



# Thermodynamic assessment of the terbium–gold binary system



Samira Otmani\*, Kamal Mahdouk

Laboratory of Thermodynamics and Energetics, Faculty of Science, Ibn Zohr University, BP 8106, 80006 Agadir, Morocco

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## ABSTRACT

The Tb–Au system was critically assessed by means of the CALPHAD technique. The liquid and the solid solution phases, fcc\_A1, bcc\_A2 and hcp\_A3, were treated with the substitutional solution model. The binary intermetallic compounds were treated as stoichiometric phases. All the thermodynamic parameters of various phases have been optimized and the calculated results are in reasonable agreement with experimental data.

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## 1. Introduction

Because of their magnetostriction property, Tb–Au alloys [1] are widely used as anti-theft markers for the sensing of physical parameters (pressure, temperature, liquid viscosity and density, fluid flow rate, humidity and gas sensing) [2]. Exposure to a time-varying magnetic field produces longitudinal vibrations in these sensors that, in turn, generate elastic waves. The elastic waves within the magnetostrictive magnetoelastic material generate a magnetic flux that can be detected remotely [3].

On the other hand gold–rare earth alloys are widely used in the industry especially in the Micro-Electro-Mechanical Systems (MEMS) packaging in order to promote bonding [4–6] and used also such electrolytes in the electronics industry [7]. In addition to their use in the green component in trichromatic lamps [8] we found them used also in the bulk of materials or at the contact surface in order to protect them against corrosion in various environments [9].

To develop an optimum material, it is essential to be able to predict its microstructure and its thermodynamic properties, but the experimental study of those alloys requires very long and very expensive process, hence the utility of the assessment which is the approach that meet those needs especially complex thermodynamic systems characterized by their high number of constituents including Tb–Au binary system assessed in this work. In this sense we found in the literature some phase diagram assessments for

binary systems involving gold and rare earth metals which are numerous but far from to be completed [10–13], which encouraged us to carry out the present work.

The aim of this work is to compile all the available experimental information, to confirm its consistency and to create an optimized set of data by using the CALPHAD (CALCulation of PHase Diagram) approach. In this method, the thermodynamic properties of the alloy systems are studied using thermodynamic models for the Gibbs energy of the available phases. The thermodynamic parameters involved in the models are optimized on the basis on experimental data and the phase diagram information from the literature.

## 2. Experimental information from the literature

The entire phase diagram for Au–Tb system had not been established before 1987, either experimentally or by thermodynamic calculations. In the following, we present the partial and lacunar data available before this date: Firstly Rider et al. [14] determined the terminal solid solubility of Tb in Au by means the lattice parameter method. Then McMasters et al. [15] determined experimentally the congruent melting behavior of the equiatomic TbAu phase and suggested a melting point of 1623 °C. In addition, the crystal structures of the seven intermetallic compounds: Tb<sub>2</sub>Au, αTbAu, βTbAu, TbAu<sub>2</sub>, TbAu<sub>3</sub>, Tb<sub>14</sub>Au<sub>51</sub> and TbAu<sub>6</sub> have been reported by means both powder and single crystal X-ray diffraction methods.

The first thermodynamic assessment of the Tb–Au system based on the available information was carried out in 1987 by Gschneidner et al. [16]. Later, in 2000 Saccone et al. [17] re-

\* Corresponding author.

E-mail address: [samira.otmani@edu.uiz.ac.ma](mailto:samira.otmani@edu.uiz.ac.ma) (S. Otmani).

established experimentally the phase relationships in this system by means the differential thermal analysis (DTA), X-ray diffraction (XRD), light optical microscopy (LOM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). Two new phases were reported they are:  $Tb_7Au_{10}$  and  $Tb_3Au_4$ . Fig 1. The 9 compounds and 16 invariant reactions established by these authors in Tb–Au system are shown in Table 1.

The unique experimental thermodynamic measurements available in the literature are the standard enthalpies of formation of the three congruent intermediate phases determined by Meschel and Kleppa [18] using direct synthesis calorimetry at  $1373 \pm 2$  K. The measured quantities are:  $-86.5 \pm 2.2$  kJ/mol,  $-81.2 \pm 1.8$  kJ/mol and  $-66.5 \pm 1.7$  kJ/mol respectively for  $TbAu$ ,  $TbAu_2$  and  $TbAu_3$ . In Table 2, we summarize the known crystallographic structure data for the Tb–Au phases.

### 3. Thermodynamic models

The thermodynamic parameters of each phase in the Tb–Au system were optimized using the PARROT [19] module of Thermo-Calc [20] software. In this module, the selected literature data were used as input for optimization by means the CALPHAD method. The philosophy of this technique is to obtain a consistent description of the phase diagram and the thermodynamic properties of stable phases in regions without or with little experimental information and for metastable states during simulations of phase transformations.

In the CALPHAD method, one collects and assesses all available experimental and theoretical information available on phase equilibria and thermochemical properties for the studied system. The thermodynamic properties of each studied phase are then described through the Gibbs free energy, applying a mathematical model containing adjustable parameters. These parameters are evaluated by optimizing the fit of the selected model to all the assessed information relative to the coexisting phases. Following this it is possible to calculate the phase diagram, as well as the

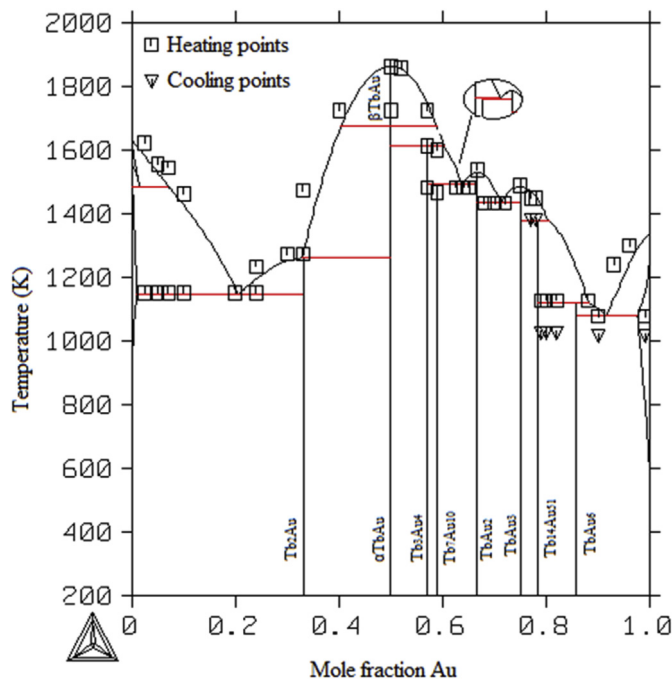


Fig. 1. Calculated Au–Tb phase diagram compared with the experimental results of Saccone et al. [17].

thermodynamic properties of all the phases and the system as a whole, and as a project to build multicomponent phase diagrams containing Au and Tb elements.

The modeling procedure includes several steps. First, the creation of the TDB file in which the Gibbs energy function of pure elements are recuperated from the Thermo-Calc database [22] while the Gibbs energies of the studied phases are mathematically expressed by means of a Redlich–Kister formalism [21] generating parameters to be optimized. The available experimental thermodynamic quantities and phase diagram information are expressed in POP files. Then the thermodynamic parameters were evaluated using a recurrent runs of the PARROT module of the Thermo-Calc software [20]. As a first step, we introduce a file in which we express the stability of the liquid phase and in order to avoid its demixing especially at high temperatures. For this reason, a positive curvature of the liquidus was added by imposing the additional constraint in the whole atomic composition range up to 4600 K [23,24]. In a next step we introduce the congruent equilibrium occurring in this system. Then we treat each invariant equilibrium separately until a better fit of the experimental phase diagram is reached. Particular attention was given to the evaluation of the optimized parameters at each step of the calculation process and each piece of experimental information is given a certain weight according to its estimated accuracy. The weights were changed systematically during the assessment until most of the selected experimental data were accounted for within the claimed uncertainty limits.

The liquid and the solid solution phases were considered as substitutional solutions. Their thermodynamic excess Gibbs energy was fitted by Redlich–Kister [21] polynomials. The intermetallic compounds were treated as stoichiometric phases.

#### 3.1. Pure elements

The Gibbs energy function:  $G_i^\phi(T) = {}^\circ G_i^\phi - H_i^{SER}(298.15K)$  for the element “i” in the phase  $\phi$  ( $\phi = \text{Liquid, hcp\_A3, fcc\_A1 and bcc\_A2}$ ) is described by an equation of the following form:

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

Where is the molar enthalpy of the element “i” at 298.15 K in its standard element reference (SER) state, hcp\_A3, bcc\_A2 for Tb and fcc\_A1 for Au.

In this work, the Gibbs energy functions are taken from the Scientific Group Thermodata Europe (SGTE) compilation of Dinsdale [22].

#### 3.2. Solution phases

The ( $\alpha$ Tb), ( $\beta$ Tb) and (Au) solution phases and liquid were modeled as substitutional solutions according to the polynomial Redlich–Kister formalism [21]. The Gibbs energy “ $G_m^\phi$ ” of one mol of formula unit of phase  $\phi$  is expressed as the sum of the reference part  $G^{ref\phi}$ , the ideal part  $G^{id\phi}$  and the excess part  $G^{exe\phi}$ :

$$G_m^\phi = {}^{ref}G^\phi + {}^{id}G^\phi + {}^{exe}G^\phi$$

As used in the thermo-calc software [20]:

$${}^{ref}G^\phi(T) = \left( {}^\circ G_{Tb}^\phi(T) - H_{Tb}^{SER}(298.15K) \right) x_{Tb} + \left( {}^\circ G_{Au}^\phi(T) - H_{Au}^{SER}(298.15K) \right) x_{Au}$$

$${}^{id}G^\phi = RT(x_{Tb} \ln x_{Tb} + x_{Au} \ln x_{Au})$$

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