Silver – Aluminium – Copper

K.C. Hari Kumar and Oger Arkens

Literature Data

The liquidus surface and isotherms were investigated by [1930Uen]. In a review article by [1977Cha] these data were corrected in order to be consistent with then accepted binary phase diagrams, especially along the Al-Cu edge. The first evaluation within the ongoing MSIT Evaluation Programs was made by [1990Ark], which is updated by the present work. Employing metallographic technique [1961Pan] determined phase equilibria near the Cu-rich corner at 500 and 700°C. Using optical microscopy, X-ray diffraction and electron microprobe analysis [1973Mas] determined phase relationships in the temperature range 575 to 625°C along the Ag-Cu side of the ternary systems. Their results are generally not in agreement with that of [1961Pan]. They also concluded that small additions of Cu to Ag_3Al(h) phase stabilizes it well below the temperature of existence in the binary. Liquidus in the region Al-Al_2Cu-Ag_2Al was investigated by [1983Liu] using thermal analysis. They identified a ternary eutectic reaction at 500°C and claimed that the section Al_2Cu-Ag_2Al is pseudobinary, with a monovariant maximum at 527°C. [1989Ado1, 1989Ado2] established isothermal phase relationships along the Ag-Cu edge of the ternary at 500, 650 and 850°C by analyzing samples prepared from high purity starting materials, employing X-ray diffraction, metallography, thermal analysis and electron microprobe analysis. Their results are in agreement with that of [1973Mas], except that they could not observe any extended stability for the Ag_3Al(h) phase. The isothermal section at 850°C should be treated as metastable since the fcc miscibility gap originating from Ag-Cu system is still present in the section. Moreover, this section is above the eutectic temperature of the Ag-Cu system and therefore liquid phase also should be present. [2000Fla] measured the partial enthalpies of components in the liquid phase and thereby integral enthalpies of mixing of liquid alloys at 873°C using a drop-calorimeter. Measurements were performed starting from pure Al to about 40 at.% Al along three sections with Ag:Cu ratios of about 1:3, 1:1 and 3:1. The partial enthalpies of mixing of the components of liquid alloys at 979°C were determined using a high-temperature isoperibolic calorimeter [2002Wit]. Measurements were performed starting from both pure Al and from binary liquid Ag-Cu alloys along sections with constant Ag:Cu ratios 1:3, 1:1, and 3:1. The integral enthalpies of mixing of these ternary alloys are calculated from the partial enthalpies of mixing using different methods. It was found that the partial enthalpy of Cu reported by [2000Fla] for all sections from are about 8 $kJ \cdot mol^{-1}$ more negative in comparison with data of [2002Wit].
[1997Lim] modelled the Gibbs energy functions of the stable phases in the ternary system using the Calphad approach. They calculated the isothermal section at 575°C and the liquidus projection pertaining to the Al-corner.

Binary Systems

The binary systems used in the present evaluations are: Al-Cu [2003Gro], Ag-Al [1995Lim] and Ag-Cu [2003Van].

Solid Phases

The known binary phases are listed in Table 1. No ternary phase is formed in the Al-rich corner up to Ag_2Al and to $CuAl_2$, and not at the Ag-Cu-side up to 37 at.% Al, 63 at.% Cu and 50 at.% Ag, 50 at.% Al.

Pseudobinary Systems

The existence of a pseudobinary section Ag_2Al-Al_2Cu is reported by [1983Liu]. Only the monovariant eutectic maximum (e_6, $L \rightleftharpoons \theta+\zeta$) is reported using DTA measurements: 527°C at the composition 21.8Ag-55.8Al-22.4Cu (at.%).

Invariant Equilibria

Certain plausible invariant equilibria in the system were discussed by [1925Got, 1976Mon, 1977Cha]. A ternary eutectic reaction L⇌(Al)+θ+ζ occurring at 500°C is reported by [1983Liu]. Composition of the liquid phase is given in Table 2.

Liquidus Surface

Figure 1 shows the liquidus projection along with few isotherms for the region Al-Al_2Cu-Ag_2Al as investigated by [1983Liu]. Liquidus data reported by [1930Uen] is not used here due to inconsistencies with binary systems. It should be noted that [1930Uen] determined the liquidus projection at a time when little was known about the binary systems and even the liquidus projection proposed by [1977Cha] ignores many reactions originating from the binaries Al-Cu and Ag-Al.

Isothermal Sections

The isothermal section at 625°C in the 0 to 40 at.% Al region is shown in Fig. 2. It is adapted from [1973Mas]. [1973Mas] also reports the 575°C isotherm, which is essentially similar to Fig. 3, except for a small three-phase region (Ag)+β_2+ζ appearing just inside the Ag-Al binary line at about 2.7 at.% Ag. Figure 3 depicts isothermal section at 500°C. It is based on the data from [1989Ado1, 1989Ado2].

Thermodynamics

The evaluated integral enthalpy of mixing of liquid alloys demonstrates that the minimum for the Ag-Al-Cu is at -17.1 $kJ \cdot mol^{-1}$ corresponding to the binary composition Al_4Cu_6. Figure 4 is taken from [2002Wit], that depicts isoenthalpy contours calculated using fitted equations.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ag) < 961.93	*cF*4 $Fm\bar{3}m$ Cu	a = 408.57	pure Ag at 25°C [Mas2]
(Al) < 660.452	*cF*4 $Fm\bar{3}m$ Cu	a = 404.96	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cu) < 1084.62	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 361.46	at 25°C [Mas2] melting point [1994Mur]
β_2, Ag_3Al(h) 600-778	*cI*2 *Im*$\bar{3}$*m* W	*a* = 324	[Mas2] [V-C2], 700°C
μ, Ag_3Al(r) < 450	*cP*20 *P4132* Mn	*a* = 694.2	[Mas2] [V-C2]
ζ, Ag_2Al < 726	*hP*2 *P63/mmc* Mg	*a* = 287.79 *c* = 462.25	22.9-41.9 at.% Al [Mas2] [V-C2] 25°C
β, Cu_3Al 1049-559	*cI*2 *Im*$\bar{3}$*m* W	*a* = 295.64	70.6 to 82 at.% Cu [1985Mur] [1998Liu] at 672°C in β + (Cu) alloy
α_2, $Cu_{1-x}Al_x$ < 363	~$TiAl_3$ long period superlattice	*a* = 366.8 *c* = 368.0	0.22 ≤ *x* ≤ 0.235 [Mas, 1985Mur] at 76.4 at.% Cu (subcell only)
γ_0, $Cu_{1-x}Al_x$ 1037-800	*cI*52 *I*$\bar{4}$*3m* Cu_5Zn_8	-	0.31 ≤ *x* ≤ 0.40 [Mas2] 0.32 ≤ *x* ≤ 0.38[1998Liu]
γ_1, Cu_9Al_4 < 890	*cP*52 *P*$\bar{4}$*3m* Cu_9Al_4	*a* = 870.68 *a* = 871.32	at 33.8 at.% Al [V-C] from single crystal [V-C]
δ, $Cu_{1-x}Al_x$ < 686	*hR** *R*$\bar{3}$*m*	*a* = 1226 *c* = 1511	0.381 ≤ *x* ≤ 0.407 [Mas2, 1985Mur] at *x* = 38.9 [V-C]
ε_1, $Cu_{1-x}Al_x$ 958-848	c**?	-	0.379 ≤ *x* ≤ 0.406 [Mas2, 1985Mur]
ε_2, $Cu_{2-x}Al$ 850-560	*hP*6 *P63/mmc* Ni_2In	*a* = 414.6 *c* = 506.3	0.47 ≤ *x* ≤ 0.78 55.0 to 61.1 at.% Cu [Mas, 1985Mur, V-C2] NiAs in [Mas2, 1994Mur]
ζ_1, ~$Cu_{47.8}Al_{35.5}$(h) 590-530	*oF*88 - 4.7 *Fmm2* $Cu_{47.8}Al_{35.5}$	*a* = 812 *b* = 1419.85 *c* = 999.28	55.2 to 59.8 at.% Cu [Mas2, 1994Mur] structure: [2002Gul]
ζ_2, $Cu_{11.5}Al_9$(r) < 570	*oI*24 - 3.5 *Imm2* $Cu_{11.5}Al_9$	*a* = 409.72 *b* = 703.13 *c* = 997.93	55.2 to 56.3 at.% Cu [Mas2, 1985Mur] structure: [2002Gul]
η_1, CuAl(h) 624-560	*o**32	*a* = 408.7 *b* = 1200 *c* = 863.5	49.8 to 52.4 at.% Cu [V-C2, Mas2, 1985Mur] Pearson symbol: [1931Pre]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
η_2, CuAl(r) < 569	*mC*20 *C2/m* CuAl(r)	*a* = 1206.6 *b* = 410.5 *c* = 691.3 β = 55.04°	49.8 to 52.4 at.% Cu [V-C2]
θ, $CuAl_2$ < 591	*tI*12 *I4/mcm* $CuAl_2$	*a* = 606.3 *c* = 487.2	31.9 to 33.0 at.% Cu [1994Mur] Single crystal [V-C2, 1989Mee]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Ag	Cu	Al
L ⇌ (Al) + θ + ζ	500	E	L	17.5	14.0	68.5

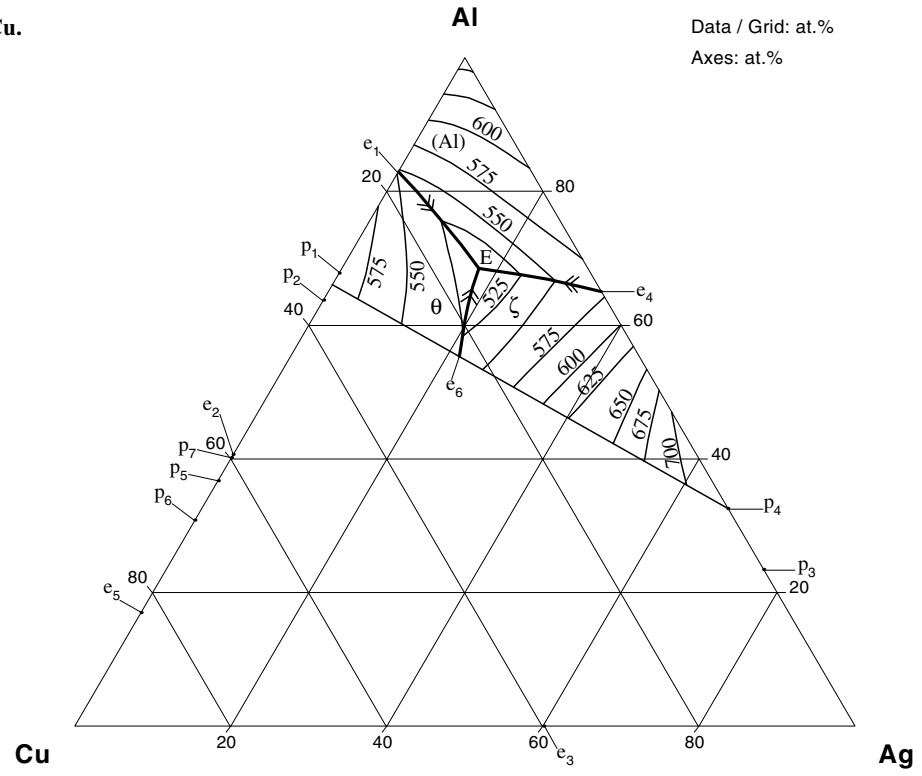

Fig. 1: Ag-Al-Cu.
Liquidus surface

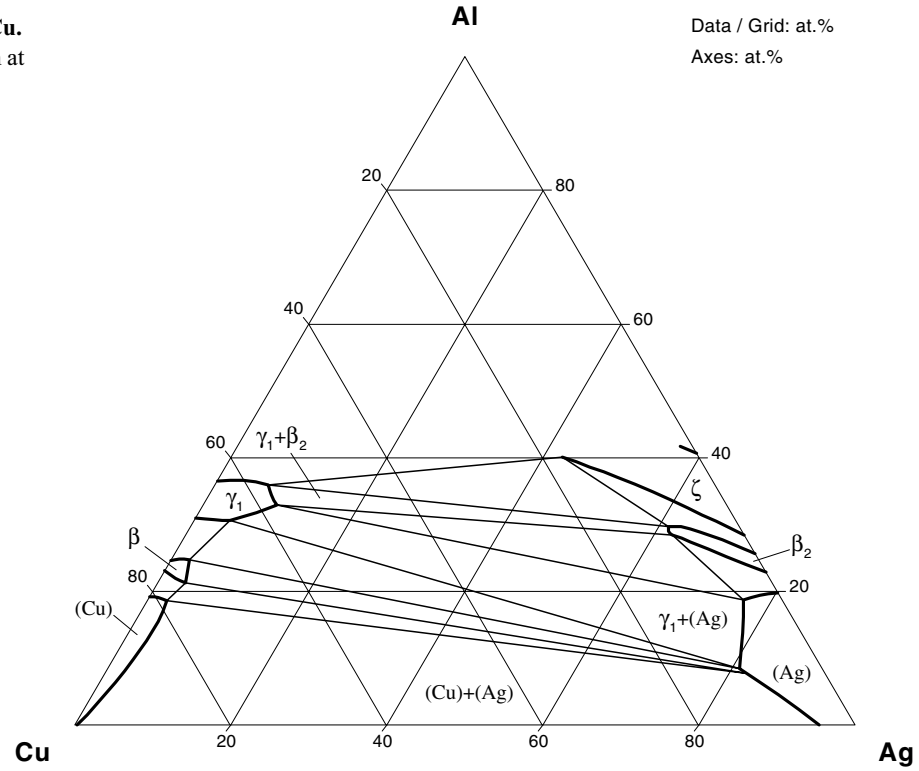

Fig. 2: Ag-Al-Cu. Isothermal section at 625°C

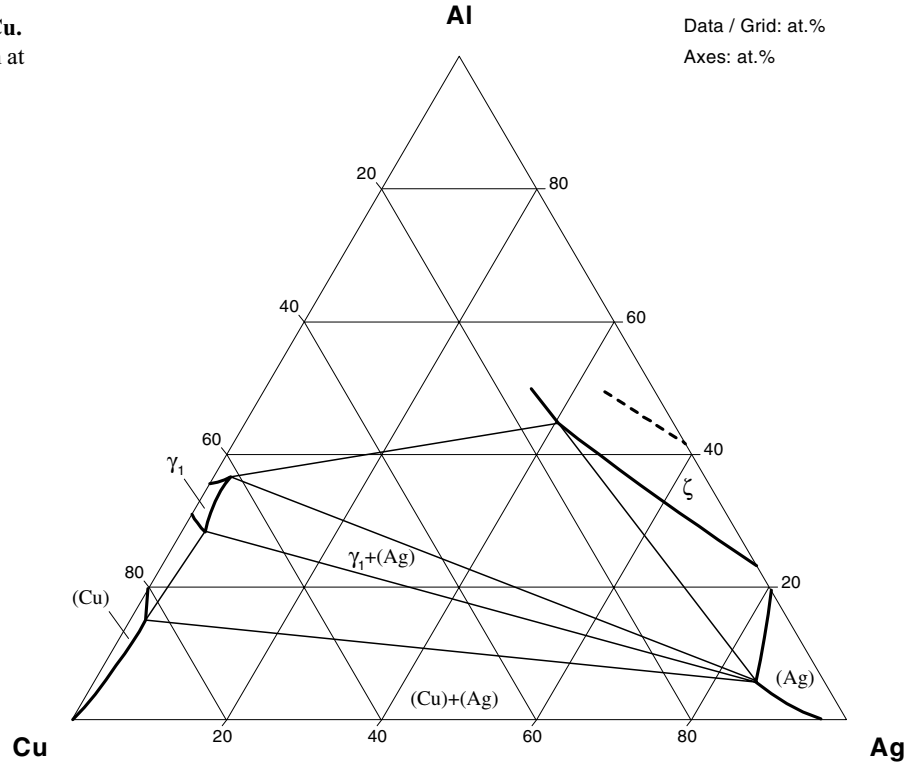

Fig. 3: Ag-Al-Cu. Isothermal section at 500°C

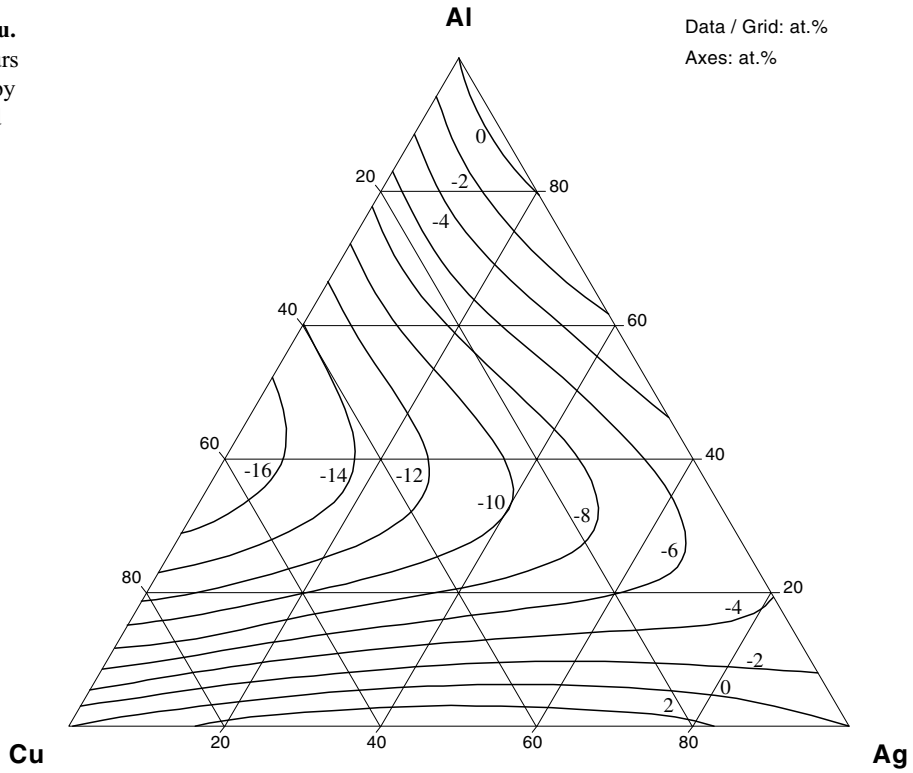

Fig. 4: Ag-Al-Cu. Isoenthalpy contours for integral enthalpy of mixing of liquid alloys at 979°C