Journal of Alloys and Compounds 683 (2016) 599–609

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Review

Thermodynamic reassessment of the cerium–gold binary system

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ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form
10 May 2016
Accepted 12 May 2016
Available online 15 May 2016

Keywords:
Ce–Au phase diagram
Thermodynamic assessment
CALPHAD method

ABSTRACT

Phase relationships in Ce–Au binary system have been thermodynamically assessed by using the CALPHAD technique through Thermo–Calc software package based on the evaluation of all available experimental data from the published literature. This data concern the phase equilibria and thermodynamic properties of the studied system. The intermetallic compounds Ce_2Au, Ce_9Au_{11}, $CeAu_2$, $Ce_{14}Au_{51}$ and CeAu6 were treated as stoichiometric phases. The two–sublattice energy model was employed to describe the CeAu intermetallic phase which presents a homogeneity range. The solution phases, including liquid, fcc_A1, hcp_A3 and bcc_A2 were treated as substitutional phases. Furthermore, the excess Gibbs energies of the studied phases were expressed with the Redlich–Kister polynomial functions. A set of self–consistent thermodynamic parameters formulating the Gibbs energy of various phases in the Ce–Au system were then obtained. A much better agreement was obtained between the calculated results and the reported experimental data.

Contents

1. Introduction

Gold–Rare Earth Elements (REEs) alloys have been widely used during recent years in the fabrication of modern electronic devices, because of their great proprieties [1–3]. REEs are potential candidate to replace Au or at least to reduce its use in the eutectic Au–20 wt % Sn solders broadly used in electronics industry in order to avoid the scarce resources and high prices of Au as well as the poor mechanical properties of the Au–Sn intermetallic compounds.

Indeed, REEs can refine the mechanical properties and improve the wettability of solders [4] and are also able to enhance the fatigue performance under slow deformation [5–7] by reducing the oxidization of solder and by cleaning the grain boundaries.

The use of REEs in corrosion protection as inhibitors is very attractive because of their non-toxicity, as compared to the common chromate inhibitors [8]. A brief analysis of literature indicates that a protective effect can be provided by small amounts of REEs [8,9]. Furthermore, REEs are becoming increasingly important in the transition to a green economy, due to their crucial role in

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http://dx.doi.org/10.1016/j.jallcom.2016.05.116
0925-8388/

permanent magnets, lamp phosphors, catalysts and rechargeable batteries [10]. On the other hand, the field of starting materials for phosphor preparation, such mixed rare earth oxides, noted a strong evolution particularly in the area of fluorescent lighting devices [11].

The progress in the performance of catalytic systems dictated by the more and more severe regulations planned in Europe and USA to lower the level of pollutant emissions arise the cerium compounds as an interesting candidates owing to their redox properties [11]. For example CeO_2acts as a water gas shift and steam reforming promoter, diminishing the amount of CO and hydrocarbons through their oxidation in globally reducing conditions. Cerium oxide also stabilizes the dispersion of the precious metal particles, avoiding sintering, which would make them inactive [12,13]. It has been widely proved [14] that it is possible to prepare gold nanoparticles deposited on metal oxide supports [15], which exhibit high catalytic activity towards oxidation reactions [16–25]. In addition, gold supported on cerium oxide has been shown to possess high activity for volatile organic compounds (VOC) oxidation [26]. Cerium has been widely used in catalysis to purify vehicle exhausts and becomes the most rare earth oxide for controlling pollutant emission.

The imbalance in the REEs supply and demand has increased the importance of recycling and extraction of REEs. An efficient recycling route has already been developed to separate REEs and noble metals from many electronic applications which have complicated architectures and often contain very small quantities of those alloys [27,28].

An important step in investigating alloy systems is the definition of their phase diagrams. Knowledge of phase equilibria, phase stability, phase transformations are important reference points in the description and understanding both of the fundamental proprieties of the alloys and of their possible technological applications. Hence, the purpose of the current work is to assess the Ce–Au binary system for which the experimental phase diagram was recently reexamined by Lomello–Tafin et al. [29] and to develop a precise thermodynamic description by means of the CALPHAD technique (CALculation of PHAse Diagram) described and presented by Refs. [30,31] and successfully applied in various computer programs in order to give a more complete and consistent description of the phases existing in the studied system and their stability. The thermodynamic optimization of the Ce–Au system is part of a research program, carried out in our laboratory, and it focuses on the study of the interaction between rare earth elements and the noble metals.

2. Review of experimental data

The first version of the Ce–Au phase diagram was experimentally determined by Vogel and Heumann [32] who reported the existence of four compounds: Ce_2Au, CeAu, $CeAu_2$ and $CeAu_3$ as well as the invariant reactions involved by these phases. Mcmasters et al. [33] investigated the crystal structures of the Ce–Au intermetallic compounds, particularly in the rich gold part, except for $CeAu_6$. They found that the previously accepted $CeAu_3$ phase turned out to be a $CeAu_{3.6}$ compound confirming the already experimental results of Donolato and Steeb [34]. By means of X–Ray Diffraction (XRD), Gschneidner et al. [35–37] reinvestigated the crystal structure of $CeAu_{3.6}$ and adopted the $Ce_{14}Au_{51}$ formulation for this phase. Concerning the equiatomic CeAu phase, Mcmasters et al. [33] gave the melting point of βCeAu, and the temperature of the αCeAu ↔ βCeAu allotropic transition. Moreau and Parthé [38] reexamined the crystal structure of CeAu6 and found that this phase is isostructural with PrAu6, which has a monoclinic structure. Later, Ferro et al. [39] observed the existence of a new Ce3Au4 phase with a hexagonal Pu3Au4–type structure. However, in a new version of the Ce–Au phase diagram redrawn by Okamoto [40], the Ce3Au4compound was represented by a dashed line, because no evidence of the existence of this phase was found in the ternary Ce–Sn–Au isothermal section studied by Boulet et al. [41] at 1023 K, and also because no crystal structure data relative to the Ce3Au4 phase were found in the Pearson's Crystal Database [42]. For this reasons, we have not considered this phase in the current optimization, in contrast with the previous work by Dong et al. [43]. Most recently, Lomello–Tafin et al. [29] have reconsidered the Ce–Au system (Fig. 1) using XRD, Differential Thermal Analysis (DTA), Optical and Scanning Electron Microscopy (SEM), Energy–Dispersive X–ray Spectroscopy (EDS) and confirmed the presence of the previously discovered phases except the Ce3Au4 phase for which these authors adopted the Ce9Au11 formula, even if the XRD patterns was indexed in the hexagonal Pu3Pd4 structure type [29]. The melting point of the CeAu2 phase, measured by Ref. [29] was 1479 K, higher by 76 K than the determined one by Vogel et al. [32]. According to [29] the difference may be due to purity of the Cerium used by Ref. [32]. Furthermore, these authors discover the existence of the δCe ↔ γCe + liquid metatectic reaction which occurs at 969 ± 3 K and established the existence of a stability domain for the βCeAu phase which extends up to 52 at.% Au at 1470 K. Lomello–Tafin et al. [29] reported also the existence of a $\alpha Ce_{14}Au_{51} \leftrightarrow \beta Ce_{14}Au_{51}$ transition at 1203 K. The extensive experimental work of [29] gave also the temperatures and compositions of the Ce–Au invariant reactions (Table 4).

The crystal structures of the various phases of the Ce–Au system are shown in Table 1.

Regarding the thermochemical information of the Ce–Au system, only a limited amount of data can be found in literature. The first calorimetric measurements were carried out by Fitzner and Kleppa [44] who reported the standard molar enthalpies of formation of the CeAu, $CeAu_2$ and $Ce_{14}Au_{51}$ phases as well as the enthalpies of mixing of the liquid phase. Later, Lomello–Tafin et al. [29] measured by means of direct reaction calorimetry at high temperature, the standard enthalpies of formation of the CeAu and $CeAu_2$ phases. Using the same technique, Ferro et al. [39] determined the enthalpy of formation of the Ce_2Au phase at high temperature. Most recently, Janghorban et al. [45] measured at 1123 K, the enthalpies of formation of the CeAu, $CeAu_2$ and $Ce_{14}Au_{51}$ congruent compounds by means of direct reaction calorimetry and deduced their standard enthalpies of formation from the relative enthalpies increment of these phases measured

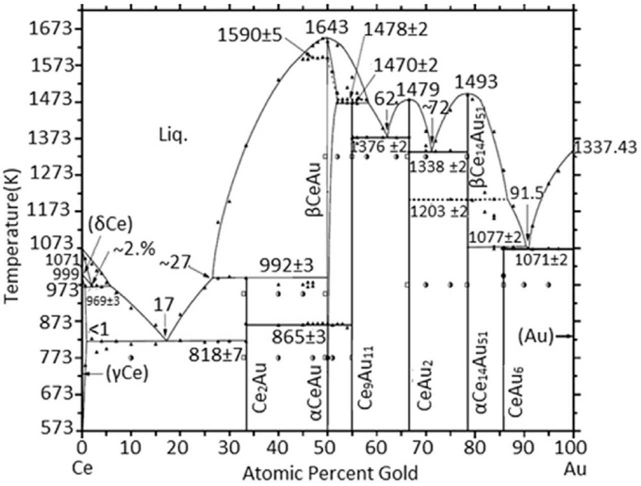

Fig. 1. Experimental Ce–Au phase diagram from Lomello–Tafin et al. [29].