

Calculation of phase diagram of Ti-Ni-O system and application to deoxidation of TiNi alloy

QIU Ai-tao, LIU Lan-jie, PANG Wei, LU Xiong-gang, LI Chong-he

Shanghai Key Laboratory of Modern Metallurgy and Materials Processing,
Shanghai University, Shanghai 200072, China

Received 18 October 2010; accepted 10 December 2010

Abstract: The Ti-Ni-O ternary system was assessed by means of Calphad method using ternary experimental data in previous study. Isothermal sections at 1 173 and 1 273 K were calculated. The result shows that the present calculated results are in good agreement with most of the experimental results. The consistent model parameter set determined in this work may provide theoretical guidance for the deoxidation of TiNi alloy.

Key words: TiNi alloy; Calphad; Ti-Ni-O system; electrochemical deoxidation

1 Introduction

Shape memory materials have attracted considerable attention recently as functional materials in a variety of industrial and medical applications. They have also been considered as important smart materials because of their ability to perform both sensing and actuating functions [1]. Among the practical shape memory materials, TiNi-based alloys are considered to be one of the most important shape memory alloys because of their excellent shape memory effect [2–3], large pseudo elasticity [4–5], high chemical corrosion resistance and good biocompatibility. Oxygen is the interstitial solute element in TiNi alloys, which must be strictly controlled, because it strongly influences the microstructure and mechanical properties.

The Ti-Ni-O system is an interesting system from the view point of the controlling of oxygen content and the deoxidation of TiNi alloy. Therefore, critically evaluated thermodynamic parameters of the Ti-Ni-O system are urgently needed in the deoxidation of TiNi alloy. The first experimental studies of the phase equilibria in the Ti-Ni-O system were performed in 1955 by ROSTOKER [6]. But even now, the Ti-Ni-O phase diagram is not known in detail, no Ti-Ni-O

thermodynamic assessment has been published.

The purpose of the present work is to thermodynamically evaluate the Ti-Ni-O ternary system so that the calculation of isothermal sections and other thermodynamic quantities become possible in the whole composition and temperature range. The present work is based on the thermodynamic descriptions of the binary systems, Ti-Ni by KEYZER et al [7], Ti-O by CANCAREVIC et al [8] and Ni-O by KOWALSKI and SPENCER [9]. The NiO-TiO₂ pseudo-binary systems were assessed. Then the thermodynamic parameters of the Ti-Ni-O system were modeled, including the ternary interaction parameters of BCC, HCP structured alloy and liquid, and some interaction parameters involving the third element, and then constructed its phase diagrams at 1 173 and 1 273 K, respectively. The oxygen potential was calculated using thermodynamic parameters of the Ti-Ni-O ternary system, and the oxygen potential can be transformed into electrical potential using Nernst equation.

2 Review of literature information

2.1 Binary systems

The Ti-Ni system was assessed previously [10–13]. Both BELLEN et al [12] and TANG et al [13] described

the B2 phase as an ordered form of the A2 phase. In the assessment by TANG et al [13], the B19' phase was also included. The upadted CALPHAD-type thermodynamic assessment was studied by KEYZER et al [7]. It was considered that the Gibbs energy expression for the pure elements in the Ni_3Ti structure should refer to the DHCP structured instead of the HCP structured phase. After changing the Gibbs energy of the pure element, parameters for Ni_3Ti were reassessed by KEYZER et al [7]. NiTi , Ni_3Ti and Ti_2Ni phases were described by the two-sublattice model in thermodynamic assessment [7]. Because the optimization showed better agreement with experiments, thermodynamic parameters [7] for the Ti-Ni system were adopted in this work.

The Ti-O system was recently assessed [8, 14–15]. FISCHER [14] published a thermodynamic calculation of the system neglecting Magneli phases and oxygen solubility of rutile. WALDNER and ERIKSSON [15] presented a complete Ti-O phase diagram from pure titanium to gaseous oxygen including Magneli phases. Most extensive evaluation of Ti-O system was done by CANCAREVIC et al [8]. The results agreed well with the experimental data and were complete thermodynamic parameters of this system, the data was used to model the Ti-Ni-O ternary system.

Ni-O system was assessed by TAYLOR and DINSDALE [16] using the ionic two-sublattice model for the description of the liquid phase. Later, the thermodynamic reevaluation of the Ni-O system was made by KOWALSKI and SPENCER [9] using an associated solution model for the liquid phase. Complete thermodynamic parameters of Ni-O system were reported in Ref. [9], and the data was used to model Ti-Ni-O ternary system.

2.2 NiO-TiO₂ pseudo-binary system

The first systematic investigation in NiO-TiO₂ pseudo binary system at high-temperature was carried out by BIRNBAUM and SCOTT [17], NiTiO_3 with ilmenite structure was described as the only binary compound. It was suggested that there also existed a phase with spinel structure, and the composition may be Ni_2TiO_4 [18]. WERNER and GEBRET [19] considered that the composition should be Ni_3TiO_5 . An improved phase diagram was published in Ref. [20]. The first complete experimental phase diagram of the NiO-TiO₂ system was reported [21], as shown in Fig. 1.

The assessment of NiO-TiO₂ pseudo-binary systems was scarcely reported. Thus, the NiO-TiO₂ system was assessed [22] (Fig. 2). The phase diagram of NiO-TiO₂ system was calculated and optimized by means of the CALPHAD method using the experimental data in precious work.

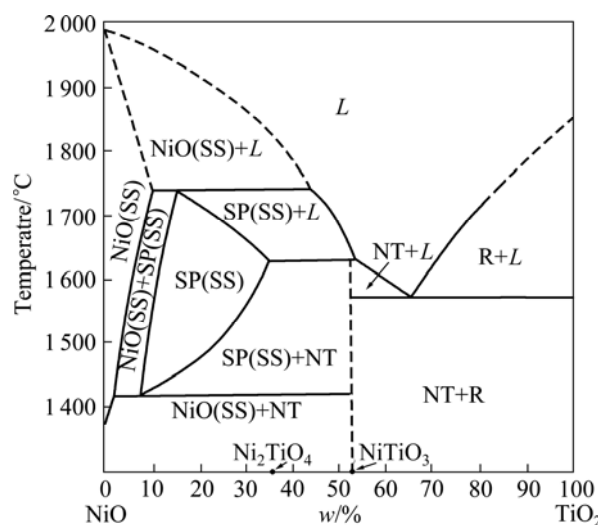


Fig. 1 Phase relations in NiO-TiO₂ system according to MUAN [21] (SP—spinel; NT— NiTiO_3 ; R—rutile; L—liquid; SS—solid solution)

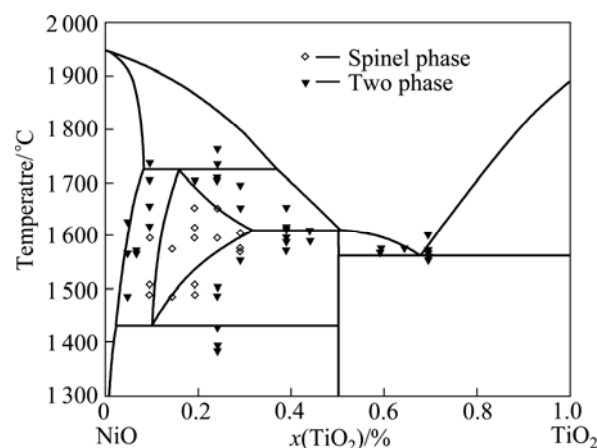


Fig. 2 Calculated NiO-TiO₂ phase diagram in this work with experimental points measured by MUAN [21]

2.3 Ti-Ni-O ternary system

Few experimental studies reported Ti-Ni-O system. ROSTOKER [6] studied the phase relation characteristics of the isothermal section of the Ti-Ni-O system at 1 173 K, the focus was concentrated on the Ti-rich region, twenty-seven alloys were used to delineate phase boundaries in the ternary section. The isothermal section with data points is shown in Fig. 3.

In order to study the influences of oxygen on the properties of TiC-base cermets, HASHIMOTO et al [23] studied the phase relation characteristics of the isothermal section of the Ti-Ni-O system at 1 000 and 2 000 °C. The isothermal section at 1 000 °C is shown in Fig. 4. The phase relationships of the Ti-Ni-O system were determined mainly in the region below 50% Ti (molar fraction). At 1 000 °C, a nickel solid solution (γ -phase) was in equilibrium with Ti_2O_3 , Ti_3O_5 , Magneli phases, TiO_2 , NiTiO_3 and NiO.

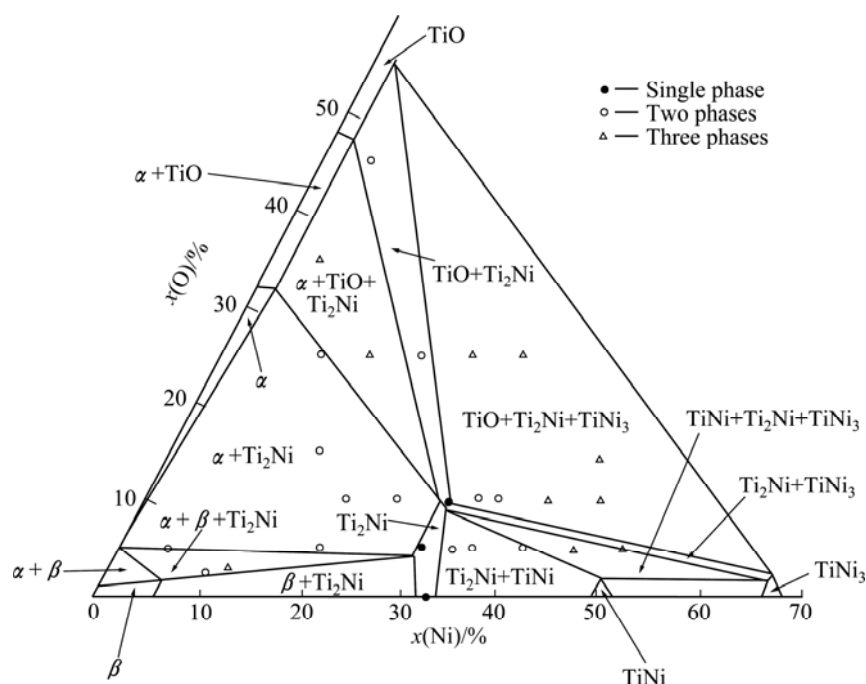


Fig. 3 Experimental phase diagram measured by ROSTOKER at 1 173 K [6]

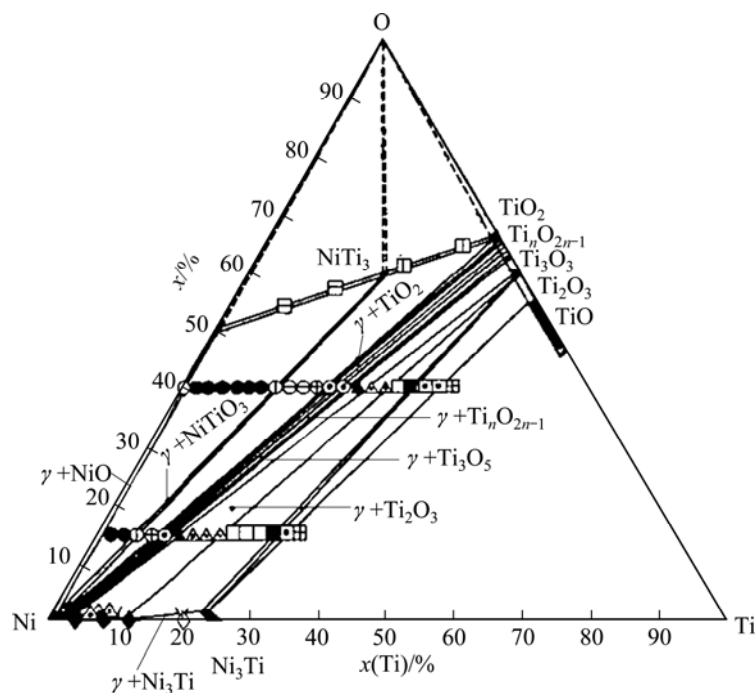


Fig. 4 Experimental phase diagram measured by HASHIMOTO et al at 1 273 K [23]

CHATTOPADHYAY and KLEYKAMP [24] re-examined the isothermal section of Ti-Ni-O system at 1 200 K in the region between Ni(Ti) solid solution and the binary oxides of titanium. The relative partial Gibbs energy of oxygen over the Ti_2O_3 - Ti_3O_5 region, as well as the Gibbs energy of formation of NiTiO_3 , Ti_3O_5 and TiNi_3 were determined between 1 100 and 1 300 K by

the use of solid electrolyte galvanic cells.

Ti-Ni-O system is an interesting system from the view point of the controlling of oxygen percent and the deoxidation of TiNi alloy. Up to now, no Ti-Ni-O thermodynamic assessment has been published. Therefore, it is of practical interests to model this ternary system based on those experimental results.

3 Thermodynamic modeling

The Gibbs energy functions of all phases are referred to the enthalpy of pure elements in their stable states at 298.15 K under 0.1 MPa. Gibbs energy functions of the pure elements were taken from the SGTE (Scientific Group Thermodata Europe) unary database [25].

3.1 Gas phase

The gas phase was described as an ideal mixture containing the species of Ti, TiO, TiO₂, O, O₂, O₃, Ni and NiO. The Gibbs energy of the gas phase is given as

$$G^{\text{gas}} = \sum_i x_i G_i^{\text{gas}} + RT \sum_i x_i \ln x_i + RT \ln(P/P^0) \quad (1)$$

where x_i is the mole fraction of the species i in the gas phase; G_i^{gas} is the standard Gibbs energy of the gaseous species i [26]; R is the gas constant and P^0 is the standard pressure of 0.1 MPa.

3.2 Liquid

The (Ti, O, TiO, TiO_{1.5}, TiO₂, Ni and NiO) model was chosen for description of liquid in the present work. The Gibbs energy of the liquid is given as

$$G^{\text{liq}} = \sum_i x_i G_i^{\text{liq}} + RT \sum_i x_i \ln x_i + G^{\text{E}} \quad (2)$$

where x_i is the mole fraction of the species i in the liquid phase; G_i^{liq} is the standard Gibbs energy of the liquid species i ; R is the gas constant and G^{E} is the excess Gibbs energy.

The excess Gibbs energy (G^{E}) is given by the general formula using the Redlich–Kister polynomial as

$$G^{\text{E}} = \sum_{i,j=1(i \neq j)}^n x_i x_j \sum_{k=0}^m L_{i,j}^k (x_i - x_j)^k + \sum_{i,j,l=1(i \neq j \neq l)}^n x_i x_j x_l \sum_{k=i,j,l} L_k V_k \quad (3)$$

where the first term represents the binary interaction terms, the second one represents the ternary interactions. $L_{i,j}^k$ is the binary interaction parameter for the i - j binary and L_k is the ternary interaction parameter. V_k is defined as

$$V_k = x_k + \frac{1 - \sum_{p=i,j,l} x_p}{n} \quad (4)$$

3.3 Interstitial solid solution phases

In Ti-Ni-O ternary system, there existed some

interstitial solid solution phases, such as BCC, HCP and FCC. In the present study, it was assumed that oxygen atoms dissolve interstitially in the BCC β -Ti and Ni-rich FCC phases as well as in HCP α -Ti phase. Therefore, these phases were described using a two-sublattice model with formula unit (Ti,Ni)_{*a*}(O,Va)_{*c*}. In this model, it was assumed that the metal elements Ti and Ni can substitute for each other on the metal sublattice and oxygen and vacancies on the interstitial sublattice. The subscripts a and c were used to denote the number of sites on each sublattice. In the case of FCC and BCC structured phases, $a=c=1$; for HCP, $a=1$ and $c=0.5$. The Gibbs free energy for one mole of formula unit can be expressed as

$$G^{\phi} = y_{\text{Ti}} y_{\text{Va}} {}^0G_{\text{Ti:Va}}^{\phi} + y_{\text{Ti}} y_{\text{O}} {}^0G_{\text{Ti:O}}^{\phi} + y_{\text{Ni}} y_{\text{Va}} {}^0G_{\text{Ni:Va}}^{\phi} + y_{\text{Ni}} y_{\text{O}} {}^0G_{\text{Ni:O}}^{\phi} + aRT(y_{\text{Ti}} \ln y_{\text{Ti}} + y_{\text{Ni}} \ln y_{\text{Ni}}) + cRT(y_{\text{Va}} \ln y_{\text{Va}} + y_{\text{O}} \ln y_{\text{O}}) + {}^{\text{E}}G^{\phi} \quad (5)$$

$${}^{\text{E}}G^{\phi} = y_{\text{Ti}} y_{\text{Ni}} y_{\text{Va}} L_{\text{Ti:Ni:Va}} + y_{\text{Ti}} y_{\text{Ni}} y_{\text{O}} L_{\text{Ti:Ni:O}} + y_{\text{Ti}} y_{\text{O}} y_{\text{Va}} L_{\text{Ti:O:Va}} + y_{\text{Ni}} y_{\text{O}} y_{\text{Va}} L_{\text{Ni:O:Va}} + y_{\text{Ti}} y_{\text{Ni}} y_{\text{O}} y_{\text{Va}} L_{\text{Ti:Ni:O:Va}} \quad (6)$$

where y_i denotes the site fraction of component i on the relevant sublattice; ${}^0G_{i:\text{Va}}$ is the Gibbs energy of pure element i and ${}^0G_{\text{Va:O}}$ is the Gibbs energy of a hypothetical state where all the interstitial sites are filled with oxygen.

3.4 Ti₂Ni

In the assessment of Ti-Ni binary system [7], Ti₂Ni phase was described using a two sublattice model with formula unit (Ti,Ni)₂(Ti,Ni)₁. In the present study, this model was extended into the ternary system by introducing one more sublattice for interstitial components, oxygen and vacancies [27]. In this study, the formula unit becomes (Ti,Ni)₂(Ti,Ni)₁(O,Va)₃. Because Ti₂Ni phase possesses the crystal structure that corresponds to FCC, the number of sites on the interstitial sublattice was given a value of 3, which is the same as that in the interstitial solid solution model. The Gibbs free energy for one mole formula unit is expressed as

$$G^{\text{Ti}_2\text{Ni}} = y_{\text{Ti}}' y_{\text{Ti}}'' y_{\text{Va}}''' {}^0G_{\text{Ti:Ti:Va}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ni}}' y_{\text{Ni}}'' y_{\text{Va}}''' {}^0G_{\text{Ni:Ti:Va}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ti}}' y_{\text{Ni}}'' y_{\text{Va}}''' {}^0G_{\text{Ti:Ni:Va}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ni}}' y_{\text{Ni}}'' y_{\text{Va}}''' {}^0G_{\text{Ni:Ni:Va}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ti}}' y_{\text{Ti}}'' y_{\text{O}}''' {}^0G_{\text{Ti:Ti:O}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ni}}' y_{\text{Ti}}'' y_{\text{O}}''' {}^0G_{\text{Ni:Ti:O}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ti}}' y_{\text{Ni}}'' y_{\text{O}}''' {}^0G_{\text{Ti:Ni:O}}^{\text{Ti}_2\text{Ni}} + y_{\text{Ni}}' y_{\text{Ni}}'' y_{\text{O}}''' {}^0G_{\text{Ni:Ni:O}}^{\text{Ti}_2\text{Ni}} + 2RT(y_{\text{Ti}}' \ln y_{\text{Ti}}' + y_{\text{Ni}}' \ln y_{\text{Ni}}') + RT(y_{\text{Ti}}'' \ln y_{\text{Ti}}'' + y_{\text{Ni}}'' \ln y_{\text{Ni}}'') + 3RT(y_{\text{O}}''' \ln y_{\text{O}}''' + y_{\text{Va}}''' \ln y_{\text{Va}}''') + {}^{\text{E}}G^{\text{Ti}_2\text{Ni}} \quad (7)$$

$$\begin{aligned}
{}^E G^{\text{TiO}_x} = & y_{\text{Ti}}' y_{\text{Ni}}'' (y_{\text{Ti}}'' y_{\text{Va}}''' L_{\text{Ti,Ni,Ti:Va}} + y_{\text{Ni}}'' y_{\text{Va}}''' L_{\text{Ti,Ni:Ni:Va}} + \\
& y_{\text{Ti}}'' y_{\text{O}}''' L_{\text{Ti,Ni,Ti:O}} + y_{\text{Ni}}'' y_{\text{O}}''' L_{\text{Ti,Ni:Ni:O}}) + \\
& y_{\text{Ti}}' y_{\text{Ni}}'' (y_{\text{Ti}}' y_{\text{Va}}''' L_{\text{Ti:Ti,Ni:Va}} + y_{\text{Ni}}' y_{\text{Va}}''' L_{\text{Ni:Ti,Ni:Va}} + \\
& y_{\text{Ti}}' y_{\text{O}}''' L_{\text{Ti:Ti,Ni:O}} + y_{\text{Ni}}' y_{\text{O}}''' L_{\text{Ni:Ti,Ni:O}}) + \\
& y_{\text{O}}''' y_{\text{Va}}''' (y_{\text{Ti}}' y_{\text{Ti}}'' L_{\text{Ti:Ti:O,Va}} + y_{\text{Ni}}' y_{\text{Ti}}'' L_{\text{Ni:Ti:O,Va}} + \\
& y_{\text{Ti}}' y_{\text{Ni}}'' L_{\text{Ni:Ti:O,Va}} + y_{\text{Ni}}' y_{\text{Ni}}'' L_{\text{Ni:Ni:O,Va}}) \quad (8)
\end{aligned}$$

3.5 NiTi (BCC_B2)

In the Ti-Ni system, there is a Ti-rich A2 phase which is the disordered form of the B2 phase and the B2 phase can be considered as an ordered state of A2 phase. In KEYZER's assessment of the Ti-Ni binary system [7], NiTi phase was described using a two sublattice model with formula unit, $(\text{Ti,Ni})_{0.5}(\text{Ti,Ni})_{0.5}$. This model was extended into the ternary system by introducing one oxygen on each sublattice. In this work, the formula unit of the NiTi phase becomes $(\text{Ti,Ni,O})_{0.5}(\text{Ti,Ni,O})_{0.5}$. In the case that two or more phases are related by an order-disorder transformation, the Gibbs energy of those phases can be written with one expression [28–29]. The Gibbs free energy of NiTi phase can be described as

$$G_m^{\text{B2}} = G_m^{\text{Dis-B2}}(x_i) + \Delta G_m^{\text{ord-B2}}(y_i^s) \quad (9)$$

The first term $G_m^{\text{Dis-B2}}(x_i)$ is independent of the ordering state of the B2 phase, it can be described using associated solution model. The second term $\Delta G_m^{\text{ord-B2}}(y_i^s)$ is the contribution due to long-range ordering, it can be expressed as

$$\begin{aligned}
\Delta G_m^{\text{ord-B2}}(y_i^s) = & y_{\text{Ti}}' y_{\text{Ti}}'' G_{\text{Ti:Ti}}^\phi + y_{\text{Ni}}' y_{\text{Ni}}'' G_{\text{Ni:Ni}}^\phi + y_{\text{O}}' y_{\text{O}}'' G_{\text{O:O}}^\phi + \\
& y_{\text{Ti}}' y_{\text{Ni}}'' G_{\text{Ti:Ni}}^\phi + y_{\text{Ti}}' y_{\text{O}}'' G_{\text{Ti:O}}^\phi + y_{\text{Ni}}' y_{\text{Ti}}'' G_{\text{Ni:Ti}}^\phi + \\
& y_{\text{Ni}}' y_{\text{O}}'' G_{\text{Ni:O}}^\phi + y_{\text{O}}' y_{\text{Ti}}'' G_{\text{O:Ti}}^\phi + y_{\text{O}}' y_{\text{Ni}}'' G_{\text{O:Ni}}^\phi + \\
& 0.5RT(y_{\text{Ti}}' \ln y_{\text{Ti}}' + y_{\text{Ni}}' \ln y_{\text{Ni}}' + y_{\text{O}}' \ln y_{\text{O}}') + \\
& 0.5RT(y_{\text{Ti}}'' \ln y_{\text{Ti}}'' + y_{\text{Ni}}'' \ln y_{\text{Ni}}'' + y_{\text{O}}'' \ln y_{\text{O}}'') + \\
& y_{\text{Ti}}' y_{\text{Ti}}'' y_{\text{O}}''' L_{\text{Ti:Ti,O}}^0 + y_{\text{O}}' y_{\text{Ti}}'' y_{\text{O}}''' L_{\text{O:Ti,O}}^0 + \\
& y_{\text{Ti}}' y_{\text{O}}'' y_{\text{Ti}}''' L_{\text{Ti:O,Ti}}^0 + y_{\text{Ti}}' y_{\text{O}}'' y_{\text{O}}''' L_{\text{Ti:O,O}}^0 + \\
& y_{\text{Ni}}' y_{\text{Ni}}'' y_{\text{O}}''' L_{\text{Ni:Ni,O}}^0 + y_{\text{O}}' y_{\text{Ni}}'' y_{\text{O}}''' L_{\text{O:Ni,O}}^0 + \\
& y_{\text{Ni}}' y_{\text{O}}'' y_{\text{Ni}}''' L_{\text{Ni:O,Ni}}^0 + y_{\text{Ni}}' y_{\text{O}}'' y_{\text{O}}''' L_{\text{Ni:O,O}}^0 + \\
& y_{\text{Ti}}' y_{\text{O}}'' y_{\text{Ni}}''' L_{\text{Ti:O,Ni}}^0 + y_{\text{Ni}}' y_{\text{Ti}}'' y_{\text{O}}''' L_{\text{Ni:Ti,O}}^0 + \\
& y_{\text{Ni}}' y_{\text{O}}'' y_{\text{Ti}}''' L_{\text{Ni:O,Ti}}^0 + y_{\text{Ti}}' y_{\text{Ni}}'' y_{\text{O}}''' L_{\text{Ti:Ni,O}}^0 \quad (10)
\end{aligned}$$

3.6 NiTiO₃ ternary phases

The ternary phase NiTiO₃, which was newly evaluated in this study, was treated as a stoichiometric compound. The (NiO, TiO₂) model was chosen for the description of NiTiO₃ in the present work. The Gibbs

free energy for one mole formula unit can be expressed as

$${}^0 G^{\text{NiTiO}_3} = {}^0 G_{\text{NiO}}^{\text{Halite}} / 2 + {}^0 G_{\text{TiO}_2}^{\text{Rutile}} / 2 + a + bT \quad (11)$$

where ${}^0 G_{\text{NiO}}^{\text{Halite}}$ is the standard Gibbs energy of halite NiO and ${}^0 G_{\text{TiO}_2}^{\text{Rutile}}$ is the standard Gibbs energy of rutile TiO₂.

3.7 Other phases

The other phases consisting in the present evaluation of Ti-Ni-O system are Ni₃Ti, Ti₃O₂, α -TiO, Ti₂O₃, Ti₅O₉, Ti₇O₁₃, Ti₃O₅, Ti₆O₁₁, Ti₈O₁₅, Ti₉O₁₇, Ti₁₀O₁₉, Ti₂₀O₃₉, halite, spinel, rutile and TiO_x binary phases. The thermodynamic descriptions for these phases were not changed from their original ones. Therefore, Ni₃Ti was described using the sublattice model, (Ni,Ti)₃(Ni,Ti)₁, halite, spinel, rutile and TiO_x phases were described using associated solution model and all the other binary phases were treated as stoichiometric compounds.

4 Optimization of thermodynamic parameters

All the thermodynamic parameters are optimized by Pan-optimizer included in the Pandat Phase Equilibrium Calculation software, which is a C/C++ software package for evaluating thermodynamic, kinetic and thermo-physical model parameters from experimental measurements. The optimization is conducted until the sum of the squares of the errors between the calculated and the experimental thermodynamic properties and the phase equilibrium is minimized.

Thermodynamic descriptions of pure elements used in the present work are from the Scientific Group Thermo data Europe databank [25]. The binary descriptions of Ti-Ni [7], Ti-O [8] and Ni-O [9] were accepted as mentioned above. The thermodynamic parameters evaluated in the present work for the Ti-Ni-O ternary description were the G and L parameters of liquid, HCP (α -Ti), BCC (β -Ti), FCC (Ni) and NiTiO₃, and the L parameters of TiNi, Ti₂Ni.

This procedure can be conducted as follows: firstly, the ternary interaction parameters of liquid, BCC, HCP and FCC were calculated; secondly, the interaction parameters involving the third element in Ti₂Ni phase were optimized; finally, the interaction parameters involving the third element in TiNi (B2) phase were optimized.

All the parameters optimized in this work are listed in Table 1.

Table 1 Thermodynamic parameters of Ti-Ni-O system

Phase	Thermodynamic parameter
Liquid	${}^0L_{\text{Ni,Ti,O}}^{\text{Liquid}} = 90\,000 - 20T$
	${}^1L_{\text{Ni,Ti,O}}^{\text{Liquid}} = 90\,000 - 20T$
	${}^2L_{\text{Ni,Ti,O}}^{\text{Liquid}} = 90\,000 - 20T$
HCP(α)	${}^0L_{\text{Ni,Ti,O}}^{\text{HCP}} = -250\,000$
	${}^0L_{\text{Ni,Ti,O,Va}}^{\text{HCP}} = -50\,000$
BCC_A2(β)	${}^0L_{\text{Ni,Ti,O}}^{\text{BCC}} = -50\,000$
	${}^0L_{\text{Ni,Ti,O,Va}}^{\text{BCC}} = -200\,000$
FCC(γ)	${}^0L_{\text{Ni,Ti,O,Va}}^{\text{FCC}} = -100\,000$
Dis_B2 (Ni, Ti, O)	${}^0G_{\text{Ni,Ti,O}}^{\text{Dis_B2}} = -250\,000$
NiTi(B2_BCC) (Ni,Ti,O) _{0.5} (Ni,Ti,O) _{0.5}	${}^0L_{\text{Ni,Ti,O}}^{\text{B2_BCC}} = -100\,000$
	${}^0L_{\text{Ti,O,Ni}}^{\text{B2_BCC}} = -100\,000$
	${}^0L_{\text{Ti,Ni,O}}^{\text{B2_BCC}} = 80\,000$
	${}^0L_{\text{Ni,O,Ti}}^{\text{B2_BCC}} = 80\,000$
NiTiO ₃ (NiO) _{0.5} (TiO ₂) _{0.5}	${}^0G_{\text{NiTiO}_3} = 0.5{}^0G_{\text{NiO}}^{\text{Halite}} + 0.5{}^0G_{\text{TiO}_2}^{\text{Rutile}} - 10\,061 + 2.226\,T$

5 Results and discussion

The calculated phase diagrams of the Ti-Ni [7], Ti-O [8] and Ni-O [9] systems are illustrated in Figs. 5–7, respectively.

Figure 8 shows the calculated isothermal section of the Ti-Ni-O ternary system at 1 173 K. Here, the experimental data by ROSTOKER [6] is also included. The calculated equilibria are in good agreement except for the equilibrium of TiO+Ti₂Ni+TiNi₃. The calculated solubility of the element O in Ti₂Ni phase is much lower than that measured by ROSTOKER [6]. This may be resulted from the solubility of the Ti₂Ni phase in the Ti-Ni binary systems assessed by KEYZER et al [7], which is very small.

Figure 9 shows the calculated isothermal section of the Ti-Ni-O ternary system at 1 273 K. Here, the experimental data by HASHIMOTO et al [23] are also included. The calculated equilibria are in good agreement with the majority of experimental results by HASHIMOTO et al [23].

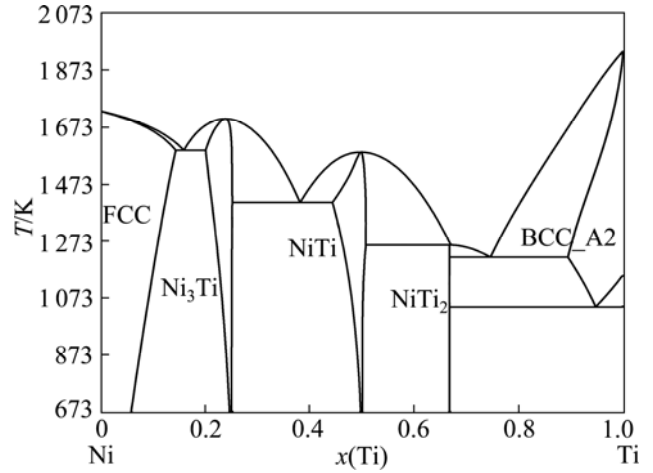


Fig. 5 Calculated Ti-Ni phase diagram using thermodynamic assessment [7]

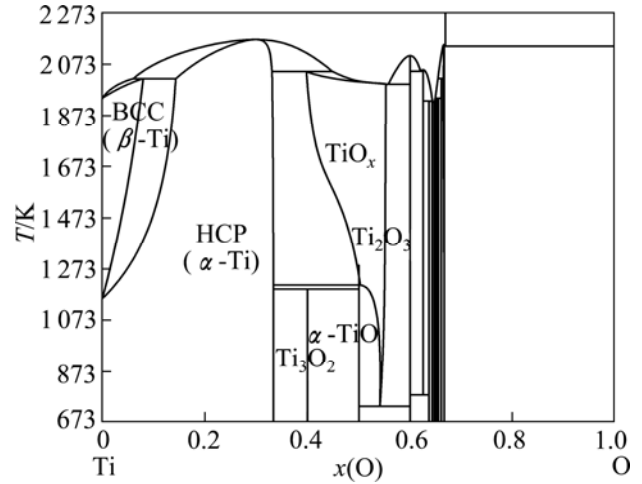


Fig. 6 Calculated Ti-O phase diagram using thermodynamic assessment [8]

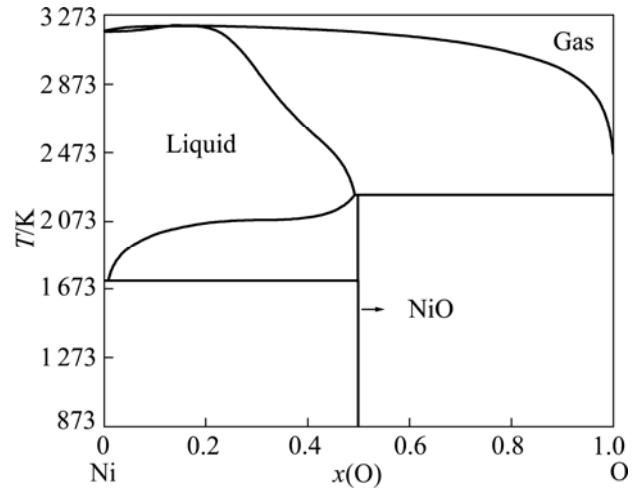


Fig. 7 Calculated Ni-O phase diagram using thermodynamic assessment [9]

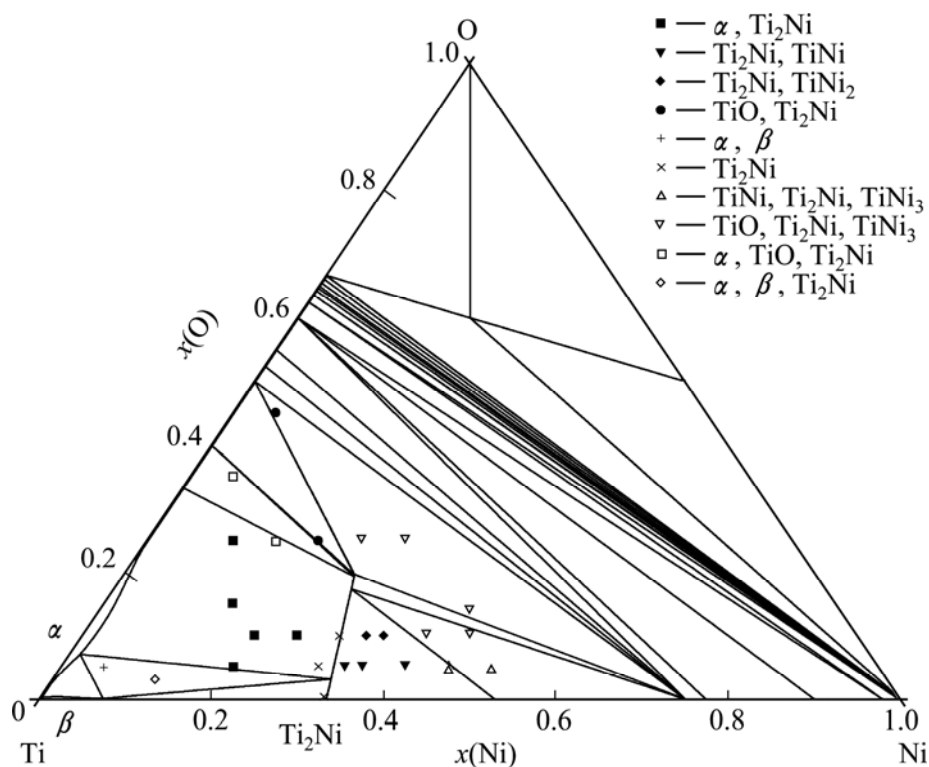


Fig. 8 Calculated 1173 K isothermal section of Ti-Ni-O in this work with experimental points measured by ROSTOKER [6]

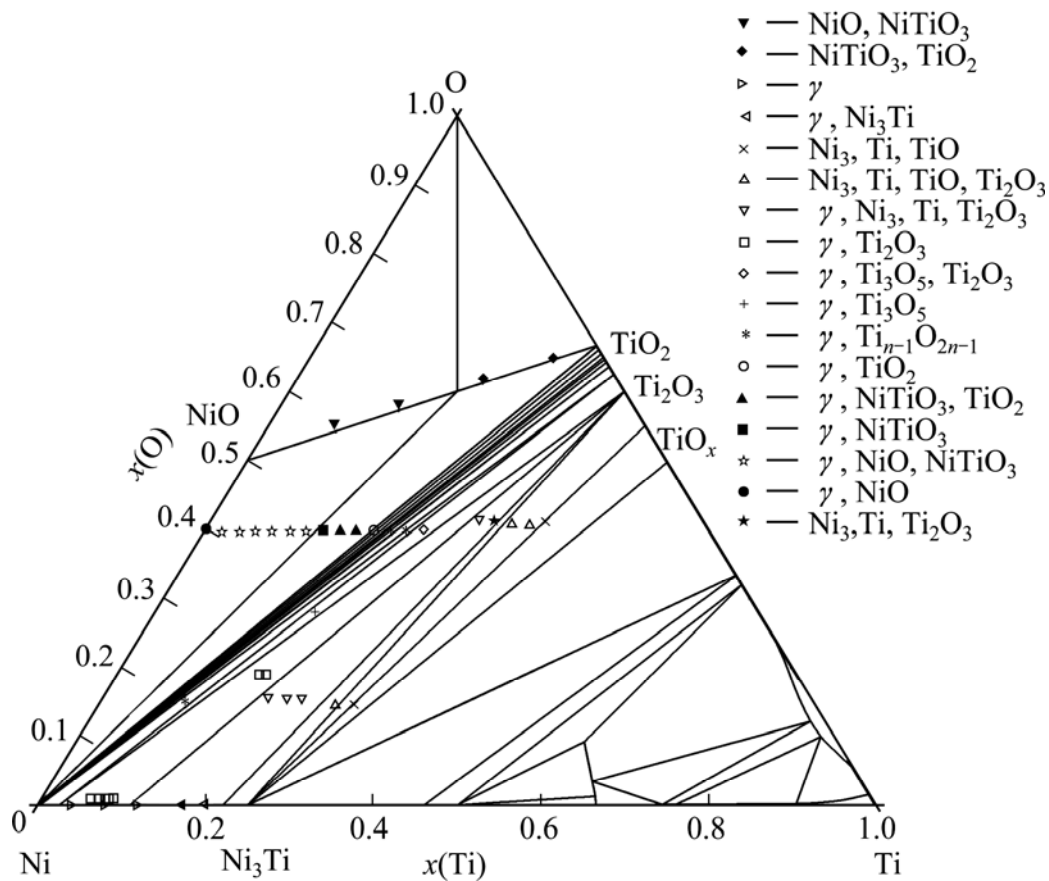


Fig. 9 Calculated 1273 K isothermal section of Ti-Ni-O in this work with experimental points measured by HASHIMOTO et al [23]

The oxygen potential can be calculated from the relevant calculation of the phase diagram of Ti-Ni-O ternary system. Then the oxygen potential is transformed into electrical potential using the Nernst equation, formulated as

$$\Delta G = RT \ln \frac{P_{O_2}}{P^0} - RT \ln \frac{P'_{O_2}}{P^0} = 2EF \quad (12)$$

where P_{O_2} is the vapor pressure of oxygen in the titanium melt and P'_{O_2} is the partial pressure of oxygen in the atmosphere. When the oxygen content of TiNi alloy is 0.08%, the vacuum is 10^{-2} Pa, the calculated electrical potential is 2.74 V at 1 773 K, through Eq. (12) (Fig. 10).

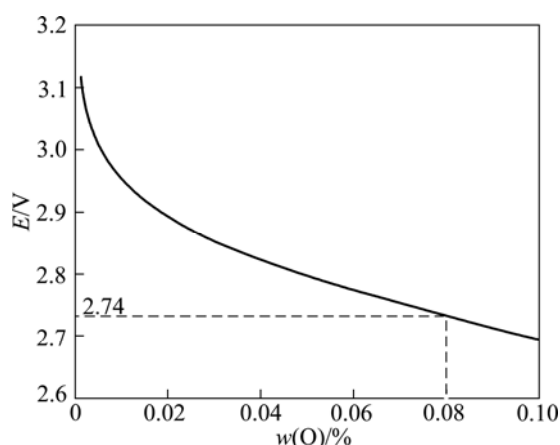


Fig. 10 Relationship between electrical potential obtained by Nernst equation and oxygen content in TiNi alloy at 1 773 K and vacuum of 10^{-2} Pa

6 Conclusions

1) Based on the previous assessed Ti-Ni, Ti-O and Ni-O systems and our evaluated NiO-TiO₂ pseudo binary systems, the thermodynamic description for the Ti-Ni-O ternary system is obtained through the extrapolation by CALPHAD method.

2) The 1 173 and 1 273 K isothermal sections are calculated. It is shown that the present thermodynamic assessment is in good agreement with the majority of experimental results. A consistent model parameter set is determined so that the calculation of isothermal sections and other thermodynamic quantities becomes possible.

3) The oxygen potential was calculated using the thermodynamic parameters of the Ti-Ni-O ternary system. Then the oxygen potential is transformed into electrical potential using Nernst equation. This result may provide theoretical guidance for the electrochemical deoxidation of TiNi alloy.

Acknowledgements

The authors are grateful to Dr. CHEN Shuang-lin from CompuTherm LLC in USA and Prof. ZHANG Jie-yu from Shanghai University in China for the helpful discussion in this work.

References

- [1] GRUMMON D S, PENCE T J. Thermottractive titanium-nickel thin films for microelectromechanical systems and active composites [J]. *Materials for Smart Systems II*, 1997, 459: 331–343.
- [2] KAHN H, HUFF M A, HEUER A H. The TiNi shape-memory alloy and its applications for MEMS [J]. *Journal of Micromechanics and Microengineering*, 1998, 8(3): 213–221.
- [3] MIYAZAKI S, OTSUKA K, SUZUKI Y. Transformation pseudoelasticity and deformation behavior in a Ti-50.6 at% Ni alloy [J]. *Scripta Metallurgica*, 1981, 15(3): 287–292.
- [4] MIYAZAKI S, OHMI Y, OTSUKA K, SUZUKI Y. Characteristics of deformation and transformation pseudoelasticity in Ti-Ni alloys [J]. *Journal de Physique Colloques*, 1982(43): C4-255–C4-260.
- [5] MIYAZAKI S, IMAI T, IGO Y, OTSUKA K. Effect of cyclic deformation on the pseudoelasticity characteristics of Ti-Ni alloys [J]. *Metallurgical and Materials Transactions A*, 1986, 17(1): 115–120.
- [6] ROSTOKER W. Selected isothermal sections in the titanium-rich corners of the systems Ti-Fe-O, Ti-Cr-O and Ti-Ni-O [J]. *Transactions of the Metallurgical Society of AIME* 203, 1955(7): 113–116.
- [7] de KEYZER J, CACCIAMANI G, DUPIN N, WOLLANTS P. Thermodynamic modeling and optimization of the Fe-Ti-Ni system [J]. *CALPHAD*, 2009, 33(1): 109–123.
- [8] CANCEREVIC M, ZINKEVICH M, ALDINGER F. Thermodynamic description of the Ti-O system using the associate model for the liquid phase [J]. *CALPHAD*, 2007, 31(3): 330–342.
- [9] KOWALSKI M, SPENCER P J. Thermodynamic reevaluation of the Cr-O, Fe-O and Ni-O systems: Remodeling of the liquid, bcc and fcc phases [J]. *CALPHAD*, 1995, 19(3): 229–243.
- [10] NASH P. Phase diagrams of binary nickel alloys [M]. Materials Park, Ohio: ASM International, 1991: 342–355.
- [11] LIANG Hai-yan, JIN Zhan-peng. A reassessment of the Ti-Ni system [J]. *CALPHAD*, 1993, 17(4): 415–426.
- [12] BELLEN P, KUMAR K C H, WOLLANTS P. Thermodynamic assessment of the Ti-Ni phase diagram [J]. *Zeitschrift für Metallkunde*, 1996, 87(12): 972–978.
- [13] TANG W, SUNDMAN B, SANDSTROM R, QIU C. New modelling of the B2 phase and its associated martensitic transformation in the Ti-Ni system [J]. *Acta Materialia*, 1999, 47(12): 3457–3468.
- [14] FISCHER E. Thermodynamic calculation of the O-Ti system [J]. *Journal of Phase Equilibria*, 1997, 18(4): 338–343.
- [15] WALDNER P, ERIKSSON G. Thermodynamic modelling of the system titanium-oxygen [J]. *CALPHAD*, 1999, 23(2): 189–218.
- [16] TAYLOR J R, DINSDALE A T. A thermodynamic assessment of the Ni-O, Cr-O and Cr-Ni-O systems using the ionic liquid and compound energy models [J]. *Zeitschrift für Metallkunde*, 1990, 81(5): 354–366.
- [17] BIRNBAUM H, SCOTT R K. X-Ray Diffraction studies of the system: Zn₂TiO₄-NiTiO₃ [J]. *Journal of the American Chemical Society*, 1950, 72(3): 1398–1399.
- [18] BAYER G, FLÖRKE O W. A new spinel-type phase in the system NiO-TiO₂-SiO₂ [J]. *Naturwissenschaften*, 1973, 60(2): 102.

- [19] WERNER H D, GEBRET W. A new compound in the system nickel oxide-titanium dioxide [J]. Neues Jahrbuch für Mineralogie-Monatshefte, 1976, 1: 44–48.
- [20] LAQUA W, SCHULTZ E W, REUTER B. Phase relations and reactions in the NiO-TiO₂ system [J]. Zeitschrift für anorganische und allgemeine chemie, 1977, 433: 167–180. (in German)
- [21] MUAN A. Equilibrium relations in the system NiO-TiO₂ in the temperature range 1 300 °C to 1 750 °C [J]. Journal of the American Ceramic Society, 1992, 75(6): 1357–1360.
- [22] QIU Ai-tao, PANG Wei, GAO Yong-hui. Optimization of the thermodynamic parameters and calculation of phase diagram of NiO-TiO₂ binary system [J]. The Chinese Journal of Process Engineering, 2010, 10(Z1): 241–245. (in Chinese)
- [23] HASHIMOTO Y, KOYAMA K, OMORI S, ARAMI Y. Isothermal phase relationships in the nickel-rich region of the nickel-titanium-oxygen system [J]. Journal of the Japan Society of Powder and Powder Metallurgy, 1980, 27(5): 155–159. (in Japanese)
- [24] CHATTOPADHYAY G, KLEYKAMP H. Phase equilibria and thermodynamic studies in the titanium-nickel and titanium-nickel-oxygen systems [J]. Zeitschrift für Metallkunde, 1983, 74(3): 182–187.
- [25] DINSDALE A T. SGTE data base for pure elements [J]. CALPHAD, 1991, 15(4): 317–425.
- [26] The SGTE substance database [M]. version 1997. Scientific Group Thermodata Europe, Grenoble, France, 1997.
- [27] LEE B J, SAUNDERS N. Thermodynamic evaluation of the Ti-Al-O ternary system [J]. Zeitschrift für Metallkunde, 1997, 88(2): 152–161.
- [28] ANSARA I, SUNDAMAN B, WILLEMIN P. Thermodynamic modeling of ordered phases in the Ni-Al system [J]. Acta Metallurgica, 1988, 36(4): 977–982.
- [29] KUSOFFSKY A, DUPIN N, SUNDMAN B. On the compound energy formalism applied to fcc ordering [J]. CALPHAD, 2001, 25(4): 549–565.

Ti-Ni-O系相图的计算及其在 TiNi合金电化学脱氧中的应用

邱爱涛, 刘岚洁, 庞 威, 鲁雄刚, 李重河

上海大学 上海市现代冶金及材料制备重点实验室, 上海 200072

摘 要: 根据文献中的实验数据, 用CALPHAD方法对Ti-Ni-O三元系进行评估优化。计算Ti-Ni-O三元系在1 173和1 273 K时的等温截面。结果表明, 计算结果与大部分实验结果吻合。通过优化获得一套自洽的热力学参数, 使其它等温截面和热力学量的计算成为可能, 为钛镍合金的脱氧提供理论指导。

关键词: TiNi合金; 计算相图; Ti-Ni-O系; 电化学脱氧

(Edited by FANG Jing-hua)