

Abstract

The Gallium-Molybdenum binary system (fig.1) [1] has been thermodynamically described and assessed using the CALPHAD (CALculation of PHase Diagrams) approach, and Thermo-calc software package. The Ga-Mo binary system contains five intermetallic compounds, the intermediate phases without a zone of homogeneity: Ga₄₁Mo₈, Ga₃₁Mo₆, Ga₂Mo and GaMo have been treated as stoichiometric phases; while the compound with homogeneity range GaMo₃ was modeled using two-sublattices model [2],[3] as (Ga)_{0.25}:(Ga,Mo)_{0.75}. The liquid phase, the Gallium (Orthorhombic) and Molybdenum (Bcc_A2) were modeled as substitutional solution phases, in which the term ^{ex}G of the Gibbs energy is described, using the linear temperature dependence of Redlich–Kister polynomial [4]. Our assessments are in good agreement with the phase diagram data and the experimental thermodynamic properties available in the literature. The optimization procedure allowed us to calculate for the first time the invariant reactions of this system and the thermodynamic properties of the liquid phase and intermetallic compounds.

Introduction

This work is part of the general framework of materials science and particularly the thermodynamics of phase equilibria. The phase diagrams have always been an important source of information for the development and design of new materials (enthalpy of formation, entropy, activities, etc). But the experimental measurement of these quantities by different experimental methods, in a system with several phases, is not always easy to carry out and requires a lot of material means which are very expensive. So the use of numerical optimization is a method that can meet the current need for characteristics of complex thermodynamic systems. It was made possible by the development of computer science and by the development of software for thermodynamic calculations.

Intermetallic alloys of rare earth metals are of great interest in many technological fields because of their richness in physical properties.

Experimental Details

The investigation of the Ga-Mo binary system was dealt with in a paper by Okamoto et al [1]. The GaMo₃, Ga₄₁Mo₈ and Ga₃₁Mo₆ phases are known from [5], [6] and [7]. Q. Han et al [8] were also experimentally studying the Ga-Mo system by different experimental methods such as X-ray diffraction, metallography and SEM / EDX, and also DTA. Concerning thermodynamic measurements it is very rare, we found just the studies of [8] and [9].

Objective

The scope of the present work is to compile experimental information and to study their consistency in comparison with the calculated results obtained by using CALPHAD approach.

Thermodynamic Models

Unary phases

The Gibbs energy function for the pure element *i*(*i*=Ga, Mo) in its stable or metastable state of the phase ϕ (ϕ =liquid, ORTHO and Bcc_A2) is described by an equation of the following form:

$$G^\phi - H_{SER}^\phi = {}^{ref}G^\phi + {}^{id}G^\phi + {}^{ex}G^\phi$$

$$= a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$$

where $H_i^{SER}(298.15K)$ is the molar enthalpy of the element *i* at 298.15 K in its standard element reference (SER) state and T is the absolute temperature; a, b, c, ..., h are the coefficients.

In the present modeling, the Gibbs energies functions are taken from the SGTE (Scientific Group Thermodata Europe) database compiled by Dinsdale.[10]

Solution phases

The substitutional solution model was employed to describe the liquid phase, its molar Gibbs energy can be expressed as the sum of the reference part, the ideal part and the excess part:

$$G_m^{liquid} = x_{Ga} {}^0G_{Ga}^{liquid} + x_{Mo} {}^0G_{Mo}^{liquid} + RT(x_{Ga} \ln x_{Ga} + x_{Mo} \ln x_{Mo}) + {}^{ex}G_m^{liquid}$$

where R is the ideal gas constant, T is the temperature in Kelvin, x_{Ga} and x_{Mo} are the mole fraction of the elements Ga and Mo, respectively.

The excess Gibbs energy, ${}^{ex}G_m^{liquid}$ is described by the Redlich–Kister polynomial [4] as follow

$${}^{ex}G_m^{liquid} = x_{Ga} x_{Mo} \sum_{i=0}^n {}^iL^{liquid} (x_{Ga} - x_{Mo})^i$$

with ${}^iL^{liquid}$ the interaction parameters between components Ga and Mo, is taken as a linear function of temperature

$${}^iL^{liquid} = a_i + b_i T$$

Where a and b two constants to be optimized in the present work.

Intermetallic compounds

In the Ga-Mo binary system four intermediates phases treated as stoichiometric phases. The Gibbs energy per mole of formula unit $G_{Ga_p Mo_q}$ is expressed as follows:

$$G_{Ga_p Mo_q}^{Ga_p Mo_q} = pGH_{SER}_{Ga} + qGH_{SER}_{Mo} + \Delta G_f^{Ga_p Mo_q} \quad \text{With } \Delta G_f^{Ga_p Mo_q} = a + bT$$

where GH_{SER}_{Ga} and GH_{SER}_{Mo} are the Gibbs energy of the pure elements Ga and Mo, respectively; a and b are optimized for each of the compounds in the present work.

Intermediate phase with homogeneity range

The GaMo₃ phase is a non-stoichiometric phase with has a large range of homogeneity on the Gallium-rich side. This compound was treated as (Ga)_{0.25}:(Ga,Mo)_{0.75} by a two-sublattice model [2,3]. The Gibbs energy function per mole of the unit of formula unit is given by the following equation:

$${}^0G_m^{GaMo_3} = Y_{Ga} {}^0G_{Ga:Mo}^{GaMo_3} + Y_{Mo} {}^0G_{Ga:Mo}^{GaMo_3} + RT(Y_{Ga} \ln Y_{Ga} + Y_{Mo} \ln Y_{Mo}) + Y_{Ga} Y_{Mo} \sum_i L_{Ga:Ga,Mo} (Y_{Ga} - Y_{Mo})^i$$

With x_{Ga} and x_{Mo} are the site part of constitutive Ga and Mo situated on two sublattices.

Assessment procedure

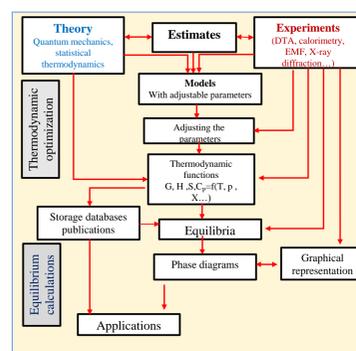


Fig. 1 Diagram illustrating the computer coupling of phase diagrams and thermochemistry approach.

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 Jansson [11] and Sundman et al. [12]. The program works by minimizing an error sum where each of the selected values is 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. Fig. 1 show an organigramme with different steps of CALPHAD method.

Results and Discussion

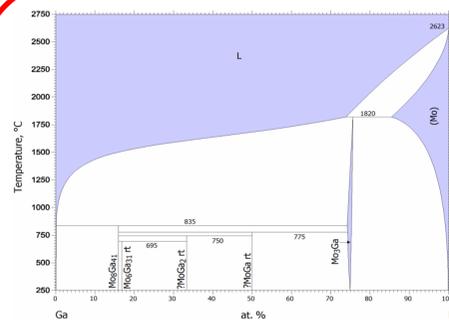


Fig. 2 The experimental phase diagram of the Ga-Mo binary system given by [1]

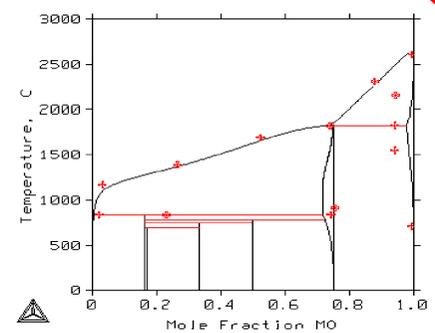


Fig. 3: Phase diagram calculated in this work compared with the experimental results drawn in the literature.

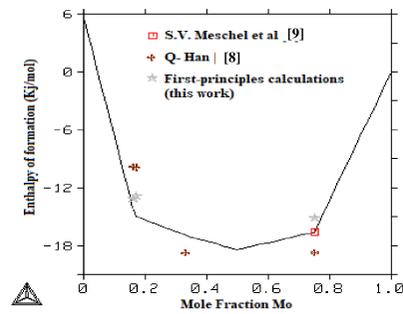


Fig. 4 Comparison between the enthalpies of formation of the intermetallic compounds calculated in this work with the experimental data.

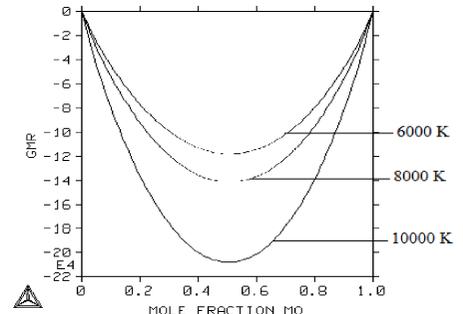


Fig. 5 Calculated Gibbs free energy of mixing (in J/mol.at) of the liquid phase at different temperatures (6000 K, 8000 and 10000 K).

Conclusion

The experimental data of the phase equilibria and the thermodynamic properties in the Ga-Mo system were critically evaluated. Based on the experimental measurements available in literatures, a set of self-consistent thermodynamic parameters of Ga-Mo binary systems was obtained. The calculation results agree with the available experimental data.

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