Thermodynamic Calculations and Experiments

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- Introduction
- Measurements of phase equilibria and thermodynamic properties
- Compatibility of thermodynamic models of phases
- Descriptions of the Ag-Cu-Zn and Ag-Al-Cu systems

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Determination of tielines by EDX using unidirectional solidification samples
Determination of tietriangle and eutectic composition in Ag-Al-Cu system by WDX and EDX techniques.
Determination of tielines in binary Ag-Al system by annealing/quenching technique
Determination of temperatures of first and second order transitions by DSC and DTA (β-phase of Ag-Cu-Zn system)
Measurement of the enthalpy change upon heating or heat capacity by DSC

Composition in wt.%:
- 14.6Ag-56.8Al-28.6Cu
- 14.2Ag-58.1Al-27.7Cu
- 14.9Ag-52.9Al-27.2Cu
- 27.0Ag-50.4Al-22.6Cu
- 50.4Ag-20.0Al-29.6Cu
- 27.8Ag-23.4Al-48.9Cu
- 42.3Ag-26.2Al-31.5Cu

Points are experimental data
Lines result from CALPHAD description of the Ag-Al-Cu system
Measurement of partial and integral enthalpies of mixing by isoperibolic calorimetry

![Graph showing ternary phase diagrams for different compositions and temperatures.](image-url)
Partial and integral enthalpies of mixing of liquid Ag-Cu-Zn alloys

![Graphs showing partial and integral enthalpies of mixing for Ag-Cu-Zn alloys](image-url)
Indirect measurement of enthalpy of formation of $\beta$- and $\gamma$-alloys of the Ag-Cu-Zn system by dissolution in liquid Zn
Enthalpy of formation at 298 K of $\beta$- and $\gamma$-alloys from fcc-Ag, fcc-Cu and hcp-Zn

\[ \Delta_f H^{\beta(\gamma)}_{298} = x_{Ag} \Delta H_{diss}^{Ag} + x_{Cu} \Delta H_{diss}^{Cu} + x_{Zn} \Delta H_{diss}^{Zn} - \Delta H_{diss}^{\beta(\gamma)} \]

$\beta$-phase

$\gamma$-phase

![Graph showing formation enthalpy vs mole fraction Cu]
Modelling of the $\gamma$-phase

Ag-Zn: Sublattice model $(\text{Ag,Zn})_2(\text{Ag})_2(\text{Ag,Zn})_3(\text{Ag,Zn})_6$ T. Gomez-Acebo, 1998.

Cu-Zn: Sublattice model $(\text{Cu,Zn})_2(\text{Cu,Zn})_2(\text{Cu})_3(\text{Zn})_6$ M. Kowalsky and P.J. Spenser, 1993.

Al-Cu: Sublattice model $(\text{Al})_4(\text{Al,Cu})(\text{Cu})_8$ N. Saunders, 1991.

Al-Cu-Zn: Substitutional, Redlich-Kister P. Liang et al., 1999

Ag-Cu-Zn: Sublattice model, $(\text{Ag,Cu,Zn})_2(\text{Ag,Cu,Zn})_2(\text{Ag,Cu})_3(\text{Zn})_6$ Present description
Binary constituents used in present description of Ag-Cu-Zn system

Comparison of experimental and calculated phase equilibria in alloys with 40wt.% Ag

E. Gerhard, G. Petzow and W. Kraus, 1962
Comparison of experimental and calculated phase equilibria in alloys with 60wt.% Ag

E. Gerhard, G. Petzow and W. Kraus, 1962
Comparison of experimental and calculated phase equilibria in alloys with 40wt.% Cu

E. Gerhard, G. Petzow and W. Kraus, 1962
Comparison of experimental and calculated phase equilibria in alloys with 60wt.% Cu

E. Gerhard, G. Petzow and W. Kraus, 1962
Comparison of calculated isothermal sections with experimental data

E. Gerhard, G. Petzow and W. Kraus, 1962
Comparison of calculated liquidus surface with literature data

E. Gerhard, G. Petzow and W. Kraus, 1962
Directional solidification experiment in Ag-Cu-Zn system

Dendritic divorced eutectic growth

(Ag) -white  (Cu) -black  β-grey

Lamellar eutectic growth
Revised description of binary Al-Cu system

- Enthalpy of formation in kJ mol
- Al (mole fraction)
- Present description
Revised description of binary Ag-Al system

Liquid phase
- Itagaki & Yazava (1969)
- Kawakami (1930)
- Description of Lim et al. (1995)
- Present description

FCC-phase
- Wittig & Schilling (1959)
- Description of Lim et al. (1995)
- Present description

Enthalpy of formation / kJ mol\(^{-1}\)

Al (mole fraction)
Revised description of binary Ag-Cu system
Experimental (points) and calculated (lines) enthalpies of formation of liquid Ag-Al-Cu alloys

standard state: Ag(l), Al(l), and Cu(l)
Vertical sections of 20, 40, 60 and 80 wt.% Ag
Vertical sections of Ag₃Al-Cu (a), CuAl₂- Ag₂Al (b), CuAl₂- Ag₃Al (c) and 90wt.% Cu (d)
Calculated and investigated by Massalski and Perepeenko isothermal sections at 625 and 575 °C
Comparison of assessed and calculated liquidus surface of the Ag-Al-Cu system

Chang et.al. 1979

calculated
Unidirectional solidification experiments in Ag-Al-Cu

Osillatory transition from *two-phase* to *three-phase* coupled zone

$v=0.08$ mm/min