Comments on the content and use of the noble metal alloy database

Description of Database

The noble metal alloy database originates from a collaboration between
The Spencer Group Inc., Trumansburg, NY, USA and
GTT-Technologies, Herzogenrath, Germany.

The database contains evaluated thermodynamic parameters for alloys of

Ag, Au, Ir, Os, Pd, Pt, Rh, Ru

alloyed amongst themselves and also in alloys with the metals

Al, As, Bi, C, Co, Cr, Cu, Fe, Ge, In, Mg, Ni, Pb, Sb, Si, Sn, Ta, Te, Ti, Tl, Zn, Zr.

The evaluated parameters in the Noble Metal Alloys Database are based on data collected from publications and internal project reports or have been assessed as part of the development of the database.

In only a few cases are the assessed parameters based on a large amount of experimental information. For many systems, very few, or even no thermodynamic measurements are available. This has necessitated use of published phase boundary information only, with a combination of estimated and optimized mixing parameters to provide a thermodynamic description of the systems concerned. For some inter-noble metal alloys, where complete ranges of solid and liquid solutions are observed, the descriptions should still be fairly reliable. For others, while a reasonable phase diagram description may have been obtained, the thermodynamic values for the different phases may have large errors associated with them.

The database provides a good starting basis for development of data for higher-order noble metal systems. At the same time, the assessed data it contains for the binary and ternary sub-systems of Au-Pd-Pt-Sn allow calculations relevant to dental alloy development.

Specific information on each alloy system can be obtained from the list of references below.

Database Applications

Noble metals and their alloys have a wide variety of applications and calculations of relevant phase equilibria in a particular case are important e.g. for optimizing suitable alloy compositions or predicting reaction products in chemically aggressive environments.
Some examples of noble metal alloy use are:

- Jewellery and decoration
- Electronic components; micro-electronic contact materials
- Solders and brazes
- Dental alloys
- Fission products
- Catalysts
- New minority alloy components, e.g. in turbine alloys
- Scientific equipment, e.g. thermocouples, crucibles, calorimeters

Because of their value, noble metal alloys undergo extensive recycling. For this reason, information on dilute ranges of impurity elements in precious metals is important with respect to different methods of refining. Among such methods are oxygen refining and some use of halogens. In such cases, the database should be used in conjunction with the SGTE Pure Substances Database to take into account relevant condensed and gaseous oxides and halides.

The database will often be used with one of the noble metals as major component, but in a number of applications, large concentrations of alloying elements are present. For this reason, and whenever possible, the assessed parameters in the noble metal alloys database cover the entire composition range of the alloys involved (see below for information on relevant ranges for specific alloys).

There are very few ternary interaction parameters available in the database and it must be realized that ***calculation of phase boundaries in higher-order systems by combination of binary alloy data only may give very unreliable results***.

In its present stage of development, the database can best be used for calculations relating to Ag-, Au-, Pd- and Pt-rich alloys containing small amounts (3-5%) of impurity or alloying elements.

The critically assessed values for the Au-Pd-Pt-Sn system allow theoretical investigation of phase equilibria in certain dental alloys.

Composition Ranges

Most of the binary alloy systems have been assessed over the entire composition range. Only a few ternary and higher-order parameters are available.

Temperature Ranges

The database is generally valid for the temperature range 300^{o}C to 2500^{o}C. Phase boundaries and thermodynamic properties measured at lower temperatures may not correspond to the equilibrium state of the alloy, even after very long annealing times.

Modeling

The database makes use of the SGTE Pure Element Data and, as such, is compatible with other SGTE Solution and Application Databases.

In the present assessments, some phases with narrow ranges of composition have been simplified to compounds with no compositional variation. Others have been modeled using the compound energy, sublattice formalism.

Systems assessed over complete range of composition:

Ag-Al: Ag-Au: Ag-Bi: Ag-Cu: Ag-Ge: Ag-In: Ag-Ir: Ag-Mg: Ag-Os: Ag-Pb: Ag-Pd: Ag-Pt: Ag-Rh: Ag-Ru: Ag-Sb: Ag-Si: Ag-Sn: Ag-Ti: Ag-Tl: Ag-Zn: Ag-Zr:

Au-Al: Au-As: Au-Bi: Au-C: Au-Cr: Au-Cu: Au-Ge: Au-In: Au-Pb: Au-Pd: Au-Pt: Au-Rh: Au-Ru: Au-Sb: Au-Si: Au-Sn: Au-Te: Au-Ti: Au-Tl:

Pd-Co: Pd-Fe: Pd-Ir: Pd-Ni: Pd-Pb: Pd-Pt: Pd-Ru: Pd-Sn:* Pd-Ti:

Pt-Co: Pt-Cr: Pt-Rh: Pt-Ru: Pt-Sn: Pt-Ta: Pt-Ti:

Rh-Ru: Sn-In: (crude description) **Sn-Zn: In-Zn:**

*** Please note that 2 descriptions of the Pd-Sn system are provided.**

The first description uses a simplified, stoichiometric modeling of the compound phases, which is compatible with the assessed parameters for the Pd-Pt-Sn and Au-Pd-Pt-Sn systems. The compound phases denoted by _gtt should be used with the LIQ-gtt and FCC_gtt phases.

The second description provides a more rigorous modeling of the binary Pd-Sn system. In this case the phases with no additional definition should be used with the LIQUID and FCC phases.

Systems assessed over a partial range of composition:

Au-Zn: to 50 at% Zn (crude description)
Pd-In: to 35 at% In
Pd-Zn: to 50 at% Zn (no reliable phase diagram information available)
Pt-In: to 30 at% In
Pt-Zn: only estimated data for the compounds Pt_3Zn and PtZn

Ag-Cu-Pb: liquid
Au-In-Pb: liquid
Au-Pd-Pt: fcc
Pd-Pt-Sn: liquid, $(Pd,Pt)_2Sn$, $(Pd,Pt)_3Sn_2$, $(PdPt)_5Sn_3$,
Pd-Pt-Ti: (Pd,Pt)Ti, $(Pd,Pt)_3Ti$

Au-Pd-Pt-Sn: (Au,Pd,Pt)Sn, $(Au,Pd,Pt)_3Sn$, $(Au,Pd,Pt)Sn_4$

The phase diagrams of all the binary systems listed above were checked, using FactSage, on 10th June, 2003.

Authorship and Contacts

Ownership of the Noble Metal Alloy Database belongs to The Spencer Group.

For questions relating to the data, please contact Dr. Philip Spencer at The Spencer Group Inc. – Tel. (1)-607-387-4038; FAX (1)-607-387-4039,
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DISCLAIMER

NOBLE METAL ALLOY DATABASE REFERENCE LIST

Pure Element Data

A.T.Dinsdale, SGTE Data for Pure Elements, Calphad **15** (1991) 317-425.

Binary Alloys

Ag-Al: S S Lim, P L Rossiter, J W Tibbals, Calphad **19** (1995) 131-142.

Ag-Au: M.Hassam, J.Agren, M.Gaune-Escard, J.P.Bros, Metall. Trans. **21A** (1990) 1877-1884.

Ag-Bi: P.Y.Chevalier, Thermochimica Acta, **130** (1988) 33-41.

Ag-Cu: Unpublished update by F.H.Hayes using unaries of A.T.Dinsdale from: F. H. Hayes, H. L. Lukas, G. Effenberg, and G. Petzow, Z. Metallkde. **77** (1986) 749-754.

Ag-Ge: P.Y.Chevalier, Thermochimica Acta **130** (1988) 25-32.

Ag-In: P.Y.Chevalier and E.Fischer, private communication to SGTE, 1998.

Ag-Ir: P.J.Spencer, 1998; based on I.Karakaya and W.T.Thompson, Bull.Alloy Phase Diagrams **7** (1986) 359.

Ag-Mg: P.J.Spencer, July 1998.

Ag-Os: P.J.Spencer, 1998; based on I.Karakaya and W.T.Thompson, Bull.Alloy Phase Diagrams **7** (1986) 361.

Ag-Pb: F.H.Hayes, H.L.Lukas, G.Effenberg; Z. Metallkde, 77 (1986) 749-754.

Ag-Pd: P.J.Spencer, 1998, based on I.Karakaya and W.T.Thompson, Bull.Alloy Phase Diagrams 1987, Vol.**8**.

Ag-Pt: P.J.Spencer, 1998, based on I.Karakaya and W.T.Thompson, Bull.Alloy Phase Diagrams **8** (1987) 334.

Ag-Rh: P.J.Spencer, 1998, based on I.Karakaya and W.T.Thompson, Bull.Alloy Phase Diagrams **7** (1986) 362.

Ag-Ru: P.J.Spencer, 1998, based on I.Karakaya and W.T.Thompson, Bull.Alloy Phase Diagrams **7** (1986) 367.

Ag-Sb: Oh, Shim, Lee and Lee, J. Alloys Compounds, **238** (1996) 155-66.

Ag-Si: P.Y.Chevalier, Thermochimica Acta **113** (1988) 33-41.

Ag-Sn: Oh, Shim, Lee and Lee, J. Alloys Compounds **238** (1996) 155-66: Data for fcc phase modified by A.T.Dinsdale due to change in fcc Sn unary data.

Ag-Ti: P.J.Spencer, July 1998, based on J.Murray, Bull.Alloy Phase Diagrams **4** (1983) 178.

Ag-Tl: H.L.Lukas, reassessment based on Zimmerman thesis, MPI, Stuttgart, 1976.

Ag-Zn: T.Gomez-Acebo, Calphad **22** (1998) 203-220.

Ag-Zr: P.J.Spencer, 1998; based on I.Karakaya and W.T.Thompson, J.Phase Equilibria **13** (1992) 143.

Au-Al: J.Murray, A.Okamoto, T.B.Massalski, Bull.Alloy Phase Diags. **8** (1987) 20: Modified by A.T.Dinsdale due to change in SGTE unary data and to prevent high temperature stability of fcc phase.

Au-As: P.J.Spencer, June 1998.

Au-Bi: P.Y.Chevalier, Thermochimica Acta **130** (1988) 15-24.

Au-C: P.J.Spencer, June 1998.

Au-Cr: P.J.Spencer, June 1998.

Au-Cu: B.Sundman, S.G.Fries, W.A.Oates, Calphad **22** (1998) 335-354: Assessment with only parameters for the disordered phases.

Au-Ge: P.Y.Chevalier, Thermochimica Acta **141** (1989) 217-226.

Au-In: I.Ansara, J.P.Nabot, Thermochimica Acta **129** (1999) 89-97.

Au-Pb: J.P.Nabot, Thesis, LTPCM, Grenoble, 1986.

Au-Pd: P.J.Spencer, 1994, based on R.Hultgren et al., `Selected Values of the Thermodynam. Props. of Binary Alloys', ASM, Metals Park, Ohio, 1971.

Au-Pt: P.J.Spencer, 1994, based on R.Hultgren et al., `Selected Values of the Thermodynam. Props. of Binary Alloys', ASM, Metals Park, Ohio, 1971.

Au-Rh: P.J.Spencer, June 1998.

Au-Ru: P.J.Spencer, June 1998.

Au-Sb: P.Y.Chevalier, Thermochimica Acta **155** (1989) 211-225.

Au-Si: P.Y.Chevalier, private communication to SGTE, July, 1998.

Au-Sn: Based on P.Y.Chevalier, Thermochimica Acta **130** (1988) 1-13: Changes to fcc and hcp pure Sn data invoked modification by A.T.Dinsdale of interaction parameters for these phases (April, 1998).

Au-Te: Y.Feutelais, D.Mounai, J.R.Didry, B.Legendre, J.Phase Equilib. **15** (1994) 380: Data for the AuTe2 phase modified by A.T.Dinsdale.

Au-Ti: K.Hack, GTT-Technologies,1996: based on J.Murray, Bull.Alloy Phase Diagrams **4** (1983) 278.

Au-Tl: P.Y.Chevalier, Thermochimica Acta **155** (1989) 211-225.

Au-Zn: P.J.Spencer, 1995. Crude description of Au-rich phase equilibria, but thermodynamic values based on experimental data and probably reasonable.

Ir-Pd: P.J.Spencer, June 1998.

Pd-Co: G.Ghosh, C.Kantner, G.B.Olson, J.Phase Equilibria **20** (1999) 295-308.

Pd-Fe: G.Ghosh, C.Kantner, G.B.Olson, J.Phase Equilibria 20 (1999) 295-308.

Pd-In: P.J.Spencer, 1994. Pd-rich range only, based on C.Colinet, A.Bessoud, A.Pasturel, Z. Metallkunde **77** (1986) 798.

Pd-Ni: G.Ghosh, C.Kantner, G.B.Olson, J.Phase Equilibria 20 (1999) 295-308.

Pd-Pb: G Ghosh, Metall Trans **30A** (1999) 5-18.

Pd-Pt: K.Hack**,** 1995.

Pd-Ru: P.J.Spencer, June 1998.

Pd-Sn: G Ghosh, Metall Trans **30A** (1999) 5-18.

Pd-Sn: M.Kowalski, 1995. Particular emphasis given to the enthalpies of formation of the compounds. Liquidus not so reliable. The data set is consistent with assessments in the Au-Pd-Pt-Sn system.

Pd-Ti: K.Hack, GTT-Technologies,1996, based on J.Murray, Bull.Alloy Phase Diagrams **3** (1982) 329.

Pd-Zn: P.J.Spencer, 1994. Crude evaluation for Pd-rich alloys based on T-H.Chiang, H.Ipser, Y.A.Chang, Z.Metallkunde **68** (1977) 141. No reliable phase diagram information in this region.

Pt-Co: P.J.Spencer, December 2002.

Pt-In: P.J.Spencer, 1994. Pt-rich range only, based on C.Colinet, A.Bessoud, A.Pasturel, Z. Metallkunde **77** (1986) 798.

Pt-Rh: P.J.Spencer, June 1998.

Pt-Ru: P.J.Spencer, June 1998.

Pt-Sn: P.J.Spencer, June 1998. Based on estimated enthalpies of formation of the compound phases (Miedema method).

Pt-Ta: P.J.Spencer, June 1998.

Pt-Ti: K.Hack, GTT-Technologies, 1996, based on J.Murray, Bull.Alloy Phase Diagrams **3** (1982) 321.

Pt-Zn: P.J.Spencer, 1994. Estimated data for Pt3Zn and PtZn only using Miedema method.

Sn-In: P.J.Spencer, 1994. Crude representation of phase equilibria, but thermodynamic values of correct order.

Zn-In: B J Lee, Calphad **20** (1996) 471-480.

Ternary Alloys

Ag-Cu-Pb: F.H.Hayes, H.L.Lukas, G.Effenberg, G.Petzow, Z.Metallkde **77** (1986) 749-754.

Au-In-Pb: J.P.Nabot, Thesis, Grenoble, 1986.

Au-Pd-Pt: A.Forstreuter, 1997. Fcc, based on Z. Metallkde, **46** (1955) Issue 7.

Pd-Pt-Sn: A.Forstreuter, 1997. Liquid, $(Pd,Pt)_3Sn$, $(Pd,Pt)_5Sn_3$, $(Pd,Pt)_3Sn_2$, based on Canadian Mineralogist, 1981, Vol.19.

Pd-Pt-Ti: Pseudo-binary mixtures (Pd,Pt)3Ti and (Pd,Pt)Ti introduced because of identical crystallographic data for binary compounds. Ideal behaviour assumed.

Quaternary Alloys

Au-Pd-Pt-Sn: A.Forstreuter, private communication to GTT, 1997.