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Phase equilibria and thermodynamic functions for Ag–Hg and Cu–Hg binary systems

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ABSTRACT

In order to facilitate the computational design of new amalgams for novel dental alloys, the phase equilibria, phase diagrams and thermodynamic functions for Ag–Hg and Cu–Hg binary systems are explored in this work, based on the CALPHAD framework and experimental characterizations. The Gibbs free energies of the solution phases as well as the stoichiometric phases are calculated, with the aid of enthalpies of mixing, activities, enthalpies of formation, and phase equilibrium data. The thermodynamic descriptions provided in this work enable the stabilities of each phase at various temperatures and compositions to be well described, which contribute to the establishment of a general database to design novel metallic dental materials.

1. Introduction

Dental amalgams are Hg-containing alloys made by combining Hg with Ag, Sn, Cu and other metallic elements. Being durable, easy-to-use, highly resistant to wear and inexpensive relative to other materials, dental amalgams feature the most thoroughly investigated restorative materials [1,2]. Although some concerns have been raised for the safety of dental amalgams, the presence of other elements renders Hg stable and safe for use, making them continue to be widely used dental materials. Phase equilibria, phase diagrams and their thermodynamic functions are indispensable in materials research and manufacturing to understand the effects from compositions and processing conditions [3], which in turn can be beneficial to harness amalgam properties during their service life. The purpose of this work is to provide contemporary and self-consistent thermodynamic descriptions for the Ag–Hg and Cu–Hg binary systems, based on the CALPHAD (CALculation of PHAse Diagrams) framework.

2. Experimental information

2.1. The Ag–Hg binary system

The phase equilibria, phase diagrams and thermodynamic functions for the Ag–Hg binary system were critically reviewed by Baren [4]. According to this reference, the Ag–Hg binary phase diagram contains one fcc solution phase which is stable within a large concentration range up to 37.3 at.% Hg, one liquid phase, and two intermetallic phases (ζ and γ).

Murphy [5] designed a new technique to overcome the difficulties arising from the difference in the physical properties of Ag and Hg. From the determination of cooling and heating curves, the liquidus between 0 and 91.1 at.% Hg were established. The liquidus around the Hg-rich portion was studied by several investigators, including Joyner [6] from 98.87 at.% Hg to 99.93 at.% Hg, Sunier and Hess [7] from 98.254 at.% Hg to 99.714 at.% Hg, DeRight [8] from 99.7108 at.% Hg to 99.9553 at.% Hg, Maurer [9] from 98.9348 at.% Hg to 99.9597 at.% Hg, Hudson [10] from 71.919 at.% Hg to 99.9442 at.% Hg, and Jangg and Palman [11] from 56 at.% Hg to 99.929 at.% Hg. The solidus and solvus data for Hg in fcc Ag are mainly obtained by Day and Mathewson [12], which were evaluated with the lattice parameters measured in specimens annealed at 549 K and 449 K, respectively. Rayson and Calvert [13] used diffusion couples to retrieve lattice parameters against composition, with the aid of XRD

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(X-ray diffraction). Such results further confirmed the solvus curve from Day and Mathewson [12]. The solubility of Ag in solid Hg, denoted by (Hg) in this work, is relatively small. According to the report of Aleksandrov and Lomonos [14], about 0.02 at.% Ag was identified at 233 K with the relative residual resistance measurement. There exists debate about the crystal structure of ζ. Seeliger and Mücke [15] suggested the composition of $Ag_{11}Hg_9$ for this phase, which is a hexagonal phase. The single-phase region of ζ region extends from 43.5 at.% Hg to 46 at.% Hg at 423 K, according to King and Massalski [16] who determined the precise lattice parameters and composition range of ζ. The crystal structure of γ phase has attracted wide investigation, and the results differ greatly, according to the review of Baren [4]. Jensen [17] utilized a neutron diffraction technique to study the structure of γ single crystals, the results of which confirmed that the $Ag_{11}Hg_{15}$ model with disorder in the 24-fold position is the most likely structure. Based on an isopiestic technique, Rayson and Alexander [18] determined the thermodynamic properties of fcc phase, including the partial Gibbs free energies of Hg at 500 and 600 K, respectively, with the Hg atomic percent ranging from 2 to 34 at.% Hg. The enthalpies of mixing of fcc phase for this concentration range were also presented, where pure fcc Ag and pure liquid Hg were used as the reference state. Hennequm et al. [19] measured the mixing enthalpies of solid Ag powders (5 μm) and liquid Hg, the results of which lead to a value of about −5.8 kJ/mol for 44 at.% Ag (γ phase). Based on such reported enthalpies for the γ phase formation as well as the temperature dependence of the Ag solubility, Guminski [20] reported the partial molar enthalpies for Ag, the value of which is 3 kJ/mol. This is related to the formation of a dilute solution from pure Ag and liquid Hg. Niessen et al. [21] also proposed a value of 8 kJ/mol for the partial molar enthalpies of Ag by the cellular model. Conant and Swofford [22] studied the activities of Hg in Ag–Hg melts at 523 K with the aid of vapor pressures measured over Ag–Hg and Hg melts. The molar fractions of Hg varied from 0.96146 to 0.99172, and the identified Hg activities in Ag–Hg melts around the Hg-rich portion show a negative deviation from the ideal solution behavior.

2.2. The Cu–Hg binary system

The phase equilibria, phase diagrams and thermodynamic functions for the Cu–Hg binary system were critically reviewed by Chakrabarti and Laughlin [23]. According to this reference, the Cu–Hg binary phase diagram is characterized by a wide miscibility gap in the liquid phase at high temperatures, and a fcc solid solution, the solubility of which is significantly smaller than that of the Ag–Hg binary system. In addition, a rhombohedral intermediate phase, denoted by Cu_7Hg_6, forms peritectically by the reaction between Cu–Hg melts and fcc phase. The liquidus around the Hg-rich portion was determined by Jangg and Palman [24]. The Cu-saturated melts equilibrated at different temperatures were analyzed chemically to explore the concentrations of the liquidus. The liquidus, solvus and solidus were established by Lugscheider and Jangg [25], based on DTA (Differential Thermal Analysis), chemical analysis, fusion and XRD. The solubility of Cu in liquid Hg at room temperature has been reported by Jangg and Palman [24], Humphreys [26], Richards and Garrod-Thomas [27], Irvin and Russell [28], and Strachan and Harris [29] by the direct method, and by Tammann and Kollmann [30], Jangg and Kirchmayr [31], Chao and Costa [32], Levitskaya and Zebreva [33], and Baletskaya et al. [34] by the calorimetric method, and by Liebl [35] by the colorimetric method. Those scattered values are characterized by higher Cu contents, likely due to incomplete filtration of Cu–Hg melts. The liquidus around the Hg-rich portion was investigated by Lange et al. [36] from 333 to 373 K, with the electrometric method. There has been no experimental report for the thermodynamic data of this binary system, except for the Gibbs free energies of formation for Cu_7Hg_6, which were derived by Lugscheider and Jangg [25] from thermal analysis.

3. Model description

The liquid phase in such two binary systems is modeled with the substitutional solution model, in which the Gibbs free energies of 1 mol atoms can be given as:

$$G_{\mathrm{m}}^{liq} = x_{\mathrm{Hg}}^{liq} \cdot {}^{0}G_{\mathrm{Hg}}^{liq} + x_{\mathrm{M}}^{liq} \cdot {}^{0}G_{\mathrm{M}}^{liq} + R \cdot T \cdot (x_{\mathrm{Hg}}^{liq} \cdot \ln x_{\mathrm{Hg}}^{liq} + x_{\mathrm{M}}^{liq} \cdot \ln x_{\mathrm{M}}^{liq}) + {}^{ex}G_{\mathrm{m}}^{liq}, \tag{1}$$

where M denotes Ag or Cu; ${}^{0}G_{\mathrm{Hg}}^{liq}$ and ${}^{0}G_{\mathrm{M}}^{liq}$ are the molar Gibbs free energies of pure liquid Hg and pure liquid M, respectively; x_{Hg}^{liq} and x_{M}^{liq} stand for the molar fractions of Hg and M in the liquid phase, respectively; T is the absolute temperature; R is the gas constant; the molar excess Gibbs free energies, denoted by ${}^{ex}G_{\mathrm{m}}^{liq}$, are expressed by the Redlich–Kister polynomial as follows:

$${}^{ex}G_{\mathrm{m}}^{liq} = x_{\mathrm{Hg}}^{liq} \cdot x_{\mathrm{M}}^{liq} \cdot \sum_{i} {}^{i}L_{\mathrm{Hg,M}}^{liq} \cdot (x_{\mathrm{Hg}}^{liq} - x_{\mathrm{M}}^{liq})^{i}, \tag{2}$$

where ${}^{i}L_{\mathrm{Hg,M}}^{liq}$ (i = 0, 1, 2,. . .) are the binary interaction parameters, which are usually temperature-dependent and can be expressed by:

$${}^{i}L_{\mathrm{Hg,M}}^{liq} = a_{i}^{liq} + b_{i}^{liq} \cdot T, \tag{3}$$

where a_{i}^{liq} and $b_{i}^{liq}\cdot$ are the parameters associated with enthalpies and entropies for the liquid phase, respectively.

The fcc phases in both binary systems are also modeled with the substitutional solution model, the molar Gibbs free energies of which can be expressed as:

$$G_{\mathrm{m}}^{fcc} = x_{\mathrm{Hg}}^{fcc} \cdot {}^{0}G_{\mathrm{Hg}}^{fcc} + x_{\mathrm{M}}^{fcc} \cdot {}^{0}G_{\mathrm{M}}^{fcc} + R \cdot T \cdot (x_{\mathrm{Hg}}^{fcc} \cdot \ln x_{\mathrm{Hg}}^{fcc} + x_{\mathrm{M}}^{fcc} \cdot \ln x_{\mathrm{M}}^{fcc}) + {}^{ex}G_{\mathrm{m}}^{fcc}, \tag{4}$$

where ${}^{0}G_{\mathrm{Hg}}^{fcc}$ and ${}^{0}G_{\mathrm{M}}^{fcc}$ are the molar Gibbs free energies of pure fcc Hg and pure fcc M, respectively; x_{Hg}^{fcc} and x_{M}^{fcc} stand for the molar fractions of Hg and M in fcc phase, respectively; the molar excess Gibbs free energies, denoted by ${}^{ex}G_{\mathrm{m}}^{fcc}$, are expressed by the Redlich–Kister polynomial as:

$${}^{ex}G_{\mathrm{m}}^{fcc} = x_{\mathrm{Hg}}^{fcc} \cdot x_{\mathrm{M}}^{fcc} \cdot \sum_{i} {}^{i}L_{\mathrm{Hg,M}}^{fcc} \cdot (x_{\mathrm{Hg}}^{fcc} - x_{\mathrm{M}}^{fcc})^{i}, \tag{5}$$

where ${}^{i}L_{\mathrm{Hg,M}}^{fcc}$ (i = 0, 1, 2. . .) are the interaction parameters defined by:

$${}^{i}L_{\mathrm{Hg,M}}^{fcc} = a_{i}^{fcc} + b_{i}^{fcc} \cdot T, \tag{6}$$

where a_{i}^{fcc} and b_{i}^{fcc} are the parameters associated with enthalpies and entropies for the fcc phase, respectively.

The three intermetallic phases, $Ag_{11}Hg_9$ and $Ag_{11}Hg_{15}$ in the Ag–Hg binary system and Cu_7Hg_6 in the Cu–Hg binary system, are treated as stoichiometric phases, whose Gibbs free energies for one mole formula unit are given as follows, respectively:

$$G_{\mathrm{m}}^{\mathrm{Ag_{11}Hg_{9}}} = 11\,{}^{0}G_{\mathrm{Ag}}^{fcc} + 9\,{}^{0}G_{\mathrm{Hg}}^{rho} + a^{\mathrm{Ag_{11}Hg_{9}}} + b^{\mathrm{Ag_{11}Hg_{9}}} \cdot T \tag{7}$$

$$G_{\mathrm{m}}^{\mathrm{Ag_{11}Hg_{15}}} = 11\,{}^{0}G_{\mathrm{Ag}}^{fcc} + 15\,{}^{0}G_{\mathrm{Hg}}^{rho} + a^{\mathrm{Ag_{11}Hg_{15}}} + b^{\mathrm{Ag_{11}Hg_{15}}} \cdot T \tag{8}$$

$$G_{\mathrm{m}}^{\mathrm{Cu_{7}Hg_{6}}} = 7\,{}^{0}G_{\mathrm{Cu}}^{fcc} + 6\,{}^{0}G_{\mathrm{Hg}}^{rho} + a^{\mathrm{Cu_{7}Hg_{6}}} + b^{\mathrm{Cu_{7}Hg_{6}}} \cdot T, \tag{9}$$

where ${}^{0}G_{\mathrm{Ag}}^{fcc}$, ${}^{0}G_{\mathrm{Cu}}^{fcc}$ and ${}^{0}G_{\mathrm{Hg}}^{rho}$ are the molar Gibbs free energies of pure fcc Ag, pure fcc Cu and pure solid Hg with a rhombohedral structure, respectively; $a^{\mathrm{Ag_{11}Hg_{9}}}$, $b^{\mathrm{Ag_{11}Hg_{9}}}$, $a^{\mathrm{Ag_{11}Hg_{15}}}$, $b^{\mathrm{Ag_{11}Hg_{15}}}$, $a^{\mathrm{Cu_{7}Hg_{6}}}$