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Thermodynamic evaluation of phase equilibria in the quasibinary TiNi–TiRu system

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Abstract

The TiNi–TiRu vertical section formed by the equiatomic phases of the Ti–Ni and Ti–Ru binary systems was constructed by the method of thermodynamic calculation, using the principle of equalities between chemical potentials of the components in coexisting phases, experimental data for the quasibinary section and thermodynamic data for the TiNi and TiRu phases. The good agreement observed between the calculated and the experimental results indicates that the adopted thermodynamic model is a reasonable approximation. The set of parameters derived from the optimization is thus recommended for use in future studies. © 1997 Elsevier Science S.A.

Keywords: Chemical potential; Phase equilibria; Quasibinary section; Thermodynamic model

1. Introduction

The study of the phase diagrams of multicomponent systems including the confining Ti–Ni system, which contains the TiNi equiatomic compound with significant ability to undergo thermoelastic transformation, is of interest for the creation of new materials demonstrating the shape memory effect. This is why multicomponent systems, containing TiNi, are of great practical interest. The Ti–Ni–Ru system is the object of investigation of this work. The most progressive method of phase diagram construction for multicomponent systems is the method of thermodynamic calculation, since its experimental investigation is a very complicated and expensive task. Modelling of alloy phase diagrams of ternary systems requires the formation of a common coordinated set of thermodynamic data for all binary and ternary phases in the system. This set is formed by means of agreement with experimental data on phase equilibria and the thermodynamic properties of phases in the system. The optimizing process is successful if reliable initial (experimental) data are used in the calculation.

State diagrams of confining binary systems were constructed experimentally. Calculations of the Ti–Ni, Ti–Ru and Ni–Ru systems were performed in Refs. [1–3]. However, the authors of these papers employed various models for the calculation of the alloy phase diagrams; this is why we cannot use their results directly for the evaluation of phase equilibria in the ternary system Ti–Ni–Ru. Therefore, in this investigation repeated calculations for confining binary systems were carried out by means of a single model.

For thermodynamic calculation of phase equilibria in the quasibinary system TiNi–TiRu interaction parameters for interaction in liquid and solid phases are required.

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2. Optimization

The chemical Gibbs potential for binary solutions is described in the quasisubregular model by the formula:

$$G = G_1 x + G_2(1-x) + G_{112}x^2(1-x) + G_{122}x(1-x)^2 + G_{1122}x^2(1-x)^2 + RT(x \ln x + (1-x)\ln(1-x)), \quad (1)$$

where G_1 and G_2 are the Gibbs potentials of the pure components, which depend on temperature following the formula:

$$G_i = A_i + B_i T + C_i T \ln T + D_i T^2, \quad (2)$$

where A_i, B_i, C_i and D_i are characteristic constants of the elements; x is the atomic fraction of component 1; T is the temperature in Kelvin; G_{ijk} and G_{ijkl} can be expressed as polynomes, which depend on temperature following:

$$G_{ijk} = A_{ijk} + B_{ijk}T + C_{ijk}T \ln T + D_{ijk}T^2, \quad (3)$$

where A_{ijk}, B_{ijk}, C_{ijk} and D_{ijk} are interaction parameters for a given solution.

The thermodynamic condition of equilibrium between two binary solutions is the equality of the chemical potentials of their components:

$$\begin{cases} \mu_1^{\mathrm{I}} = \mu_1^{\mathrm{II}}, \\ \mu_2^{\mathrm{I}} = \mu_2^{\mathrm{II}} \end{cases} \quad (4)$$

where μ_j^i are the chemical potentials of component j in phase i. The chemical potentials for the components of a solution are obtained by means of differentiating Eq. (1).

Thermodynamic potentials of the compounds are represented by the formula:

$$G_0 = A_0 + b_0 T + C_0 T \ln T + D_0 T^2, \quad (5)$$

where A_0, B_0, C_0 and D_0 are the stability constants of the compound.

The thermodynamic condition of equilibrium for a solution with a constant composition phase is:

$$G_0 = \mu_1 x_0 + \mu_2(1-x_0), \quad (6)$$

where G_0 is the thermodynamic potential for the constant composition phase and μ_1 and μ_2 are the chemical potentials of the phase components.

As well as in a binary system we used the thermodynamic Gibbs potential for variable composition phases in a ternary system following the formula:

$$G = G_1 x + G_2 y + G_3 z + G_{112}x^2 y + G_{122}xy^2 + G_{133}xz^2 + G_{113}x^2 z + G_{223}y^2 z + G_{233}yz^2 + G_{1122}x^2y^2 + G_{1133}x^2z^2 + G_{2233}y^2z^2 + G_{1123}x^2yz + G_{1223}xy^2z + G_{1233}xyz^2 + RT(x \ln x + y \ln y + z \ln z), \quad (7)$$

where G_1, G_2 and G_3 are the Gibbs potentials for the pure components, which depend on temperature as in Eq. (2); T is the temperature in Kelvin; G_{ijk} and G_{ijkl} (G_{112}, G_{122}, G_{133}, G_{113}, G_{223}, G_{233}, G_{1122}, G_{1133}, G_{2233}, G_{1223}, G_{1123}, G_{1233}) are the polynomes, which depend on temperature in the same manner as in Eq. (3).

The Gibbs potentials for the solid phase in the quasibinary system TiNi–TiRu are described by the formula:

$$G = G_1 x + G_2 y + G_{112}x^2 y + G_{122}xy^2 + G_{1122}x^2y^2 + RT(x \ln x + y \ln y), \quad (8)$$

where x is the composition of TiNi; G_1 and G_2 are the Gibbs potentials for TiRu and TiNi, which depend on temperature as in Eq. (5); G_{112} and G_{122} can be expressed as polynomes, which depend on temperature as in Eq. (3).

Table 1
Interaction parameters for the binary system Ti–Ni

Phase	Gibbs potential	A (J mol^{-1})	B (J mol^{-1} K^{-1})	C (J mol^{-1} K^{-1})	D (J mol^{-1} K^{-2})
L	G_{112}	−112804.82	29.24616	0	0
L	G_{122}	−188008.04	54.30832	0	0
α	G_{112}	−44287.64	29.24616	0	0
α	G_{122}	−44287.64	29.24616	0	0
β	G_{112}	−81910.168	29.24616	0	0
β	G_{122}	−209292.04	54.30832	0	0
γ	G_{112}	−90244.696	29.24616	0	0
γ	G_{122}	−182158.8	54.30832	0	0
Ti_2Ni	G_0	−26927.805	116.3223	−21.52417	-4.1124×10^{-3}
TiNi	G_0	−4, 706.112	135.5544	−23.65863	-3.5743×10^{-3}
$TiNi_3$	G_0	−35310.24	156.3288	−26.86044	-2.7677×10^{-3}

Equalities of chemical potentials in coexisting phases for the quasibinary system TiNi–TiRu are described by the expressions:

$$\begin{cases} m_1 = \mu_1 x_1 + \mu_2 y_1 + \mu_3 z_1, \\ m_2 = \mu_1 x_2 + \mu_2 y_2 + \mu_3 z_2, \end{cases} \quad (9)$$

and m_1 and m_2 are the chemical potentials of TiNi and TiRu, which are described by the formulas:

$$m_1 = G + G'y, \quad (10)$$

$$m_2 = G - G'x, \quad (11)$$

and μ_1, μ_2 and μ_3 are the chemical potentials for the components, which are expressed as:

$$\mu_1 = G + \frac{dG}{dx} - \lambda,$$

$$\mu_2 = G + \frac{dG}{dy} - \lambda,$$

$$\mu_3 = G + \frac{dG}{dz} - \lambda,$$

where

$$\lambda = x\frac{dG}{dx} + y\frac{dG}{dy} + z\frac{dG}{dz};$$

x_1, y_1, z_1 and x_2, y_2, z_2 are the coordinates of TiNi and TiRu.

3. Results of optimization and discussion

Thermodynamic data [4,5] for the enthalpy of formation of TiRu, Ti_2Ni, TiNi and $TiNi_3$ were used for the calculation of the stability constants of these compounds. It was accepted that TiRu, Ti_2Ni, $TiNi_3$ and TiNi are the constant composition phases.

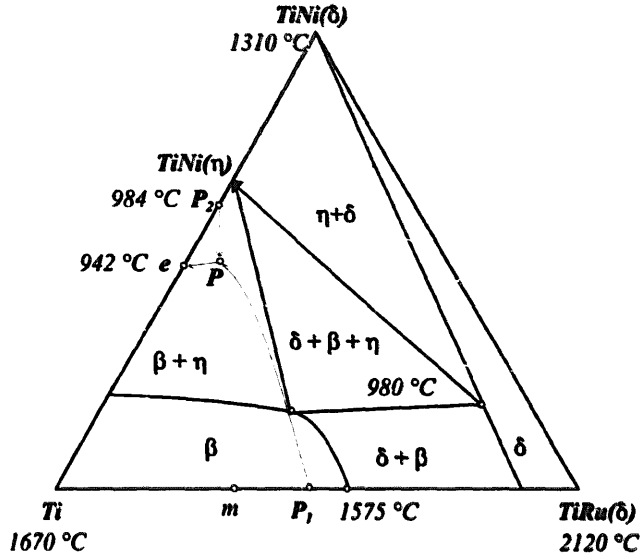

Fig. 1. Preliminary version of the Ti–Ni–Ru alloy phase diagram in the Ti–TiNi–TiRu region [9].

Gibbs potentials of variable composition phases, based on ⟨Ti⟩, ⟨Ru⟩, ⟨Ni⟩ and liquid (for the Ti–Ni and Ni–Ru systems), were described as an approximation of subregular solutions (G_{112}, G_{122} interaction parameters are not equal to zero); the Ti–Ru system was calculated previously as an approximation of a quasisubregular solution. The model of quasisubregular solutions is shown to account for the Gibbs potentials of variable composition phases, based on L, if the interaction parameters G_{112}, G_{122} and G_{1122} are taken

Table 2
Interaction parameters in the binary system Ti–Ru

Phase	Gibbs potential	A (J mol^{-1})	B (J mol^{-1} K^{-1})	C (J mol^{-1} K^{-1})	D (J mol^{-1} K^{-2})
L	G_{112}	264 403.12	−243.14865	0	0
L	G_{122}	−387 737.47	0	0	0
L	G_{1122}	188 280	104.6	0	0
α	G_{112}	−171 605.14	−66.771924	0	0
α	G_{122}	317 467.52	0	0	0
β	G_{112}	3 043 170	−1863.1626	0	0
β	G_{122}	−2 117 416.7	946.34122	0	0
β	G_{1122}	578 611.88	0	0	0
TiRu	G_0	−79 137.129	119.74866	−21.937379	-4.1446×10^{-3}

Table 3
Interaction parameters in the binary system Ni–Ru

Phase	Gibbs potential	A (J mol^{-1})	B (J mol^{-1} K^{-1})	C (J mol^{-1} K^{-1})	D (J mol^{-1} K^{-2})
L	G_{112}	26 186.358	−13.95615	0	0
L	G_{122}	237 983.82	−121.1603	0	0
α	G_{112}	−5705.2521	343.55451	−44.790138	0
α	G_{122}	−684.45219	343.55451	−44.790138	0
γ	G_{112}	60 014.961	250.13165	−37 932813	0
γ	G_{122}	8515.7788	121.24311	−15.756023	0

Table 4
Interaction parameters in the liquid phase in the ternary system Ti–TiNi–TiRu

Phase	A_{1123} (J mol^{-1})	A_{1223} (J mol^{-1})	A_{1233} (J mol^{-1})
L	−418400	−292880	−292880

Table 5
Interaction parameters in the solid phase in the quasibinary system TiNi–TiRu

Phase	A_{112} (J mol^{-1})	A_{122} (J mol^{-1})
S	8368	8368

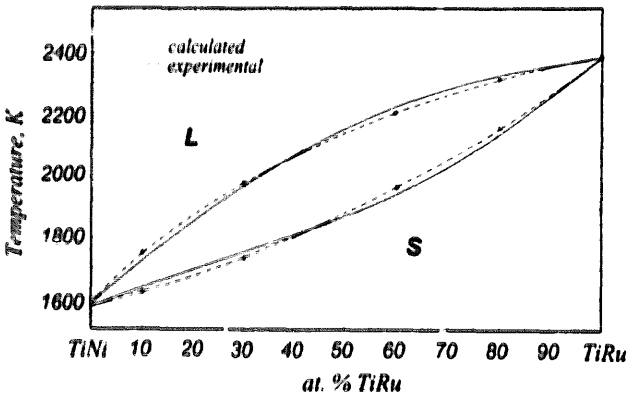

Fig. 2. Comparison of calculated TiNi–TiRu quasibinary system with experimental data.

into consideration. The thermodynamic properties of the elements are represented by Eq. (2). Stability constants for Ti and Ni phases are taken from Ref. [6]. Initial data for the calculation of stability constants for Ru are represented as entropy and enthalpy values, which are given in Ref. [7], and differences of thermodynamic potentials for various phases of Ru are taken from Ref. [8].

So, the basic binary systems calculation (the description of the L phase for all binary systems) needed for the calculation in the ternary system Ti–Ni–Ru was obtained. It is shown in Tables 1–3.

We used experimental data for nonvariant equilibria with the liquid phase [9] in the subsystem Ti–TiRu–TiNi (Fig. 1) in order to obtain a thermodynamic description of the liquid phase in the ternary system. Using data for coordinates of $p.P$ we obtained interaction parameters A^{L}_{1123}, A^{L}_{1223} and A^{L}_{1233} (Table 4).

A thermodynamic description of the solid phase based on Ti($Ni_{1-x}Ru_x$) was obtained using thermodynamic data for TiNi and TiRu (Tables 1 and 2), interaction parameters in the liquid phase, and experimental data for the quasibinary system TiNi–TiRu [10], principally by means of equalities between chemical potentials of the components in the coexisting phases. Interaction parameters in the solid phase are given in Table 5.

Thus, the quasibinary system TiNi–TiRu was calculated using interaction parameters in the liquid and solid phases. A comparison between the calculated and experimental alloy phase diagrams is given in Fig. 2. The good agreement observed between calculated and experimental results indicates that the adopted thermodynamic model is a reasonable approximation. The set of parameters derived from the optimization is thus recommended for use in future studies.

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