

Thermodynamic Description of the Cadmium–Nickel System

H. Azza*, N. Selhaoui, L. Bouirden

Laboratory of Thermodynamics and Energy (L.T.E), Faculty of science, University IbnZohr, Agadir, Morocco

***Corresponding Author:** H. Azza, Laboratory of Thermodynamics and Energy (L.T.E), Faculty of science, University IbnZohr, Agadir, Morocco

Abstract: The thermodynamic description of the Cd-Ni binary system was carried out with the help of CALPHAD of PHASE Diagram (CALPHAD) method. The solution phases (Liquid, HCP_A3 (Cd) and FCC_A1 (Ni)) were modeled with the Sublattice formalism and the excess term of the Gibbs energy with the Redlich-Kister equation. The intermetallic compounds Cd_5Ni and $CdNi$ which a narrow homogeneity range, were modeled using a two-sublattice model with a mutual substitution of Cd and Ni on both sublattices. The calculations based on the thermodynamic modeling are in good agreement with the phase diagram data and experimental thermodynamic values.

Keywords: Cd-Ni system; Thermodynamic description; Phase diagram; Calphad method; Redlich–Kister equation.

1. INTRODUCTION

The Nickel–cadmium (Ni–Cd) batteries are rechargeable energy sources widely used in portable electronic devices. This huge demand occurs because these electrochemical systems have several advantages, like low cost, high energy density and high storage capacity [1]. Also are used extensively in aerospace systems, because of their relatively high energy and power densities and their excellent cycling capabilities [2-5] and recognizing the need to keep battery weight to an absolute minimum, efforts continue to improve the cycle life particularly to high depths of discharge.

The cycle lives of Ni-Cd batteries are limited by irreversible structural and physicochemical changes that occur in the porous nickel electrodes as the batteries are cycled between the charged and discharged states. Due to cadmium and nickel concentration levels of about 14% and 24.5% respectively, these batteries are economically attractive candidates for recycling operations, being even considered as secondary sources for those metals. Unfortunately, also due to their high levels of metals, they also constitute hazardous residues, and their inadequate disposal is a potential source of contamination in soil and water bodies [6–9]. Cadmium is a toxic metal with cumulative character, classified as a carcinogenic agent for humans [10], while nickel, besides being a toxic material, induces some harmful health effects from mere allergy to risk of lung and gastrointestinal cancer, being responsible for the increase in the incidence of malign tumors [11]. Various models have been developed that provide a good phenomenological simulation of the loss of capacity. [12-13] However, a complete understanding of the degradation mechanisms requires a careful analysis of the cell thermodynamics so that the voltage and energy efficiencies can be placed on a rational basis.

In order to define the processing conditions for making these alloys and subsequent treatments to obtain the optimum engineering properties, a knowledge of the phase diagram and thermodynamic properties of these alloys is essential. The binary and ternary systems used for energy storage have attracted much attention for the theoretical study of the solid state and for many industrial purposes.

This present work deals with an assessment of the thermodynamic description of the Cd-Ni system using the Calphad method [14]. In this method, the thermodynamic models for the Gibbs energy of all the individual phases are studied using the Parrot module in the Thermo-Calc Software [15]. The thermodynamic parameters involved in the models are optimized from the experimental thermodynamic and phase diagram data.

2. THERMODYNAMIC DATA

First investigations of the phase equilibria restricted to Cd-rich part of the Cd-Ni system have been performed by Voss [16] and Swartz et al. [17] using thermal analysis, micrographic observations and

chemical analysis of equilibrated samples. Chasanov et al [18] has determined the liquidus up to 14.5 at% Ni. Ekman et al [19] has stated that an intermediate phase $Cd_{21}Ni_5$ exists by using X-ray diffractogram, instead of another stoichiometry as Voss [16] and Swartz et al. [17] has proposed. Ljung et al. [20] stated that this phase has the stoichiometry Cd_5Ni indenting X-ray diffraction analysis but Goldschmidt et al. [21] have found a homogeneity range of this phase from about 13 to 20 at % Ni melt at 723 K, whereas Nowotny et al. [22] reported for the Cd-rich boundary 9.2 at% Ni at 673 K by using magnetic susceptibility.

Further on, Lihl et al. [23] had observed and investigated another intermediate phase CdNi, between 47 at % Ni and 48.5 at%. Ni and later confirmed by Lott et al. [24] and Goldschmidt et al. [21] From thermal and metallographic analyses and Thermal and metallographic observations, X-ray diffractogram respectively.

On the basis of these findings Shunk et al. [25] have drawn an assessed phase diagram, which was taken as a basis for **Fig. 1**.

It should be mentioned that Lihl et al. [23] have found by an amalgamation process a third intermediate phase in this system which is Cd_5Ni_2 . From thermal analysis and metallographic investigations there is some evidence for the existence of this phase, too confirmed by Lott et al. [24]. Also, by the x-ray diffraction, Cd_5Ni_2 could be detected in sintered Cd-Ni alloys Pozin et al. [26] and Terentev et al. [27]. On the other hand, Goldschmidt et al. [21] were not able to find this phase. Obviously, Cd_5Ni_2 is a metastable phase and has not been included in the assessed diagram by Shunk et al. [25]. The crystal structures and list of various phases are reported in **Table 1**.

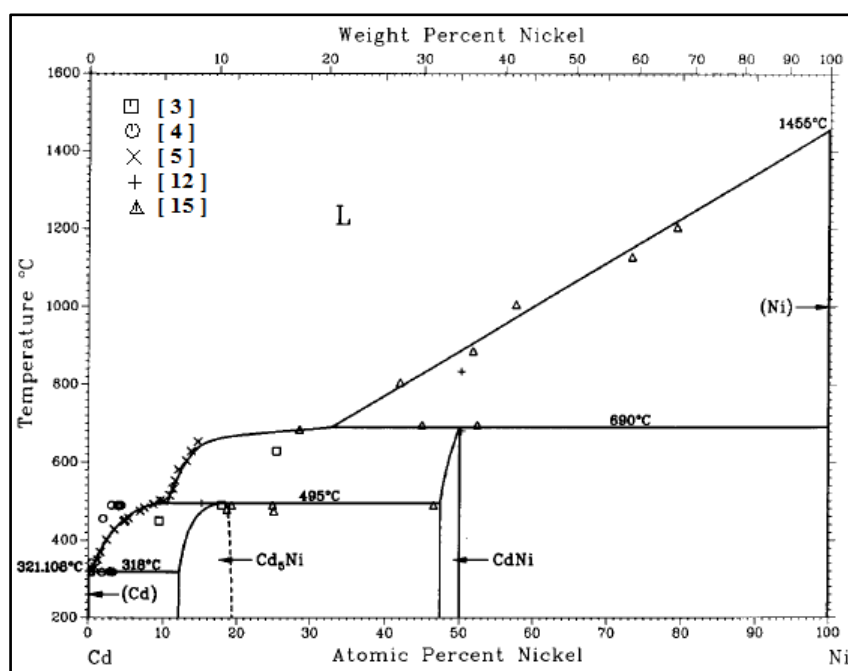


Fig1. Assessed Cd-Ni phase diagram with select experimental data [3-5, 12, 15]

As limited thermodynamic information is available in literature on Cd–Ni system, calorimetric investigation of this system was undertaken. The intermetallic compounds Cd_5Ni and CdNi melt peritectically and have narrow non-stoichiometric range of stability according to [28]. Enthalpy increments and enthalpies of formation of these two compounds were measured by Agarwal et al. [29] using high temperature Calvet calorimeter.

Table 1. Symbols and crystal structures of the stable solid phases in the Cd-Ni system. [16].

Diagram symbol	Composition at.% Ni	Pearson symbol	Symbol used in Thermo-Calc data file	Struktur-bericht Designation	Prototype
(Cd)	0	hP2	HCP_A3	A3	Mg
Cd_5Ni	12 to 18.5	cP52	Cd_5Ni	D8 ₃	Cu_9Al_4
Cd_5Ni_2	27.5 to 29	D8 ₃	...
CdNi	48 to 50	cF112	CdNi	E9 ₃	Fe_3W_3C
(Ni)	100	cF4	FCC_A1	A1	Cu

3. THERMODYNAMIC MODELS

3.1. Pure Elements

The Gibbs energy of the pure element i ($i = \text{Cd, Ni}$) in the phase ϕ ($\phi = \text{Liquid, HCP_A3 and FCC_A1}$), referred to the enthalpy of its stable state at 298.15 K, is described as a function of temperature by:

$$G_i^\phi(T) = {}^0 G_i^\phi - H_i^{SER}(298.15\text{K}) = a + bT + cT \ln T + dT^2 + eT^3 + fT^7 + gT^{-1} + hT^{-9} \quad (1)$$

Where $H_i^{SER}(298.15\text{K})$ is the molar enthalpy of the element i ($i = \text{Cd, Ni}$) at 298.15 K in its standard element reference (SER) state, HCP_A3 for Cd and FCC_A1 for Ni.

In this article, The Gibbs energy functions are taken from the SGTE compilation of Dinsdale [30].

3.2. Solution Phases

The solution phases (liquid, HCP_A3 (Cd) and FCC_A1 (Ni)) were modeled as substitution solution according to the polynomial Redlich–Kister model [31]. The solid solution HCP_A3 (Cd) and FCC_A1 (Ni) with negligible solubility are considered as pure elements. The Gibbs energy of one mol of formula unit of phase ϕ is expressed as the sum of the reference part ${}^{ref} G_i^\phi$, the ideal part ${}^{id} G_i^\phi$,

and the excess part ${}^{exc} G_i^\phi$:

$$G_m^\phi = {}^{ref} G^\phi + {}^{id} G^\phi + {}^{exc} G^\phi \quad (2)$$

As used in the Thermo-Calc software [15]:

$${}^{ref} G^\phi(T) = ({}^0 G_{Cd}^\phi(T) - H_{Cd}^{SER}(298.15\text{K}))x_{Cd} + ({}^0 G_{Ni}^\phi(T) - H_{Ni}^{SER}(298.15\text{K}))x_{Ni} \quad (3)$$

$${}^{id} G^\phi = RT(x_{Cd} \ln x_{Cd} + x_{Ni} \ln x_{Ni}) \quad (4)$$

Where R is the gas constant, T the temperature, in Kelvin, x_{Ni} and x_{Cd} are the fraction of elements Ni and Cd, respectively.

The excess terms of all the solution phases (liquid, HCP_A3 (Cd) and FCC_A1 (Ni)) were modelled by the Redlich-Kister [31] formula:

$${}^{exc} G_m^\phi(T) = x_{Ni} x_{Cd} \left[{}^0 L_{Ni,Cd}^\phi(T) + {}^1 L_{Ni,Cd}^\phi(T)(x_{Ni} - x_{Cd}) + {}^2 L_{Ni,Cd}^\phi(T)(x_{Ni} - x_{Cd})^2 + \dots \right] \quad (5)$$

$${}^i L_{Ni,Cd}^\phi(T) = a_i + b_i T \quad (6)$$

Where ${}^i L_{Ni,Cd}^\phi(T)$ is the interaction parameter between the elements Ni and Cd, which is evaluated in the presentwork, the coefficients a_i and b_i are optimized using the PARROT module [15].

3.3. Intermediate Phases

The intermetallic compounds of the Cd_5Ni and CdNi (Cd_mNi_n) phases (substoichiometric in Ni) in the Cd-Ni binary systems have an experimental small homogeneity range, they were treated by a two-sublattice model as $(\text{Ni})_n(\text{Ni,Cd}\%)_m$. The symbol % denotes the major component in the considered sublattice. The Gibbs energy function per mole of the formula unit $(\text{Ni})_n(\text{Ni, Cd}\%)_m$ is the following:

$$G^{Cd_m Ni_n} - H_{Cd_m Ni_n}^{SER} = y_{Ni}^1 y_{Cd}^2 {}^0 G^{Ni: Cd} + y_{Ni}^1 y_{Ni}^2 {}^0 G^{Ni: Ni} + RT \left[m \left(y_{Cd}^2 \ln y_{Cd}^2 + y_{Ni}^2 \ln y_{Ni}^2 \right) + n y_{Ni}^1 \ln y_{Ni}^1 \right] + {}^{xs} G_m \quad (7)$$

$$H_{Cd_m Ni_n}^{SER} = m H_{Cd}^{SER} + n H_{Ni}^{SER} \quad (8)$$

Where $y_{Ni}^1 = 1$ denote the site fractions of Ni in the first Sublattice, y_{Ni}^2 and y_{Cd}^2 the site fractions of Ni and Cd in the second Sublattice, $G^{Cd_m Ni_n}$ is the Gibbs energies of the hypothetical compound $\text{Cd}_m \text{Ni}_n$

^{xs} G_m is the excess Gibbs energy expressed by the following expression:

$$^{xs} G_m = y_{Cd}^2 y_{Ni}^2 \left(L_{Ni,Cd: Cd}^{Cd_m Ni_n} \right) \quad (9)$$

Where $L_{Ni,Cd: Cd}^{Cd_m Ni_n}$ represent the interaction parameters between the element Ni and Cd in the related first while the second Sublattice is only by the element Ni.

These excess parameters are temperature dependent as:

$$L_{Ni,Cd: Cd}^{Cd_m Ni_n} = a + bT \quad (10)$$

4. OPTIMIZATION AND DISCUSSIONS

Most of the experimental information mentioned above is selected in this study. The optimization is carried out by means of the Thermo-Calc software [12] which can take various kinds of experimental data.

The thermodynamic optimization of the model parameters of the Gibbs energy expressions is an application of the CALPHAD technique with the help of the PARROT module of the Thermo-Calc software developed by Sundman et al. [4] and Jansson [32].

The program works by minimizing an error sum where each of the selected data values are given a certain weight. The weight is chosen by personal judgment and changed by trial and error during the work until most of the selected experimental information is reproduced within the expected uncertainty limits. No enthalpy of mixing of the liquid was available in the literature.

In order to avoid the formation of an unwanted inverted miscibility gap in the liquid phase of the Cd-Ni system, thermodynamic constraints were imposed during the optimization with the Redlich–Kister formalism [31], a positive curvature of the liquidus by optimizing $d^2G/dx^2 > 0$ in the atomic composition range $0 < x(Ni) < 1$ and every 50 degrees from the liquidus temperature up to 6000 K, was therefore optimized, enthalpy and entropy of same sign.

The thermodynamic parameters for the intermediate and liquid phases were optimized at the first stage based on the enthalpies of formation of the intermetallic compounds measured by Agarwal et al [29].

The optimization was carried out in two steps. In the first treatment, CdNi and Cd₅Ni was assumed to be a stoichiometric compound, and in the second, it was treated using a two-sublattice model. The parameters obtained from the first treatment were used as starting values for the second.

The liquid was treated as a substitution solution. Both intermetallic compounds have homogeneity ranges, and were treated as (Ni)_n(Ni,Cd%)_m by a two-Sublattice model. The compositions of the phases and the temperatures involved in the invariant reactions mainly based on the phase diagram of the Cd-Ni system evaluated by Shunk [25] were used and all the thermodynamic parameters were optimized and listed in **Table 2**. **Fig. 2** shows the calculated equilibrium phase diagram with the numerous experimental data result reported by Shunk et al. [16] used in the optimization. A satisfactory agreement is noted.

Table 2. Optimized thermodynamic parameters of the Cd-Ni system

Phase	Thermodynamic models	Parameters (J/mol at)
Liquid	(Cd, Ni) ₁	${}^0L^{liq} = 4302 - 4.9 * T$ ${}^1L^{liq} = -34607 + 24 * T$
HCP_A3	(Cd, Ni) ₁ (Va) ₁	${}^1L^{HCP_A3} = 93948 - 39.9 * T$
FCC_A1	(Cd, Ni) ₁ (Va) ₃	${}^0L^{FCC_A1} = 66982 - 6.75 * T$ ${}^1L^{FCC_A1} = -65581 + 0.65 * T$
<i>Cd₅Ni</i>	(Cd) _{0.83} :(Cd, Ni) _{0.17}	$G_{Cd: Cd}^{Cd_5 Ni} - H_{Cd}^{298.15} = 5000 + G_{Cd}^{HCP_A3}$ $G_{Cd: Ni}^{Cd_5 Ni} - 0.83 * H_{Cd}^{HCP_A3} - 0.17 H_{Ni}^{FCC_A1}$ $= 0.83 GHSERCd - 0.17 GHSERNi - 8500 + 5.22T$ $G_{Cd: Ni, Cd}^{Cd_5 Ni} = -12399 + 11.35T$
<i>CdNi</i>	(Cd) _{0.50} :(Cd, Ni) _{0.50}	$G_{Cd: Cd}^{Cd_5 Ni} - H_{Cd}^{298.15} = 5000 + G_{Cd}^{HCP_A3}$ $G_{Cd: Ni}^{Cd_5 Ni} - 0.50 H_{Cd}^{HCP_A3} - 0.50 H_{Ni}^{FCC_A1}$ $= 0.5 GHSERCd - 0.5 GHSERNi - 18640 + 14.68T$ $G_{Cd: Ni}^{Cd Ni} - 0.5 * H_{Cd}^{298.15} - 0.5 H_{Ni}^{298.15}$

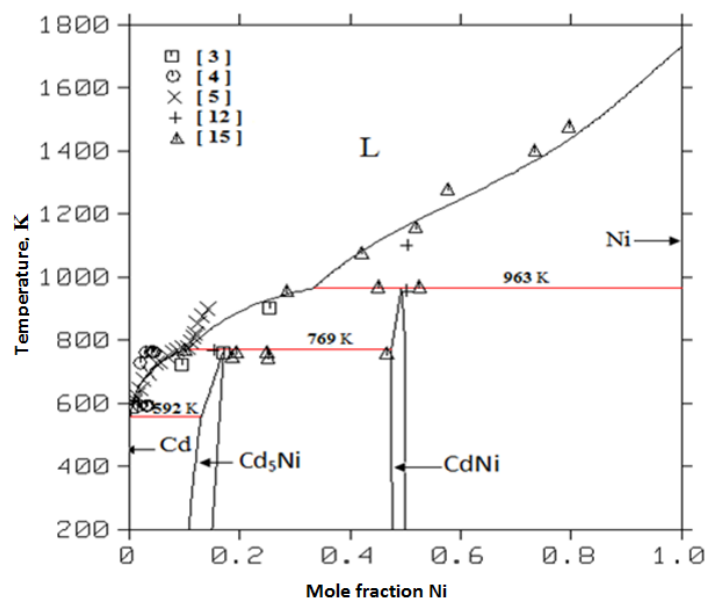


Fig2. Comparison of the Cd-Ni calculated phase diagram with the experimental data

The liquidus on the Ni-rich side calculated in the present work is in best agreement with the experimental data than the one calculated by Lott et al [24] and Goldschmidt et al [21]. The limit between the (Cd₅Ni + Liq) two-phase domain and the (Cd) terminal solid solution is in very satisfactory agreement with the data in [18]. The temperature of this Liq ↔ Cd₅Ni + Cd eutectic reaction is calculated at 591.1K and is therefore in very good agreement with the data of Shunk et al [25] at 592 K), as well as the Ni compositions of the liquid eutectic and the (Cd) terminal solid solution.

The assessed enthalpies of formation of Cd-Ni intermetallic compounds compared with experimental measured by Agarwal et al. [29] obtained by tin solution calorimetry are plotted in Table 3, also presented in Fig. 4. The agreement is very good.

Table3. Calculated and measured enthalpies of formation of the intermetallic compounds

Phase	Enthalpy of formation (kJ mol ⁻¹)	
	Agarwal et al.[29]	This work
Cd ₅ Ni	-8.140	-8.139
CdNi	-18.640	-23.057

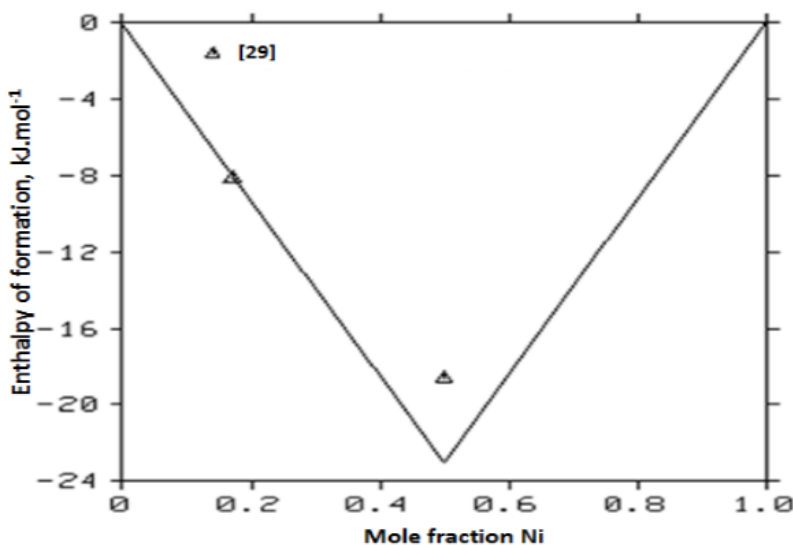


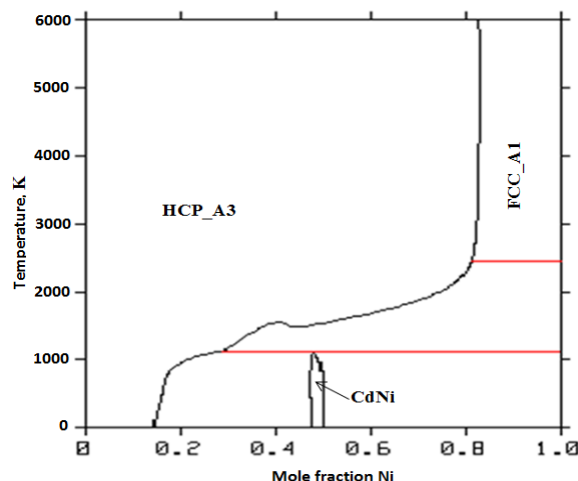
Fig3. Calculated and measured enthalpies of formation of the intermetallic compounds.

The invariant reactions in the Cd-Ni system are listed in **Table 4** and compared with the results from [16]. A very good agreement is obtained between the calculations and the experiments for the temperatures and compositions.

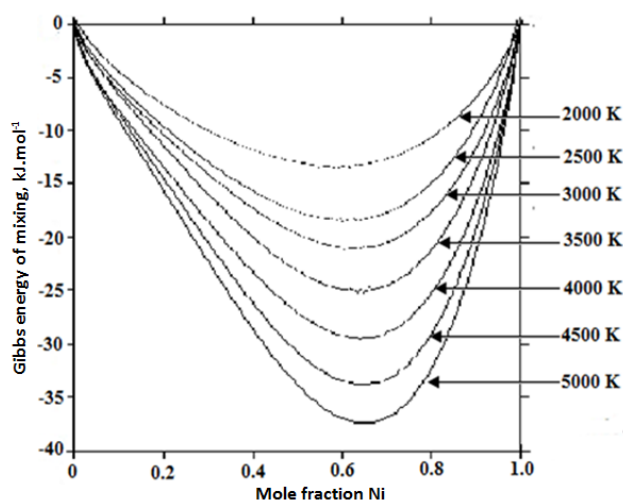
Table 4. Invariant reactions in the Cd–Ni system

Reaction	Type	Experimental Values		Ref	This work	
		T (K)	x(Ni) at		T (K)	x(Ni) at
$\text{Liq} \leftrightarrow \text{Cd} + \text{Cd}_5\text{Ni}$	Eutectic	591	0.00633	[4]	592.1	0.00426
$\text{Liq} + \text{CdNi} \leftrightarrow \text{Cd}_5\text{Ni}$	Peritectic	768	0.10400	[9]	769.7	0.10490
$\text{Liq} + \text{Ni} \leftrightarrow \text{CdNi}$	Peritectic	963	0.33300	[8]	963.0	0.33300

As first stated by [33], we verified that when the liquid phase is suspended during the calculation of the Cd-Ni phase diagram the intermetallic compounds are no more stable at high temperatures; see **Fig. 4**. At high temperatures, the FCC_A1 and the HCP_A3 terminal solid solution is stable on the Ni-rich side, and on the Cd-rich side respectively, between these single-phase domains the two-phase domain (HCP_A3 + FCC_A1) is well calculated.


Fig 4. Calculated Cd-Ni phase diagram when the liquid phase is suspended

Finally, we verified that no miscibility gap was calculated with our thermodynamic optimized parameters as commended in [34]. **Fig. 5** shows the evolutions of Gibbs energy for the liquid phase as a function of temperature (T), when T is increasing up to 5000 K, the Gibbs energy for the liquid phase decreases. No anomaly is detected on all the curves.


Fig 5. Gibbs energy of mixing of the liquid phase at different temperature, the reference states were Cd and Ni liquids.

5. CONCLUSION

The present work reviewed critically the experimental information on phase diagram and a thermodynamic property of the Cd-Ni binary system has been optimized using the CALPHAD method. A set of self-consistent thermodynamic parameters formulating the Gibbs energies of various phases in the Cd-Ni binary system was obtained, which can reproduce well most of the experimental data on thermodynamic properties and phase diagram. The computed values are in good agreement with the experimental data.

REFERENCES

- [1] M. Freitas, T.R. Penha, S. Sirtoli, J. Power Sources. 163 (2007) 1114.
- [2] P. C. Milner and U. B. Thomas, Advances in Electrochemistry and Electrochemical Engineering.5 (1967)1.
- [3] G. Halpert, J. Power Sources, 15 (1985) 119.
- [4] J. K. McDermott, *ibid*, 18 (1986) 265.
- [5] L. Miller, J. Brill, and G. Dodson, *ibid*. 29 (1990) 533.
- [6] B.R. Reddy, D.N. Priya, S.V. Rao, P. Radhika, Hydrometallurgy 77 (2005) 253–261.
- [7] B.R. Reddy, D.N. Priya, K.H. Park, Sep. Purif. Technol. 50 (2006) 161.
- [8] C.A. Nogueira, F. Margarido, Waste Manage. 27 (2007) 1570.
- [9] M. Safarzadeh, M.S. Bafghi, D. Moradkhani, M. Ilkhchi, Miner. Eng. 20 (2007) 211.
- [10] M.P. Waalkes, J. Inorg. Biochem. 79 (2000) 241.
- [11] E.L.B. Novelli, R.T. Hernandez, J.L.V.B. Novelli Filho, L.L. Barbosa, Environ. Pollut. 103 (1998) 295.
- [12] D. D. Macdonald, B. G. Pound, and S. J. Lenhart, *ibid*. 29 (1990) 447.
- [13] D.D. Macdonald, M. Urquidi-Macdonald, S. D. Bhatka, and B. G. Pound, This Journal, 138 (1991) 1359.
- [14] L. Kaufman and H. Bernstein, Computer Calculations of Phase Diagrams, Academic Press, NY. (1970).
- [15] B. Sundman, B. Jansson, and J. Andersson, the Thermodynamic Databank System, Calphad. 9(2) (1985) 153.
- [16] G. Voss, Z. Anorg. Allg. Chem. 57 (1908) 34.
- [17] C. E. Swartz, A. J. Phillips, Trans. AIME. 111 (1934) 333.
- [18] M. G. Chasanov, P.D. Hunt, I. Johnson, H.M. Feder, Trans. AIME. 224 (1962) 935.
- [19] W. Ekman. Z. Physik. Chhem. B 12 (1931) 69.
- [20] H. Ljung, S. Westman, Acta Chem. Scand. 24 (1970) 611.
- [21] H.J. Goldschmidt, M.J. Walker, J. Appl. Crystallogr. 2 (1969) 273.
- [22] H. Nowotny, H. Bittner, Monatsh. Chem. 81 (1950) 887.
- [23] F. Lihl, E. Buhl, Z. Metallkde. 46 (1955) 787.
- [24] R.J. Lott, Critchley, J.K. Nature 200 (1963) 773.
- [25] F.A. Shunk and P. Nash, 8 (2) (1987) 122.
- [26] Yu.M. Pozin, N.K. Terentev, N.A. Makhalov, Porosh. Metall. (1971) 18.
- [27] N.K. Terentev, Yu.M. Pozin, Porosh. Metall. (1973) 45.
- [28] T.B. Massalski, M. Okamoto, L. Kacprzak, in: 2nd Edition, Binary Alloy Phase Diagrams. (1990) 2.
- [29] R. AGARWAL, R. PRASAD, V. Venugopal, Journal of Alloys and Compounds, 320 (2001) 103.
- [30] A.T. Dinsdale, SGTE data for pure elements. Calphad, 15 (1991) 317.
- [31] O. Redlich, A. Kister, Ind. Eng. Chem, 40 (1948) 345.
- [32] B. Jansson, Ph.D. Thesis, Royal Institute of Technology, Stockholm Sweden, (1984).
- [33] G. Kaptay, CALPHAD, 28 (2004) 115.
- [34] S.L. Chen, S. Daniel, F. Zhang, Y.A. Chang, W.A. Oates, R. Schmid-Fetzer, J. Phase Equilib, 22 (2001) 373.

Citation: H. Azza et al., "Thermodynamic Description of the Cadmium–Nickel System", *International Journal of Advanced Research in Physical Science (IJARPS)*, vol. 5, no. 5, pp. 17-23, 2018.

Copyright: © 2018 Authors, This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.