16 Ag-Al-Ti

Silver – Aluminium – Titanium

Hans Leo Lukas

Literature Data

Köster and Sampaio [1957Koe] investigated ternary isothermal sections at 800°C, 1000°C and 1100°C by X-ray and metallographic analyses ($x_{Ti} > 25$ at.% and $x_{Ag} < 42$ at.%). At these temperatures they found the binary Al-Ti phases in equilibrium with an Ag-rich melt or with the silver solid solution, (Ag).

Hashimoto et al. [1983Has] determined the 800°C isothermal section (x_{Al} < 75 at.%) and a vertical section from Ti+51 at.% Al to Ag+7.5 at.% Al by electron microprobe, X-ray diffraction, scanning electron microscopy and DTA. These authors analyzed also the ternary solubilities of the (Ag) solid solution at 800°C.

Mabuchi et al. [1990Mab] detected a ternary phase $Ti(Al_{1-x}Ag_x)_3$ of the $AuCu_3$ type (L1₂) with 0.1<x<0.25. This phase has also a considerable homogeneity range with respect to the ratio Ti:(Al+Ag), 25-30 at.% Ti at 1000°C. [1957Koe] did not investigate the area of this phase and [1986Has] investigated one alloy in this area (65 at.% Al+10 at.% Ag), reported it as single phase at 800°C, but interpreted it as a solid solution of the $TiAl_3$ phase.

Several papers [1991Dur, 1992Dur, 1993Nak, 1999Yam] compare $L1_2$ phases $Ti(A1_{1-x}X_x)_3$ with different elements X (Ag, Co, Cr, Cu, Fe, Mn, Ni, Pd, Zn) but similar compositions of X. Yamamoto et al. [1999Yam] reported the homogeneity range of the $L1_2$ phase at 1177°C. Tian and Nemeto [2002Tia] studied the precipitation of TiAl and TiAl₂ from the $L1_2$ phase, homogenized at 1000°C, as well as that of $L1_2$ from TiAl during annealing at lower temperatures (700-900°C). The present evaluation updates that of [1990Luk].

Binary Systems

The three binary systems are accepted from the SGTE assessments in Landolt-Börnstein [2002LB]. For Ag-Ti [2002Li] and Al-Ti [2003Sch] the MSIT Workplace provides assessments with nearly equivalent contents. For Al-Ti the [2003Sch] evaluation states, that there is still some uncertainty, especially on the area between TiAl and TiAl₃.

The Ag-Ti system used by [1957Koe] assumed a much higher temperature of peritectic formation of the Ti_2Ag phase (1280°C) than [2002LB] (940°C).

All three [2002LB] diagrams are based on thermodynamic calculations, two of them published before: Ag-Al [1995Lim], Al-Ti [1998Sau].

Solid Phases

A single ternary phase, τ , of the AuCu₃ (L1₂) type was found near TiAl₃. Like TiAl₃, TiAl₂, Ti₅Al₁₁, TiAl and Ti₃Al it is an ordered form of a close packed crystal structure [1991Dur, 1992Dur]. Some more binary Al-Ti phases between TiAl and TiAl₃ were not considered as stable phases in the accepted binary Al-Ti system. All solid phases regarded to be stable in the Landolt-Börnstein evaluations are summarized in Table 1.

Invariant Equilibria

A tentative reaction scheme was given by [1957Koe]. Due to the discrepancies between the binary systems used by [1957Koe] and those accepted here, it needs modification. Using the approximate thermodynamic description given below in section "Thermodynamics" a tentative reaction scheme above 800° C can be calculated. Figure 1 shows the result. The temperatures and phase compositions of the ternary invariant reactions must be taken as tentative only, therefore no table of invariant reactions is given. Below 800° C the system is nearly degenerate and the reaction scheme is equal to the binary Ag-Al system with either the τ phase or TiAl₃ being in equilibrium with the Ag-Al phases, but not taking part in the reactions.

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After the calculation the Ag solubility in the (Ti)(r) phase decreases very rapidly above 1000°C and thus there appears twice a four phase reaction between liquid, (Ti)(r), (Ti)(h) and Ti₃Al (at 1280 and 1033°C). This may be an artefact, although the three phase field liquid+(Ti)(h)+Ti₃Al between these two temperatures is supported by the 1100°C isothermal section reported by [1957Koe].

Isothermal Sections

The sections at 1100, 1000 and 800°C , (Fig. 2, Fig. 3 and Fig. 4), are drawn from thermodynamic calculations using the description given in the next section. The homogeneity range of the τ phase as well as the (Ti)(r)+(Ti)(h)+liquid equilibrium at 1000°C are modified to fit to the reported measured points of [1957Koe, 1986Has, 1990Mab]. The sections differ from those of [1957Koe] due to the differences in the accepted binary systems and due to the consideration of the τ phase. In Köster's diagrams Ti₂Ag appears as stable above 1100°C and all phases between Ti₃Al and TiAl were not yet known. The 800°C section of [1983Has] differs from that given by [1957Koe] for the same temperature mainly by the equilibria containing the Ag-Ti phases TiAg and Ti₂Ag. The calculation strongly supports the equilibria given by [1983Has]. The Ti solubility measurements in liquid and solid Ag reported by [1983Has] gave significantly lower values than compatible with the Ag-Ti system of [2002LB]. Also [1983Has] did not consider the TiAl₂ phase between TiAl and TiAl₃ and they did not distinguish τ from TiAl₃. The Ag solubilities in Ti₃Al, TiAl and TiAl₃ are accepted from [1957Koe].

Thermodynamics

The thermodynamic data sets as used in [2002LB] allow approximate calculation of the ternary system. Without the introduction of ternary parameters, however, the homogeneity ranges of the (Ti)(h) and (Ti)(r)) solid solutions in this calculation disagree significantly with [1957Koe] and [1986Has]. For phases with only small ternary solubilities the calculated equilibria agree fairly well with those reported by [1957Koe] and [1986Has].

Using the thermodynamic descriptions of the binary systems [2002LB] with additional ternary terms of $+120000\,x_{\mathrm{Ag}}x_{\mathrm{Al}}x_{\mathrm{Ti}}\,\mathrm{J\cdot mol}^{-1}$ for G^{bcc} and $(+80000-12T)x_{\mathrm{Ag}}x_{\mathrm{Al}}x_{\mathrm{Ti}}\,\mathrm{J\cdot mol}^{-1}$ for G^{hcp} the ternary system can be approximately calculated. The ternary phase τ can be roughly approximated by a stoichiometric phase $\mathrm{Ti}_{0.27}\mathrm{Ag}_{0.12}\mathrm{Al}_{0.61}$ with the Gibbs energy of formation G^{τ} -0.27- $G^{\mathrm{hcp}}_{\mathrm{Ti}}$ -0.12 $G^{\mathrm{fcc}}_{\mathrm{Ag}}$ -0.61 $G^{\mathrm{fcc}}_{\mathrm{Al}}$ =-36500+7 $T\,\mathrm{J\cdot mol}^{-1}$.

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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
(Ti)(h) 1715-882	cI2 Im3m W	a = 330.65	pure element, 900°C [Mas2]
(Ti)(r) < 1500	hP2 P6 ₃ /mmc Mg	a = 295.06 c = 468.35	pure element, 25°C [Mas2]
(Ag) < 962	cF4 <i>Fm3m</i> Cu	a = 408.57	pure element, 25°C [Mas2]
(Al) < 661	<i>cF</i> 4 <i>Fm</i> 3 <i>m</i> Cu	a = 404.96	pure element, 25°C [Mas2]
Ti ₂ Ag < 940	tI6 I4/mmm MoSi ₂	a = 295 c = 1180	[1965Sch]
TiAg < 1020	<i>tP</i> 4 <i>P</i> 4/ <i>nmm</i> TiCu	a = 290 c = 814	[1965Sch]
Ti ₃ Al < 1190	hP8 P6 ₃ /mmc Ni ₃ Sn	a = 577.5 c = 463.8	[2001Bra]
TiA1 < 1444	<i>tP4</i> <i>P4/mmm</i> CuAu	a = 399.8 c = 407.6	[2001Bra]
TiAl ₂ < 1181	tI24 I4 ₁ /amd HfGa ₂	a = 397.6 c = 2497	[1962Poe, 1990Sch]
Ti ₅ Al ₁₁ 1379-996	tI16 I4/mmm ZrAl ₃	a = 391.7 c = 1652.4	[1965Ram, 1990Sch]
TiAl ₃ < 1373	tI8 I4/mmm TiAl ₃	a = 384 c = 857.9	[1965Ram, 1990Sch]
Ag ₃ Al(h) 780-610	cI2 Im3m W	a = 330.2	700°C [V-C2]
Ag ₃ Al(r) < 448	cP20 P4 ₁ 32 βMn	a = 693.4	[V-C2]
Ag ₂ Al < 727	hP2 P6 ₃ /mmc Mg	a = 288.5 c = 458.2	[V-C2]
$\star \tau$, Ti(Al _{1-x} Ag _x) ₃	cP4 Pm3m AuCu ₃	<i>a</i> = 399.0 to 400.4	[1990Mab]

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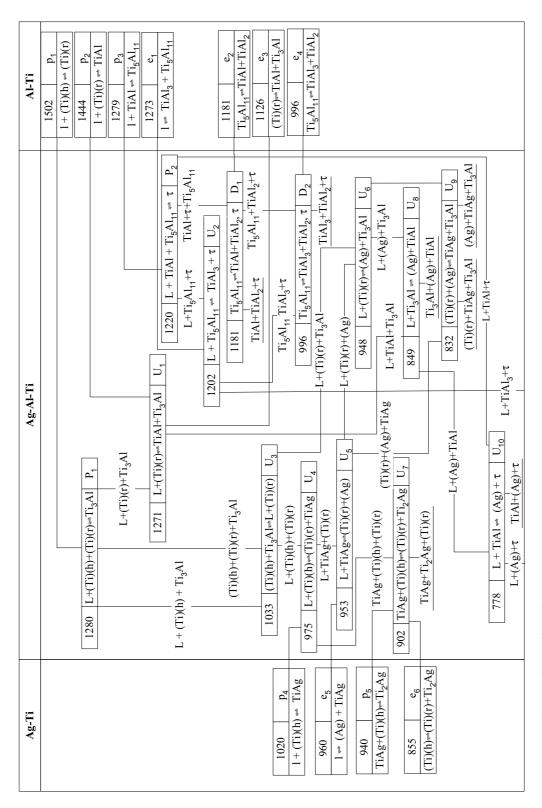


Fig. 1: Ag-Al-Ti. Tentative reaction scheme

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Fig. 2: Ag-Al-Ti. Isothermal section at 1100°C

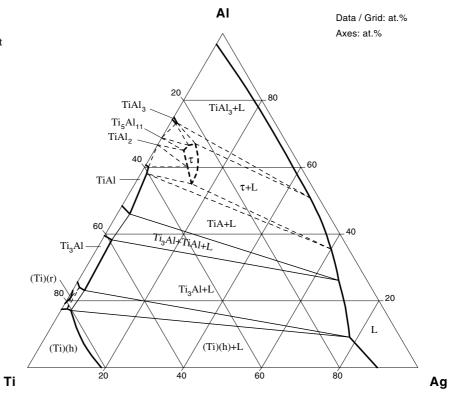
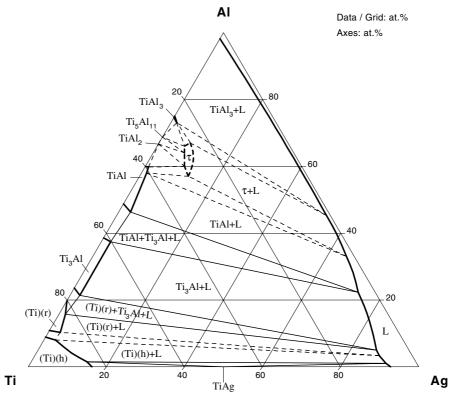
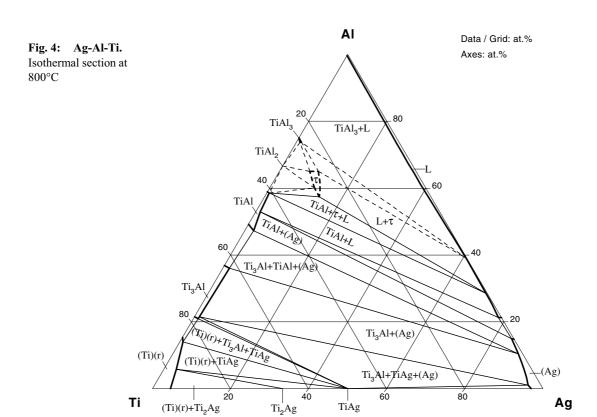


Fig. 3: Ag-Al-Ti. Isothermal section at 1000°C



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