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## Thermodynamic modelling of the Ag-Cu-Ti ternary system

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Ag-Cu-Ti system is important for brazing applications and mainly for ceramic joining. This system is characterized by numerous intermetallics in the Cu-Ti binary and the existence of a miscibility gap in the liquid phase. For applications, the knowledge of phase equilibria, invariant reactions in the temperature range of interest and thermodynamic activity values (mainly of Ti) are important. Thermodynamic model parameters for all the stable phases in the Ag-Cu, Cu-Ti and Ag-Ti systems, previously obtained using the Calphad method and available in the literature are used. New thermodynamic description for the ternary interaction parameter of the liquid is obtained from experimental informations.  $\text{Ti}_2\text{Cu}$  and  $\text{Ti}_2\text{Ag}$  which have the same crystallographic structure were modelled as a single phase. The same was done for  $\text{TiCu}$  and  $\text{TiAg}$ . Finally, solid solubility of Ag in the Ti-Cu intermetallics is taken into account. The parameters obtained in this assessment are later used for the calculation of selected sections that can be useful for research and applications in the field of joining with Ti activated Ag-Cu braze.

keywords: Calphad; braze alloys; phase diagram; Ag-Cu-Ti

## 1 Introduction

The Ag-Cu binary consists in a simple eutectic ([1] modified by [2] and hereby noted as [3] in the following). Ag-Ti is characterized by the existence of two intermetallics with peritectic decomposition (see figure 1 from [4]) while in the Cu-Ti system 6 intermetallic phases are stable, where only one melts congruently (see figure 2 from [5]).

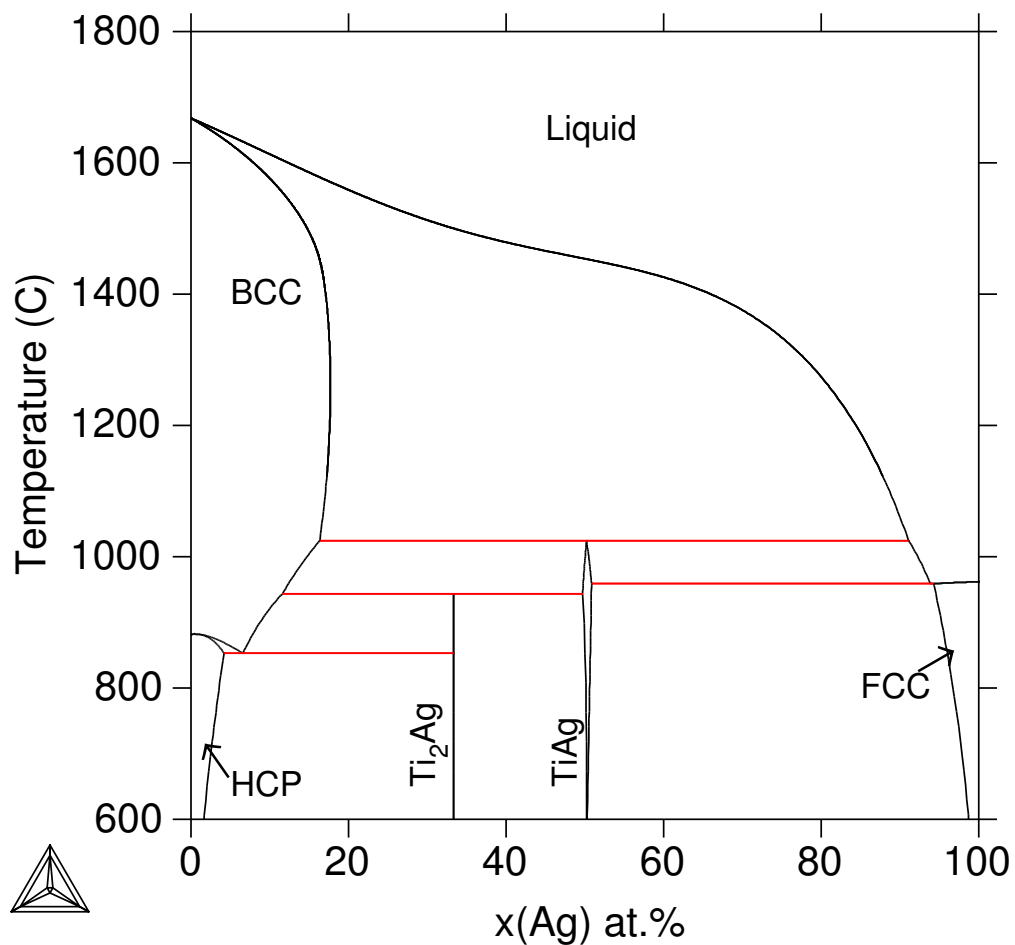


Figure 1: Calculated Ag-Ti phase diagram, using thermodynamic assessment by Arroyave [4].

Concerning the ternary system, it is mainly characterized by two features: the first one

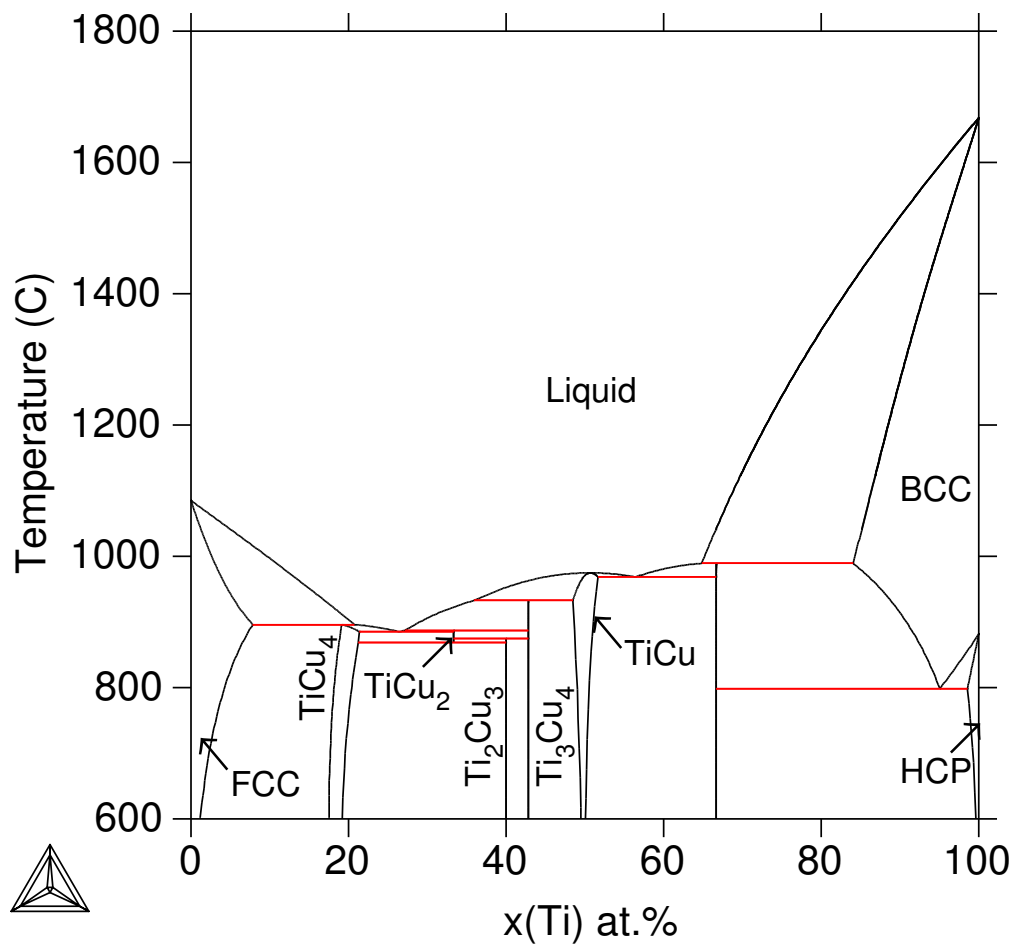


Figure 2: Calculated Cu-Ti phase diagram, using thermodynamic assessment by Hari Kumar et al. [5].

is the continuous solid solution between the  $\text{Ti}_2\text{Cu}$  and  $\text{Ti}_2\text{Ag}$  compounds, the second is the existence of a miscibility gap in the liquid state between a Ag-rich and a Ti-rich liquids. Since this miscibility gap is not observed in the binary sub-systems, it is assumed to have a closed topology.

Alloys of the Ag-Cu-Ti ternary system are often used for brazing ceramics to metals in the temperature range 800-900 °C [6]. The low liquidus temperature of the Ag-Cu eutectic allows brazing at reasonably low temperatures, while the presence of Ag increases the activity of Ti very noticeably [7], promoting interfacial reactions with most of ceramic materials [6, 8]. Depending on its activity, Ti can form compounds with a partially metallic character on various ceramic solids thus leading to an improvement of wettability [9, 10]. A thorough knowledge of the Ag-Cu-Ti phase diagram from room temperature up to 900 °C is then required when trying to understand the mechanisms of reactive wetting or to develop high performance metal/ceramic brazed joints, more especially when the metal is a titanium base alloy [11, 12, 13]. Although the Ag-Cu-Ti system has been modelled before [14], no thermodynamic description has been made available. In this paper, a model for the ternary Ag-Cu-Ti system is proposed and phase diagram and thermochemical calculations are compared with the experimental evidence available.

## 2 Experimental data

The only systematic experimental study of this system is due to Eremenko et al. [15, 16, 17]. The system was later critically reevaluated by Chang et al. [18] and more recently by Kubachewski et al. [19]. Only some formal changes have been made and no new experimental information have been given. One of the main experimental feature reported by Eremenko et al. is the existence of a liquid miscibility gap that divides the liquid into Ag rich and Ti rich solutions. This miscibility gap has been confirmed experimentally by Paulasto et al. [14].

No ternary compounds has been found in the Ag-Cu-Ti system. Crystallographic data of the phases of the Ag-Ti and Cu-Ti systems are listed in Table 1 (data from [19]). According to Eremenko et al. a continuous solid solution exists between iso-structural  $\text{Ti}_2\text{Ag}$  and  $\text{Ti}_2\text{Cu}$  and the dependence of lattice parameters in this solid solution obeys Vegards law [15, 17, 16]. The two other iso-structural solids  $\text{TiCu}$  and  $\text{TiAg}$  do not form a continuous solid solution and are not even in equilibrium with each other at any temperature. However, both phases exhibit noticeable penetration in the ternary composition triangle: Eremenko et al. reported solubility limits at 700 °C which are respectively 5 at.% Ag in  $\text{TiCu}$  and 2 at.% Cu in  $\text{TiAg}$  [17]. The solubility of Ag in  $\text{TiCu}$  is highly sensitive to the temperature and it has been measured as about 13 at.% at 950 °C [14]. Concerning the other solid phases (Cu rich  $\text{Cu}_x\text{Ti}_y$  compounds) the Ag solubility seems to decrease continuously as Cu increases: at 700 °C Eremenko et al. gave a generic value that is lower than 2 at.% while Paulasto et al. measured an Ag content up to 2.8 at.% in  $\text{Ti}_3\text{Cu}_4$  at 950 °C.

Recent experimental investigations on the Ag-Cu-Ti system by isothermal diffusion experiments have reported an Ag content in the Cu-rich Cu-Ti compounds ( $\text{Ti}_3\text{Cu}_4$ ,  $\text{Ti}_2\text{Cu}_3$  and  $\text{TiCu}_4$ ) up to 1.5 at.% at 790 °C [20, 21] that confirm previous results. The decomposition of  $\text{Ti}_3\text{Cu}_4$ ,  $\text{Ti}_2\text{Cu}_3$  and  $\text{TiCu}_4$  compounds in the ternary system occurs by ternary transition reaction with the liquid phase and Ag solid solution at temperatures varying from 783 °C to 860 °C according to [16, 19] (see table 2).

## 3 Thermodynamic modelling

### 3.1 Literature survey

In the Ag-Cu-Ti system, reliable descriptions for the Cu-Ti [5] and Ag-Cu [3] binaries are available in the literature and will be used as a starting description in this work. The third Ag-Ti binary had been thermodynamically assessed both by Arroyave [4] and Li et al. [22] and the parameters of the first one are used in the following. The first attempt of assessment

Strukturbericht	Diagram symbol	Symbol used in Thermo-Calc data file	Pearson symbol/ Space group/ Prototype	Lattice parameter (pm)
A1	(Ag) (Cu)	FCC_A1 Fm $\bar{3}$ m	cF4  Cu	a=408.57 a=361.46
A3	$\alpha$ -Ti	HCP_A3	hP2 P6 $_3$ /mmc Mg	a=330.65
A2	$\beta$ -Ti	BCC_A2	cI2 Im $\bar{3}$ m W	a=295.06 c=468.35
	TiCu $_4$	TiCu $_4$	oP20 Pnma ZrAu $_4$	a=452.5 b=434.1 c=1295.3
	TiCu $_2$	TiCu $_2$	oC12 Amm2 VAu $_2$	a=436.3 b=797.7 c=447.3
	Ti $_2$ Cu $_3$	Ti $_2$ Cu $_3$	tP10 P4/nmm Ti $_2$ Cu $_3$	c=1395
	Ti $_3$ Cu $_4$	Ti $_3$ Cu $_4$	tI14 I4/mmm Ti $_3$ Cu $_4$	a=313 c=1994
C11 $_b$	Ti $_2$ Cu Ti $_2$ Ag	Ti $_2$ M	tI6 I4/mmm MoSi $_2$	a=295.3 c=1073.4 a=295.2 c=1185
B11	TiAg TiCu	TiM	tP4 P4/nmm TiCu	a=290.3 c=574 a=310.8 to 311.8 c=588.7 to 592.1

Table 1: Symbols and crystal structures of the stable phases in the ternary Ag-Cu-Ti system (lattice parameters from [19]).

of the Ag-Cu-Ti ternary systems has been performed by Paulasto et al. in 1995 [14]. They proposed some isothermal sections at high temperature and optimised the value of an excess ternary parameter in the liquid phase in order to describe satisfactorily the miscibility gap. Unfortunately, the whole set of parameters used was not reported. More recently, Arroyave started a new assessment of this ternary system that has been partly reported in its PhD [4]. Since this period, the work has been further pursued and the whole assessment is detailed in the present paper.

### 3.2 Unary phases

For the thermodynamic functions of the pure elements in their stable and metastable states, the phase stability equations compiled by Dinsdale [23] were used.

### 3.3 The solution phases

The liquid phase and the solid solution phases (fcc,hcp and bcc) were described by the Redlich-Kister substitutional solution model.. The Gibbs energy function of the solution phase  $\Phi$  ( $\Phi = \text{liquid, bcc, hcp, and fcc}$ ) for 1 mole of atoms is described by the following expression:

$$G_m^\Phi = \sum_i x_i^\Phi \circ G_i^\Phi + RT \sum_i x_i^\Phi \ln(x_i^\Phi) + {}^{ex}G_i^\Phi \quad (1)$$

$${}^{ex}G_i^\Phi = \sum_i^{n-1} \sum_{j=i-1}^n x_i^\Phi x_j^\Phi L_{i,j}^\Phi + x_i^\Phi x_{j \neq i \neq k}^\Phi x_{k \neq i \neq j}^\Phi L_{i,j,k}^\Phi \quad (2)$$

where elements Ag, Cu and Ti are identified as 1,2,3; n is equal to 3,  $x_i^\Phi$  is the molar fraction of element;  $\circ G_i^\Phi$  corresponds to the Gibbs energy of the pure element in the state  $\Phi$ ;  ${}^{ex}G_i^\Phi$  is the excess Gibbs energy which is expressed in the Redlich-Kister polynomial; and  $L_{i,j}^\Phi$  the binary interaction parameter between elements  $i$  and  $j$  that can be further expanded as:

$$L_{i,j}^{\Phi} = \sum_k {}^k L_{i,j}^{\Phi} (x_i^{\Phi} - x_j^{\Phi})^k \quad (3)$$

$${}^k L_{i,j}^{\Phi} = {}^k a + {}^k b T \quad (4)$$

In order to describe the existence of a liquid miscibility gap in the central region, a ternary interaction parameter ( ${}^{\Phi}L_{i,j,k}$  in equation 2) was incorporated into the description of the excess Gibbs energy of the liquid phase. For solid solution phases (fcc, hcp, and bcc), the existing descriptions of the binaries are used [3, 5, 4] and no ternary parameter added.

### 3.4 Binary phases extending into the ternary system

#### 3.4.1 Extension of stoichiometric binary compounds into the ternary

In the Cu-Ti binary system,  $\text{Ti}_3\text{Cu}_4$  and  $\text{Ti}_2\text{Cu}_3$  are essentially stoichiometric and therefore they are modelled as line compounds. In this work, in order to take into account the small, but important Ag solubility detected in those phases [20, 17, 14, 21], the models are modified by considering the presence of Ag in the Cu rich sublattice, leading to  $(\text{Ti})_p(\text{Cu,Ag})_q$  where  $p$  and  $q$  are stoichiometric numbers, respectively 3-4 and 2-3 for  $\text{Ti}_3\text{Cu}_4$  and  $\text{Ti}_2\text{Cu}_3$ . As a consequence the expression of the Gibbs energy function may be written as:

$$\begin{aligned} G^{Ti_pCu_q} &= y'_{Ti} y''_{Cu} \circ G^{Ti_pCu_q}_{Ti:Cu} + y'_{Ti} y''_{Ag} \circ G^{Ti_pAg_q}_{Ti:Ag} \\ &+ RT(y'_{Ti} \ln y'_{Ti} + y''_{Cu} \ln y''_{Cu}) \\ &+ RT(y'_{Ti} \ln y'_{Ti} + y''_{Ag} \ln y''_{Ag}) + {}^{ex}G^{Ti_pCu_q} \end{aligned} \quad (5)$$

where  $y_i^s$  is the site fraction of component  $i$  in sublattice  $s$ , and  $\circ G^{Ti_pCu_q}_{Ti:Cu}$ ,  $\circ G^{Ti_pAg_q}_{Ti:Ag}$  are the Gibbs energies of the stoichiometric compounds  $\text{Ti}_p\text{Cu}_q$  and  $\text{Ti}_p\text{Ag}_q$  formed when each of the sublattices is occupied by only one component:

$${}^{\circ}G_{Ti:Ag}^{Ti_pAg_q} = p {}^{\circ}G_{Ti}^{hcp} + q {}^{\circ}G_{Ag}^{fcc} + A \quad (6)$$

where  $A$  is an optimised parameter. As the Gibbs energies of  $Ti_2Cu_3$  and  $Ti_3Cu_4$  in the binary are approximately the same, and because their compositions and decomposition temperatures are also very close in the ternary, the same value of parameter  $A$  was assumed for both of them.  ${}^{ex}G^{Ti_pCu_q}$  is the excess Gibbs energy and its composition dependence is assumed to conform with a Redlich-Kister polynomial. Due to the restricted number of experimental data the temperature dependence of the excess Gibbs energy is neglected and only the subregular solution term of the Redlich-Kister serie was used:

$${}^{ex}G^{Ti_pCu_q} = y''_{Cu}y''_{Ag}(y'_{Ti} L_{Ti:Cu,Ag}^{Ti_pCu_q}) \quad (7)$$

$$L_{Ti:Cu,Ag}^{Ti_pCu_q} = a_{pq}^0(y''_{Cu} - y''_{Ag}) \quad (8)$$

Finally, for  $Ti_3Cu_4$  and  $Ti_2Cu_3$  the parameters to be optimised are  $A$  (eq. 6) and the two Redlich-Kister coefficient  $a_n$  (eq. 8).

Eremenko et al. [17] concluded that the  $Ti_2Cu$  and  $Ti_2Ag$  phases are iso-structural with a complete solid solubility between the two phases. Therefore, these two phases are modeled as a single phase by using the sublattice formalism  $(Ti)_2(Cu,Ag)_1$  [24], allowing random mixing of Cu and Ag in the second sublattice. The derived expressions of the Gibbs energy functions are similar to those obtained for  $Ti_3Cu_4$  and  $Ti_2Cu_3$  and detailed above (see eqns. 5 and 6).

### 3.4.2 Extension of non-stoichiometric binary compounds in the ternary

In the Cu-Ti binary system,  $TiCu_4$  and  $TiCu$  are non stoichiometric compounds with an homogeneity range of, respectively, about 3 at.% Ti and 4 at.% Ti around their ideal compositions of 20 at.% Ti and 50 at.%Ti. As  $Ti_2Cu$  and  $Ti_2Ag$ , the  $TiCu$  and  $TiAg$  phases

are iso-structural [17] and TiAg is also non stoichiometric with an homogeneity range of about 2 at.% Ti. Therefore, they are described as a single phase using the model proposed by Hari Kumar et al. [5] allowing for mixing of all three atoms in the two sublattices:  $(\text{Cu,Ag,Ti})_1(\text{Cu,Ag,Ti})_1$ . Therefore the Gibbs energies for this phase can be represented by:

$$\begin{aligned}
G^{TiM} = & y'_{Cu}y''_{Cu} \circ G_{Cu:Cu}^{TiM} + y'_{Ti}y''_{Cu} \circ G_{Ti:Cu}^{TiM} + y'_{Cu}y''_{Ti} \circ G_{Cu:Ti}^{TiM} \\
& + y'_{Ag}y''_{Ag} \circ G_{Ag:Ag}^{TiM} + y'_{Ti}y''_{Ag} \circ G_{Ti:Ag}^{TiM} + y'_{Ag}y''_{Ti} \circ G_{Ag:Ti}^{TiM} \\
& + y'_{Ag}y''_{Cu} \circ G_{Ag:Cu}^{TiM} + y'_{Cu}y''_{Ag} \circ G_{Cu:Ag}^{TiM} \\
& + RT \left( \sum_{i=Ti,Cu,Ag} (y'_i \ln y'_i + \sum_{i=Ti,Cu,Ag} (y''_i \ln y''_i)) \right. \\
& + \sum_{i=Ag,Cu,Ti} y'_i y''_{Cu} y''_{Ti} L_{i:Cu,Ti}^{TiM} + \sum_{i=Ag,Cu,Ti} y'_{Cu} y'_{Ti} y'_i L_{Cu,Ti:i}^{TiM} \\
& + \sum_{i=Ag,Cu,Ti} y'_i y''_{Ag} y''_{Ti} L_{i:Ag,Ti}^{TiM} + \sum_{i=Ag,Cu,Ti} y'_{Ag} y'_{Ti} y'_i L_{Ag,Ti:i}^{TiM} \\
& + y'_{Cu} y'_{Ag} y''_{Ag} L_{Cu,Ag:Ag}^{TiM} + y'_{Cu} y'_{Ag} y''_{Cu} L_{Cu,Ag:Cu}^{TiM} + y'_{Cu} y'_{Ag} y''_{Ti} L_{Cu,Ag:Ti}^{TiM} \\
& \left. + y'_{Cu} y''_{Cu} y''_{Ag} L_{Cu:Cu,Ag}^{TiM} + y'_{Ag} y''_{Cu} y''_{Ag} L_{Ag:Cu,Ag}^{TiM} + y'_{Ti} y''_{Cu} y''_{Ag} L_{Ti:Cu,Ag}^{TiM} \right)
\end{aligned} \tag{9}$$

where the parameters  $\circ G_{i:j}^{TiM}$  with  $i, j = \text{Cu or Ag}$ ,  $L_{i:Cu,Ag}^{TiM}$  and  $L_{Cu,Ag:i}^{TiM}$  are the parameters to be optimised, the other ones coming either from [5] for the TiCu phase or from [4] for the TiAg phase.

Concerning the last  $\text{TiCu}_4$  compound, the existing description assumed the existence of defects on both sublattices that are anti-structure atoms represented by the sublattice notation  $(\text{Ti}\%,\text{Cu})_1:(\text{Cu}\%,\text{Ti})_p$  [5]. Introduction of Ag in this compound can lead to a dramatic increase of the number of interaction parameters between the elements in each sublattice. However, the only available experimental data that can be used during the optimisation to refine these parameters is the value of Ag solubility. It is thus important to restrict the number of adjustable parameters. For that purpose, in the present work it was firstly assumed Ag is present only in the second sublattice, where Cu is the major component leading to  $(\text{Ti}\%,\text{Cu})_1:(\text{Cu}\%,\text{Ag,Ti})_4$  in sublattice notation. Assuming that the interaction

between constituents in different sublattice are independent, the Gibbs energy of this phase is expressed as in Eq. 10:

$$\begin{aligned}
G^{TiCu_4} &= y'_{Ti} y''_{Cu} \circ G_{Ti:Cu}^{TiCu_4} + y'_{Ti} y''_{Ag} \circ G_{Ti:Ag}^{TiCu_4} + y'_{Ti} y''_{Ti} \circ G_{Ti:Ti}^{TiCu_4} \\
&+ y'_{Cu} y''_{Cu} \circ G_{Cu:Cu}^{TiCu_4} + y'_{Cu} y''_{Ag} \circ G_{Cu:Ag}^{TiCu_4} + y'_{Cu} y''_{Ti} \circ G_{Cu:Ti}^{TiCu_4} \\
&+ RT[(y'_{Ti} \ln y'_{Ti} + y'_{Cu} \ln y'_{Cu}) + 4(y''_{Ti} \ln y''_{Ti} + y''_{Cu} \ln y''_{Cu} + y''_{Ag} \ln y''_{Ag})] \\
&+ \sum_{i=Ti,Cu} y'_i y''_{Ti} y''_{Cu} L_{i:Ti,Cu}^{TiCu_4} + \sum_{i=Ti,Cu} y'_i y''_{Ti} y''_{Ag} L_{i:Ti,Ag}^{TiCu_4} \\
&+ \sum_{i=Ti,Cu} y'_i y''_{Cu} y''_{Ag} L_{i:Cu,Ag}^{TiCu_4} + \sum_{i=Ti,Cu,Ag} y'_{Ti} y'_{Cu} y''_i L_{Ti,Cu:i}^{TiCu_4}
\end{aligned} \tag{10}$$

where the parameters  $\circ G_{i:j}^{TiCu_4}$  with  $i, j = Cu$  or  $Ti$  and  $L_{i:Ti,Cu}^{TiCu_4}$  are directly taken from the Cu-Ti binary system obtained by Hari Kumar et al. [5]. The two other lattice stabilities are given by:

$$\circ G_{Ti:Ag}^{TiCu_4} = \circ G_{Ti}^{hcp} + 4 \circ G_{Ag}^{fcc} + 5B \tag{11}$$

$$\circ G_{Cu:Ag}^{TiCu_4} = \circ G_{Cu}^{fcc} + 4 \circ G_{Ag}^{fcc} + 5B \tag{12}$$

$B$ ,  $L_{i:Ti,Ag}^{TiCu_4}$ ,  $L_{i:Cu,Ag}^{TiCu_4}$  and  $L_{Ti,Cu:i}^{TiCu_4}$  are the parameters to be optimised. Note that only the regular-solution terms in the Redlich-Kister serie were considered.

## 4 Optimisation procedure

Optimisation was performed using the PARROT module of the Thermo-Calc software [25], that uses weighted experimental data as input. For this optimisation, the different sets of phases were optimised in different stages. For the  $Ti_2M$  phase, a positive zeroth-order interaction parameter was used to allow the phase to become less stable at the central regions of the  $Ti_2Ag$ - $Ti_2Cu$  iso-compositional line in order to avoid making the phase undesirably

Reaction	Type	Reference	T (°C)	Phase	Composition ( at.%)		
					Ag	Cu	Ti
$L_1 + (\beta\text{Ti}) \rightleftharpoons L_2 + \text{Ti}_2\text{Cu}$	U <sub>1</sub>	[19]	982	L <sub>1</sub>	13	30	57
		This work	996	L <sub>2</sub>	88	10	2
				L <sub>1</sub>	8	36	56
		L <sub>2</sub>	79	13	8		
$L_3 \rightleftharpoons L_4 + \text{Ti}_2\text{Cu} + \text{TiCu}$	E <sub>1</sub>	[19]	954	L <sub>3</sub>	10	38	52
$L_3 + L_4 \rightleftharpoons \text{Ti}_2\text{Cu} + \text{TiCu}$	U <sub>2</sub>	This work	985	L <sub>4</sub>	84	14	2
				L <sub>3</sub>	7.8	38.2	54
				L <sub>4</sub>	78	14	8
$L + (\beta\text{Ti}) \rightleftharpoons \text{Ti}_2\text{Cu} + \text{TiAg}$	U <sub>3</sub>	[19]	960	-	-	-	-
		This work	971	L	87.5	5	7.5
$L + \text{TiAg} \rightleftharpoons \text{Ti}_2\text{Cu} + (\text{Ag})$	U <sub>4</sub>	[19]	929	-	-	-	-
		This work	935	L	89	5	6
$L + \text{Ti}_2\text{Cu} \rightleftharpoons \text{TiCu} + (\text{Ag})$	U <sub>5</sub>	[19]	908	-	-	-	-
		This work	910	L	84	11	5
$L_5 + \text{TiCu} \rightleftharpoons L_6 + \text{Ti}_3\text{Cu}_4$	U <sub>6</sub>	[19]	900	L <sub>5</sub>	6	61	33
		This work	907	L <sub>6</sub>	66	32	2
				L <sub>5</sub>	9.6	61.6	28.8
				L <sub>6</sub>	60.5	35	4.51
$\text{Ti}_3\text{Cu}_4 + \text{TiCu}_2 \rightleftharpoons L + \text{Ti}_2\text{Cu}_3$	U <sub>7</sub>	[19]	875-851	-	-	-	-
		This work	884	L	2.5	70.7	26.8
$\text{TiCu}_2 \rightleftharpoons L + \text{Ti}_2\text{Cu}_3 + \text{TiCu}_4$	E <sub>2</sub>	[19]	851	L	5	72	23
		This work	882	L	4.7	68.9	26.4
$L_7 + \text{Ti}_3\text{Cu}_4 \rightleftharpoons L_8 + \text{Ti}_2\text{Cu}_3$	U <sub>8</sub>	This work	879	L <sub>7</sub>	11.8	66	22.2
				L <sub>8</sub>	52.6	43	4.4
$L + \text{TiCu} \rightleftharpoons \text{Ti}_3\text{Cu}_4 + (\text{Ag})$	U <sub>9</sub>	[19]	860	-	-	-	-
		This work	847	L	73	24	2
$L_9 + \text{Ti}_2\text{Cu}_3 \rightleftharpoons L_{10} + \text{TiCu}_4$	U <sub>10</sub>	This work	836	L <sub>9</sub>	18.5	69.2	12.3
				L <sub>10</sub>	36.3	58	5.7
$L + \text{Ti}_3\text{Cu}_4 \rightleftharpoons \text{Ti}_2\text{Cu}_3 + (\text{Ag})$	U <sub>11</sub>	[19]	843	-	-	-	-
		This work	826	L	69	29	2
$L + \text{Ti}_2\text{Cu}_3 \rightleftharpoons \text{TiCu}_4 + (\text{Ag})$	U <sub>12</sub>	[19]	808	-	-	-	-
		This work	796	L	61.3	37	1.7
$L + \text{TiCu}_4 \rightleftharpoons (\text{Cu}) + (\text{Ag})$	U <sub>13</sub>	[19]	783	-	-	-	-
		This work	786	L	58.4	40	1.6

Table 2: Invariant equilibria in the Ag-Cu-Ti ternary system. Comparison of the values accepted by [19] and calculated in this work.

more stable in the central region than at the end members because of the ideal entropic contribution. As noted above, the liquid phase presents a liquid miscibility gap in the central region of the system because of Cu-Ti interactions that are negative whereas the Ag-Ti are positive. Due to this fact, it was decided to introduce a ternary interaction parameter as shown in equation 2. For the TiM phase, in order to limit the number of adjustable parameters, all the interactions parameters  $L_{i:Cu,Ag}^{TiM}$  and  $L_{Cu,Ag:i}^{TiM}$  involving only Ag and Cu ( $i = \text{Ag or Cu}$ ) are considered as equal. Finally, the  $L_{Ti:Cu,Ag}^{TiM}$  parameter is described by the zeroth- and first order interaction coefficients. All these parameters were optimised during a first step by using the phase equilibria, invariant reaction [15, 16, 14] and activity values [7] at high temperature (above 900 °C).

Next, the invariant reactions at lower temperature (see table 2) and Ag solubilities in Ti-Cu compounds were used to optimised the remaining parameters of the  $\text{Ti}_3\text{Cu}_4$ ,  $\text{Ti}_2\text{Cu}_3$  and  $\text{TiCu}_4$  phases (about 1.5 at.% at 790 °C - see section 2). To perform this optimisation step, it was necessary to reduce the number of independent model parameters by introducing certain assumptions. For the lattice stabilities corresponding to hypothetical compounds like  $\text{Ti}_p\text{Ag}_q$  and  $\text{TiAg}_4$  or  $\text{CuAg}_4$ , the parameters  $A$  and  $B$  in Eqns. 6 and 12 were arbitrarily assumed to be +5000 J.mol<sup>-1</sup>. For the same reasons, the following simplifications were introduced in the description of  $\text{TiCu}_4$ :

$${}^\circ L_{Cu:Ti,Ag}^{TiCu_4} = {}^0 L_{Cu:Cu,Ag}^{TiCu_4} = {}^\circ L_{Ti:Ti,Ag}^{TiCu_4} = {}^\circ L_{Ti:Cu,Ag}^{TiCu_4} = {}^\circ L_{i:j,Ag}^{TiCu_4} \quad (13)$$

Finally, three regular-solution interaction parameters were optimised in this second step:

$${}^\circ L_{Ti:Cu,Ag}^{Ti_3Cu_4}, {}^\circ L_{Ti:Cu,Ag}^{Ti_2Cu_3} \text{ and } {}^\circ L_{i:j,Ag}^{TiCu_4}.$$

At the end of optimisation, rounding off of the optimised coefficients was done according to the procedure described in [26].

## 5 Results and discussion

### 5.1 Comparison with experimental results

Optimised values of the whole set of model parameters are given in appendix A.

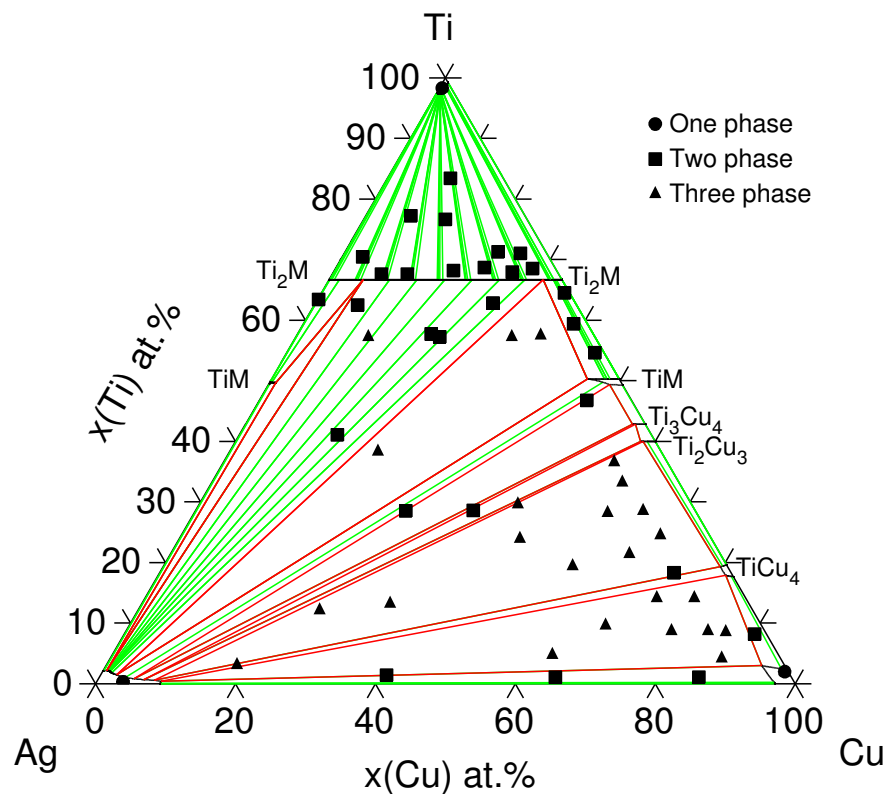


Figure 3: Calculated and experimental phase diagram of the Ag-Cu-Ti system at 700 °C. The experimental data was obtained from [17].

Figure 3 and 4 presents the calculated Ag-Cu-Ti phase diagram, along with experimental data points obtained from the literature (See [17, 14]). In general, the agreement is quite good. Figure 3 shows the calculated and experimental [17] Ag-Cu-Ti phase diagram at 700 °C. As can be seen, in most of the compositional triangle the agreement is excellent and the single, two- and three-phase fields have adequate compositional ranges and all the important features of the experimental diagram are reproduced. Figure 4 shows the experimental [14] and calculated ternary Ag-Cu-Ti phase diagram at 950 °C. As can be seen,

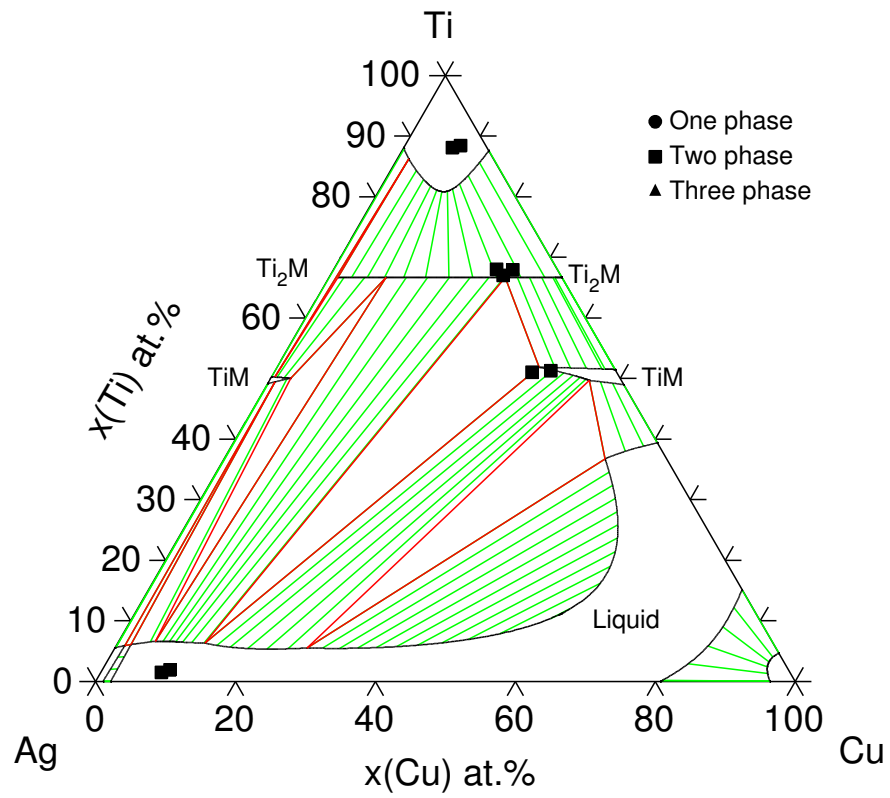


Figure 4: Calculated and experimental phase diagram for the Ag-Cu-Ti system at 950 °C. Experimental data after [14].

the composition of TiM and Ti<sub>2</sub>M phases involved in the three phase equilibrium with the Ag-rich liquid are well-reproduced. Composition of the liquid is given by Paulasto et al. [14] as being the composition of the Ag solid solution after solidification. However, the fine precipitation of Ti-Cu intermetallics during cooling leads to an underestimation of the Ti content in the liquid that could explain the discrepancy observed in figure 4. The direction of the tie-lines indicating regions across the miscibility gap at thermochemical equilibrium also correspond to reported experimental results [17].

The consistency between experimental and calculated invariant equilibria constitutes a good indicator of the validity of the thermodynamic descriptions used. Table 2 presents a comparison between the calculated and experimental invariant points (from [19]), including reaction temperatures (see also figure 5 for partial vertical section focused on the temperature range interesting for brazing). The agreement is fairly good on the whole temperature range and mainly at high temperature, although the discrepancy increases at lower temperature. The biggest discrepancy between experiments and calculations is the nature of the invariant reaction involving Ti<sub>2</sub>Cu, TiCu and the liquid phase. Eremenko proposed a eutectic reaction whereas this reaction has a transition type character ( $L_3 + L_4 \rightleftharpoons \text{Ti}_2\text{Cu} + \text{TiCu}$ ) in our assessment. This is a direct consequence of the stabilization of TiCu by addition of Ag.

In brazing of ceramics to metals, the chemical activity of Ti in the liquid braze is perhaps the most important factor when trying to predict the reaction products formed at the ceramic/metal interface. Thus, a reasonable calculation of the chemical activity of Ti in liquid Ag-Cu-Ti melts is desired. Figure 6 shows the comparison between experimental values (EMF measurement from [7]) and calculated Ti chemical activities in eutectic Ag-Cu melts. The agreement can be considered as being satisfactory. It is important to note, however, that the calculated values are higher than the experimental ones. This implies a higher calculated positive deviation from ideality than experimentally observed. It should be noted that Rongti et al. [27] reported activity values that are 1 or 2 order of magnitude lower. This major discrepancy between two experimental studies, that highlights the difficulty of

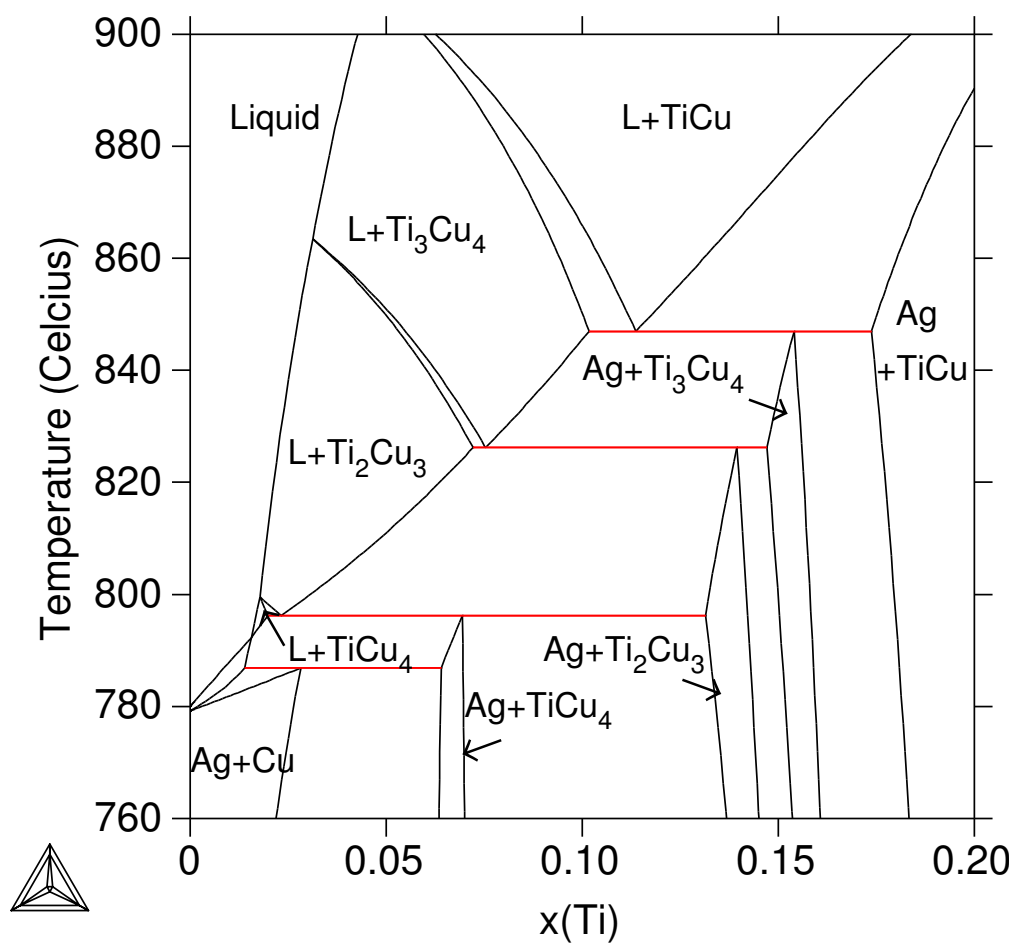


Figure 5: Calculated partial vertical section for 60 at.% of Ag.

such measurements, has already been discussed by Arroyave [4]. The low activity values of Rongti et al. are associated with negative values for the enthalpy of Ti at infinite dilution in liquid Ag, about  $-27850 \text{ J.mol}^{-1}$  [27, 28] against  $+25000 \text{ J.mol}^{-1}$  the value obtained by Arroyave [4] from the thermodynamic optimisation using phase diagram data. Such a negative value has major impact on the calculation of phase diagram that are not compatible with the literature [4, 22].

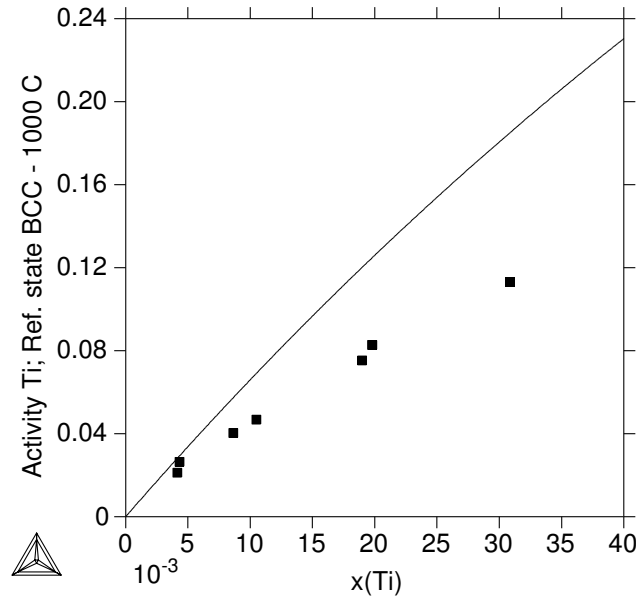


Figure 6: Calculated and experimental chemical activity of Ti in the eutectic melt Ag-Cu at 1000 °C. The experimental data points are taken from [7]

## 5.2 Calculations with the assessed thermodynamic model

Figure 7 presents the calculated isothermal section of the ternary system at 850 °C that is typically the recommended temperature for brazing with a Ti activated Ag-Cu braze. Since the formation of the first liquid droplet, at 780 °C in the Ag-Cu binary, the domain of liquid has extended widely with the appearance of a horn reflecting the tendency to demixion. The miscibility gap is already formed and all the Ti-Cu intermetallics are still in equilibrium with the liquid phase. This figure, associated with the list of invariant points (see 2) highlights the complexity of processes that occur for this system in a very narrow range of temperature

from 800 to 900 °C.

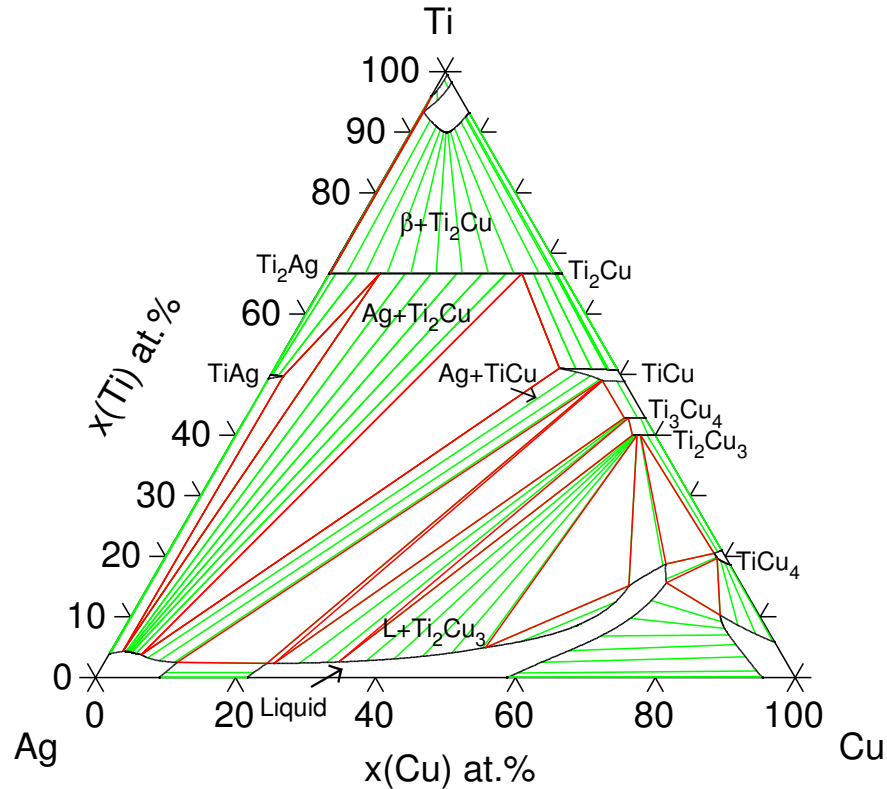


Figure 7: Isothermal section at 850 °C of the ternary Ag-Cu-Ti system calculated according to the present assessment (parameters given in appendix).

The projection on the Gibbs triangle of the monovariant lines is presented in figure 8. Some discrepancies exist with the projection reported by Eremenko et al. [15]: the most important is the extension of the liquid miscibility gap at low temperature. The calculated value is about 838 °C against 850 °C. The difference is small but has important consequences as the calculated miscibility gap intercepts more monovariant lines descending from the invariant points in the Cu-Ti binary to the Ag-Cu eutectic, leading to the appearance of two new invariant reactions that are not reported in the reaction scheme suggested by Eremenko et al. [15]. However, if the experimental results of Eremenko et al. allow the determination of the primary phase crystallization, the extension of liquid miscibility gap at low temperature can hardly be deduced. Moreover, the existence of successive invariant peritectic transfor-

mations at relatively low temperature and in narrow temperature and composition ranges can also hardly be detected by thermal analysis method or micrographs obtained on as-cast samples. For these reasons, the calculated projection can be considered as acceptable even if some additional experimental results would be necessary to clarify the extension of the liquid miscibility gap.

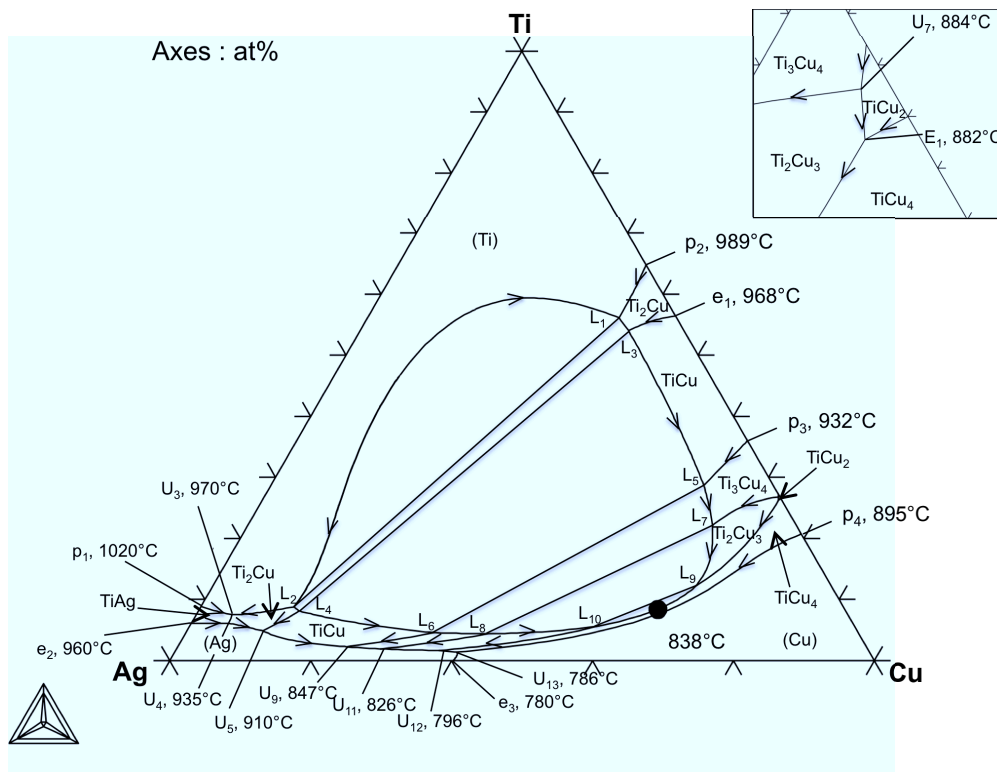


Figure 8: Calculated projection of the monovariant lines of the Ag-Cu-Ti system according to the present description. The labelling of the invariant reactions corresponds to table 2. Temperatures are given in Celsius.

### 5.3 Some consequences on brazing processes

Thermodynamic approach can be useful to understand the mechanism of a classical brazing process with Ti activated braze at about 850 °C. First of all, it has been recently shown by Differential Thermal Analysis (performed on Mettler-Toledo TMA/SDTA 840) in the range 750 to 800 °C and by isothermal diffusion at 790 °C that TiCu<sub>4</sub> is the first phase to form when a transient Ag-Cu eutectic liquid spreads onto solid Ti between 780 and 790 °C

[20]. Next, during the temperature rise toward 850 °C, dissolution of Ti in the AgCu melt proceeds across the  $Ti_xCu_y$  intermetallic compounds that formed by solid state diffusion between  $TiCu_4$  and Ti [21]. The kinetics of enrichment in Ti of the liquid phase is limited by the dissolution rate of  $Ti_xCu_y$  and in particular  $TiCu_4$ . As a consequence, the Ti amount available in the liquid state is strongly dependent on the way Ti is brought to the brazing filler (thickness and size are not the same for colaminated sheets, powder embedded in a paste, screen printing of a Ti paste, etc.) and on the temperature used for the isothermal step of the brazing process. For example, the results of Kozlova et al. at 840 °C, [29] show that the dissolution of 1-20  $\mu m$  Ti particles is not complete after 15 min of contact (presence of  $Ti_3Cu_4$  phase embedded in big round  $TiCu_4$  particles formed during heating and isothermal treatment). At the opposite, Shiue et al. [30] observed complete dissolution after only 180 s of a few micrometers thick Ti foil at 900 °C, a temperature higher than the decomposition temperature of  $TiCu_4$ .

Figure 9 and 10 presents the isothermal sections with the respective plots of the Ti activity (reference state is hcp-Ti) at 800 and 850 °C respectively which are data valuable for direct use during active brazing process ( $a_{Ti} = \frac{x_{Ag}}{x_{Ag}+x_{Cu}}$ ). It appears that the Ti activity of a liquid in equilibrium with  $TiCu_4$  is about 0.18 in the 800-850 °C temperature range. This activity is particularly important for reactive brazing of ceramic materials because the nature of the reaction product that is formed at the liquid/solid interface is determined by this value [9, 29, 31]. Fortunately, the Ti activity varies hardly with the nominal Ti amount in Ag-Cu braze whatever the nature of the Ti-Cu intermetallic phase involved in the liquid/solid equilibrium. This is revealed by the upper limit of liquid domain on figure 10 that is nearly flat. However, in order to avoid a dramatic decrease of Ti activity because of its consumption by chemical reaction with the substrates, it is recommended to use high Ti amount and to bring Ti to the brazing filler in the form of small particles. The temperature can hardly be increased above 850 °C because of the appearance of a liquid miscibility gap between a Ag rich and a Cu-Ti rich liquid [14]. Finally, it should be emphasized that in

the case of heterogeneous brazing of a ceramic with a metal, the interaction between the reactive element and the elements contained in the metallic solid have to be taken into account.

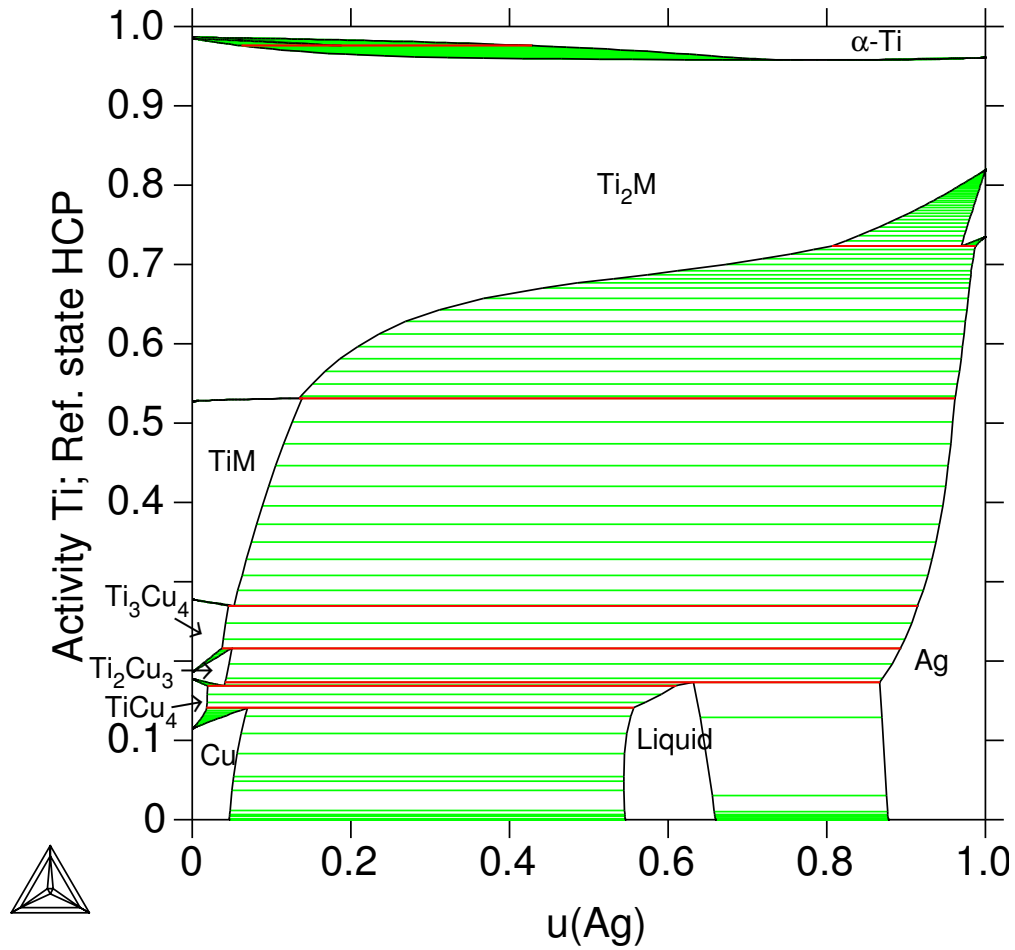


Figure 9: Activity of Ti as a function of  $u_{Ag} = \frac{x_{Ag}}{x_{Ag} + x_{Cu}}$  at 800 °C

## Acknowledgements

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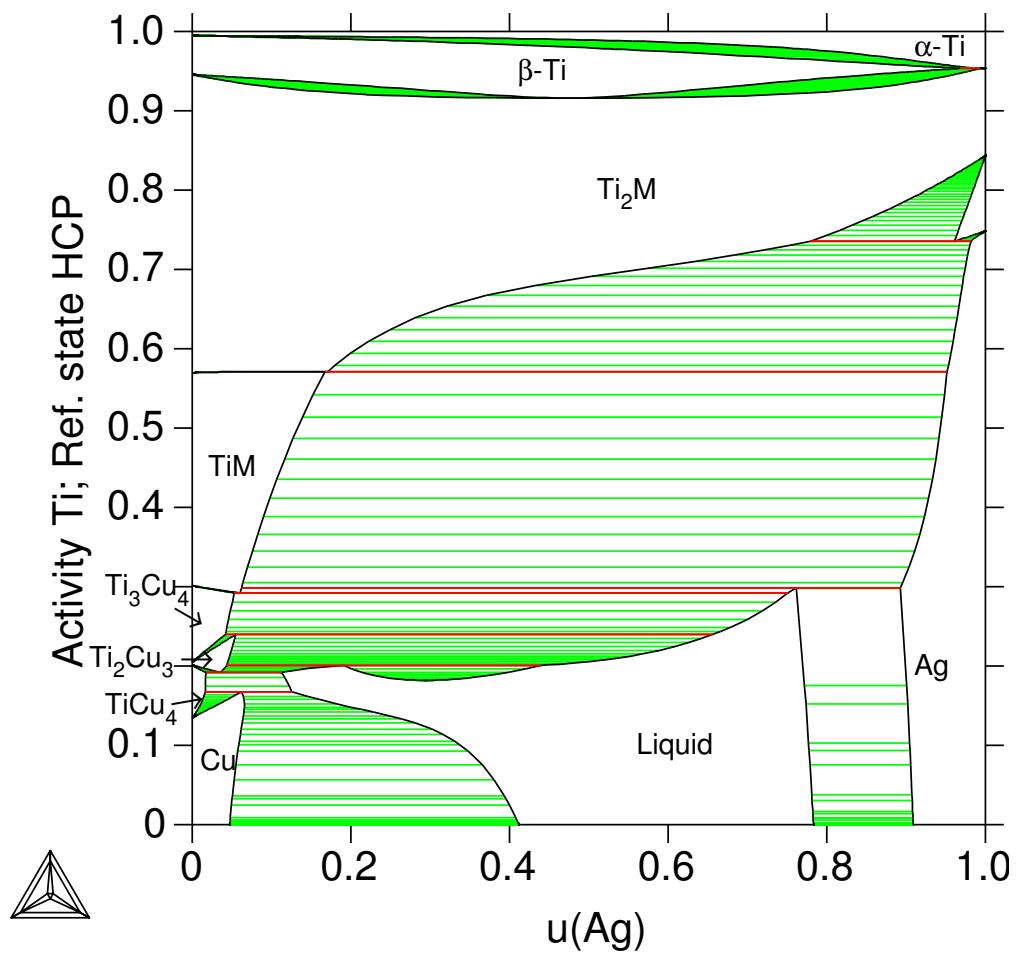


Figure 10: Activity of Ti as a function of  $u_{\text{Ag}} = \frac{x_{\text{Ag}}}{x_{\text{Ag}} + x_{\text{Cu}}}$  at  $850\text{ }^\circ\text{C}$

# A Thermodynamic description of the Ag–Cu–Ti ternary system

## Functions

$$R = 8.3145100$$

$$\text{RTLNP} = +R T \ln(1 \cdot 10^{-5} P)$$

$$\text{GHSERAG} = \quad \quad \quad [23]$$

$$298.14 \leq T < 1235.08 : -7209.512 + 118.200733 T - 23.8463314 T \ln(T) - .001790585 T^2 - 3.98587 \cdot 10^{-7} T^3 - 12011 T^{-1}$$

$$1235.08 \leq T < 3000.00 : -15095.314 + 190.265169 T - 33.472 T \ln(T) + 1.412186 \cdot 10^{29} T^{-9}$$

$$\text{GHSERCU} = \quad \quad \quad [23]$$

$$298.14 \leq T < 1358.02 : -7770.458 + 130.485403 T - 24.112392 T \ln(T) - .00265684 T^2 + 1.29223 \cdot 10^{-7} T^3 + 52478 T^{-1}$$

$$1358.02 \leq T < 3200.00 : -13542.33 + 183.804197 T - 31.38 T \ln(T) + 3.64643 \cdot 10^{29} T^{-9}$$

$$\text{GHSERTI} = \quad \quad \quad [23]$$

$$298.14 \leq T < 900.00 : -8059.921 + 133.687208 T - 23.9933 T \ln(T) - .004777975 T^2 + 1.06716 \cdot 10^{-7} T^3 + 72636 T^{-1}$$

$$900.00 \leq T < 1155.00 : -7811.815 + 133.060068 T - 23.9887 T \ln(T) - .0042033 T^2 - 9.0876 \cdot 10^{-8} T^3 + 42680 T^{-1}$$

$$1155.00 \leq T < 1941.00 : +908.837 + 67.048538 T - 14.9466 T \ln(T) - .0081465 T^2 + 2.02715 \cdot 10^{-7} T^3 - 1477660 T^{-1}$$

$$1941.00 \leq T < 4000.00 : -124526.786 + 638.878871 T - 87.2182461 T \ln(T) + .008204849 T^2 - 3.04747 \cdot 10^{-7} T^3 + 36699805 T^{-1}$$

## Liquid (Ag,Cu,Ti)

$${}^{\circ}G_{\text{Ag}}^{\text{Liquid}} - {}^{\circ}H_{\text{Ag}}^{\text{FCC-A1}} = \quad \quad \quad [23]$$

$$298.14 \leq T < 1235.08 : +11025.293 - 8.890146 T - 1.0322 \cdot 10^{-20} T^7 + \text{GHSERAG}$$

$$1235.08 \leq T < 3000.00 : +11507.972 - 9.300495 T - 1.412186 \cdot 10^{29} T^{-9} + \text{GHSERAG}$$

$${}^{\circ}G_{\text{Cu}}^{\text{Liquid}} - {}^{\circ}H_{\text{Cu}}^{\text{FCC-A1}} = \quad \quad \quad [23]$$

$$298.14 \leq T < 1358.02 : +12964.84 - 9.510243 T - 5.83932 \cdot 10^{-21} T^7 + \text{GHSERCU}$$

$$1358.02 \leq T < 3200.00 : +13495.4 - 9.920463 T - 3.64643 \cdot 10^{29} T^{-9} + \text{GHSERCU}$$

$${}^{\circ}G_{\text{Ti}}^{\text{Liquid}} - {}^{\circ}H_{\text{Ti}}^{\text{HCP-A3}} = \quad \quad \quad [23]$$

$$298.14 \leq T < 900.00 : +4134.494 + 126.7062 T - 23.9933 T \ln(T) - .004777975 T^2 + 1.06716 \cdot 10^{-7} T^3 + 72636 T^{-1}$$

$$900.00 \leq T < 1155.00 : +4382.601 + 126.0791 T - 23.9887 T \ln(T) - .0042033 T^2 - 9.0876 \cdot 10^{-8} T^3 + 42680 T^{-1}$$

$$1155.00 \leq T < 1300.00 : +13103.253 + 60.0676 T - 14.9466 T \ln(T) - .0081465 T^2 + 2.02715 \cdot 10^{-7} T^3 - 1477660 T^{-1}$$

$$1300.00 \leq T < 1941.00 : +369519.198 - 2553.9505 T + 342.059267 T \ln(T) - .163409355 T^2 + 1.2457117 \cdot 10^{-5} T^3 - 67034516 T^{-1}$$

$$1941.00 \leq T < 4000.00 : -19887.066 + 298.8087 T - 46.29 T \ln(T)$$

$${}^0L_{\text{Ag,Cu}}^{\text{Liquid}} = +17323.4 - 4.46819 T \quad [3]$$

$${}^1L_{\text{Ag,Cu}}^{\text{Liquid}} = +1654.38 - 2.35285 T \quad [3]$$

$${}^0L_{\text{Ag,Cu,Ti}}^{\text{Liquid}} = 32400 \quad [4]$$

$${}^0L_{\text{Ag,Ti}}^{\text{Liquid}} = 25632 \quad [4]$$

$${}^1L_{\text{Ag,Ti}}^{\text{Liquid}} = -327 \quad [4]$$

$${}^0L_{\text{Cu,Ti}}^{\text{Liquid}} = -19330 + 7.651 T \quad [5]$$

$${}^2L_{\text{Cu,Ti}}^{\text{Liquid}} = +9382 - 5.448 T \quad [5]$$

### FCC – A1 (Ag,Cu,Ti)<sub>1</sub>(Va)<sub>1</sub>

$$\circ G_{\text{Ag:VA}}^{\text{FCC-A1}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} = +\text{GHSERAG} \quad [23]$$

$$\circ G_{\text{Cu:VA}}^{\text{FCC-A1}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} = +\text{GHSERCU} \quad [23]$$

$$\circ G_{\text{Ti:VA}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = +6000 - .T + \text{GHSERTI} \quad [23]$$

$${}^0L_{\text{Ag,Cu:VA}}^{\text{FCC-A1}} = +36061.88 - 10.44288 T \quad [3]$$

$${}^1L_{\text{Ag,Cu:VA}}^{\text{FCC-A1}} = -4310.12 \quad [3]$$

$${}^0L_{\text{Ag,Ti:VA}}^{\text{FCC-A1}} = 23405 \quad [4]$$

$${}^0L_{\text{Cu,Ti:VA}}^{\text{FCC-A1}} = -9882 \quad [5]$$

$${}^1L_{\text{Cu,Ti:VA}}^{\text{FCC-A1}} = 15777 \quad [5]$$

### HCP – A3 (Ag,Cu,Ti)<sub>1</sub>(Va)<sub>.5</sub>

$$\circ G_{\text{Ag:VA}}^{\text{HCP-A3}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} = +300 + .3 T + \text{GHSERAG} \quad [23]$$

$$\circ G_{\text{Cu:VA}}^{\text{HCP-A3}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} = +600 + .2 T + \text{GHSERCU} \quad [23]$$

$$\circ G_{\text{Ti:VA}}^{\text{HCP-A3}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = +\text{GHSERTI} \quad [23]$$

$${}^0L_{\text{Ag,Cu:VA}}^{\text{HCP-A3}} = +35000 - 8 T \quad [3]$$

$${}^0L_{\text{Ag,Ti:VA}}^{\text{HCP-A3}} = 50050 \quad [4]$$

$${}^1L_{\text{Ag,Ti:VA}}^{\text{HCP-A3}} = 27000 \quad [4]$$

$${}^0L_{\text{Cu,Ti:VA}}^{\text{HCP-A3}} = 16334 \quad [5]$$

### BCC – A2 (Ag,Cu,Ti)<sub>1</sub>(Va)<sub>3</sub>

$$\circ G_{\text{Ag:VA}}^{\text{BCC-A2}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} = +3400 - 1.05 T + \text{GHSERAG} \quad [23]$$

$$\circ G_{\text{Cu:VA}}^{\text{BCC-A2}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} = +4017 - 1.255 T + \text{GHSERCU} \quad [23]$$

$$\begin{aligned} \circ G_{\text{Ti:VA}}^{\text{BCC-A2}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} &= \quad \quad \quad [23] \\ 298.15 \leq T < 1155.00 &: -1272.064 + 134.78618 T - 25.5768 T \ln(T) - 6.63845 \cdot 10^{-4} T^2 - \\ & \quad 2.78803 \cdot 10^{-7} T^3 + 7208 T^{-1} \\ 1155.00 \leq T < 1941.00 &: +6667.385 + 105.438379 T - 22.3771 T \ln(T) + 0.0121707 T^2 - \\ & \quad 8.4534 \cdot 10^{-7} T^3 - 2002750 T^{-1} \\ 1941.00 \leq T < 4000.00 &: +26483.26 - 182.354471 T + 19.0900905 T \ln(T) - 0.02200832 T^2 + \\ & \quad 1.228863 \cdot 10^{-6} T^3 + 1400501 T^{-1} \end{aligned}$$

$${}^0 L_{\text{Ag,Cu:VA}}^{\text{BCC-A2}} = +35000 - 8 T \quad [3]$$

$${}^0 L_{\text{Ag,Ti:VA}}^{\text{BCC-A2}} = +22900 + .5 T \quad [4]$$

$${}^1 L_{\text{Ag,Ti:VA}}^{\text{BCC-A2}} = 1500 \quad [4]$$

$${}^0 L_{\text{Cu,Ti:VA}}^{\text{BCC-A2}} = 3389 \quad [5]$$

### **Cu<sub>2</sub>Ti** (Cu)<sub>2</sub>(Ti)<sub>1</sub>

$$\circ G_{\text{Cu:Ti}}^{\text{Cu}_2\text{Ti}} - 2 \circ H_{\text{Cu}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = -17628 + 2 \text{GHSERCU} + \text{GHSERTI} \quad [5]$$

### **Cu<sub>3</sub>Ti<sub>2</sub>** (Ag,Cu)<sub>3</sub>(Ti)<sub>2</sub>

$$\circ G_{\text{Ag:Ti}}^{\text{Cu}_3\text{Ti}_2} - 3 \circ H_{\text{Ag}}^{\text{FCC-A1}} - 2 \circ H_{\text{Ti}}^{\text{HCP-A3}} = +25000 + 3 \text{GHSERAG} + 2 \text{GHSERTI} \quad \text{This work}$$

$$\circ G_{\text{Cu:Ti}}^{\text{Cu}_3\text{Ti}_2} - 3 \circ H_{\text{Cu}}^{\text{FCC-A1}} - 2 \circ H_{\text{Ti}}^{\text{HCP-A3}} = -46245 + 10.86 T + 3 \text{GHSERCU} + 2 \text{GHSERTI} \quad [5]$$

$${}^0 L_{\text{Ag,Cu:Ti}}^{\text{Cu}_3\text{Ti}_2} = 27800 \quad \text{This work}$$

### **Cu<sub>4</sub>Ti** (Ag,Cu,Ti)<sub>4</sub>(Cu,Ti)<sub>1</sub>

$$\circ G_{\text{Ag:Cu}}^{\text{Cu}_4\text{Ti}} - 4 \circ H_{\text{Ag}}^{\text{FCC-A1}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} = +25000 + 4 \text{GHSERAG} + \text{GHSERCU} \quad \text{This work}$$

$$\circ G_{\text{Cu:Cu}}^{\text{Cu}_4\text{Ti}} - 5 \circ H_{\text{Cu}}^{\text{FCC-A1}} = +25000 + 5 \text{GHSERCU} \quad [5]$$

$$\circ G_{\text{Ti:Cu}}^{\text{Cu}_4\text{Ti}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} - 4 \circ H_{\text{Ti}}^{\text{HCP-A3}} = +80055 - 11.693 T + \text{GHSERCU} + 4 \text{GHSERTI} \quad [5]$$

$$\circ G_{\text{Ag:Ti}}^{\text{Cu}_4\text{Ti}} - 4 \circ H_{\text{Ag}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = +25000 + 4 \text{GHSERAG} + \text{GHSERTI} \quad \text{This work}$$

$$\circ G_{\text{Cu:Ti}}^{\text{Cu}_4\text{Ti}} - 4 \circ H_{\text{Cu}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = -30055 + 11.693 T + 4 \text{GHSERCU} + \text{GHSERTI} \quad [5]$$

$$\circ G_{\text{Ti:Ti}}^{\text{Cu}_4\text{Ti}} - 5 \circ H_{\text{Ti}}^{\text{HCP-A3}} = +25000 + 5 \text{GHSERTI} \quad [5]$$

$$\begin{aligned}
{}^0L_{\text{Ag,Ti:Cu}}^{\text{Cu}_4\text{Ti}} &= 102000 && \text{This work} \\
{}^0L_{\text{Ag,Cu:Cu}}^{\text{Cu}_4\text{Ti}} &= 102000 && \text{This work} \\
{}^0L_{\text{Ag,Cu,Ti:Cu}}^{\text{Cu}_4\text{Ti}} &= 102000 && \text{This work} \\
{}^0L_{\text{Cu,Ti:Cu}}^{\text{Cu}_4\text{Ti}} &= 17089 && [5] \\
{}^0L_{\text{Cu:Cu,Ti}}^{\text{Cu}_4\text{Ti}} &= -15767 && [5] \\
{}^0L_{\text{Ti:Cu,Ti}}^{\text{Cu}_4\text{Ti}} &= -15767 && [5] \\
{}^0L_{\text{Ag,Ti:Ti}}^{\text{Cu}_4\text{Ti}} &= 102000 && \text{This work} \\
{}^0L_{\text{Ag,Cu:Ti}}^{\text{Cu}_4\text{Ti}} &= 102000 && \text{This work} \\
{}^0L_{\text{Ag,Cu,Ti:Ti}}^{\text{Cu}_4\text{Ti}} &= 102000 && \text{This work} \\
{}^0L_{\text{Cu,Ti:Ti}}^{\text{Cu}_4\text{Ti}} &= 17089 && [5]
\end{aligned}$$

### **Cu<sub>4</sub>Ti<sub>3</sub>** (Ag,Cu)<sub>4</sub>(Ti)<sub>3</sub>

$$\circ G_{\text{Ag:Ti}}^{\text{Cu}_4\text{Ti}_3} - 4 \circ H_{\text{Ag}}^{\text{FCC-A1}} - 3 \circ H_{\text{Ti}}^{\text{HCP-A3}} = +25000 + 4 \text{ GHSERAG} + 3 \text{ GHSERTI} \quad \text{This work}$$

$$\circ G_{\text{Cu:Ti}}^{\text{Cu}_4\text{Ti}_3} - 4 \circ H_{\text{Cu}}^{\text{FCC-A1}} - 3 \circ H_{\text{Ti}}^{\text{HCP-A3}} = -68236 + 15.946 T + 4 \text{ GHSERCU} + 3 \text{ GHSERTI} \quad [5]$$

$${}^0L_{\text{Ag,Cu:Ti}}^{\text{Cu}_4\text{Ti}_3} = 51300 \quad \text{This work}$$

### **CuTi** (Ag,Cu,Ti)<sub>1</sub>(Ag,Cu,Ti)<sub>1</sub>

$$\circ G_{\text{Ag:Ag}}^{\text{CuTi}} - 2 \circ H_{\text{Ag}}^{\text{FCC-A1}} = +10000 + 2 \text{ GHSERAG} \quad [4]$$

$$\circ G_{\text{Cu:Ag}}^{\text{CuTi}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} = +25000 + \text{ GHSERCU} + \text{ GHSERAG} \quad \text{This work}$$

$$\circ G_{\text{Ti:Ag}}^{\text{CuTi}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = +24080 - 1.32 T + \text{ GHSERAG} + \text{ GHSERTI} \quad [4]$$

$$\circ G_{\text{Ag:Cu}}^{\text{CuTi}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} = +25000 + \text{ GHSERCU} + \text{ GHSERAG} \quad \text{This work}$$

$$\circ G_{\text{Cu:Cu}}^{\text{CuTi}} - 2 \circ H_{\text{Cu}}^{\text{FCC-A1}} = +10000 + 2 \text{ GHSERCU} \quad [5]$$

$$\circ G_{\text{Ti:Cu}}^{\text{CuTi}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = +42412 - 6.544 T + \text{ GHSERCU} + \text{ GHSERTI} \quad [5]$$

$$\circ G_{\text{Ag:Ti}}^{\text{CuTi}} - \circ H_{\text{Ag}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = -4080 + 1.32 T + \text{ GHSERAG} + \text{ GHSERTI} \quad [4]$$

$$\circ G_{\text{Cu:Ti}}^{\text{CuTi}} - \circ H_{\text{Cu}}^{\text{FCC-A1}} - \circ H_{\text{Ti}}^{\text{HCP-A3}} = -22412 + 6.544 T + \text{ GHSERCU} + \text{ GHSERTI} \quad [5]$$

$$\circ G_{\text{Ti:Ti}}^{\text{CuTi}} - 2 \circ H_{\text{Ti}}^{\text{HCP-A3}} = +10000 + 2 \text{ GHSERTI} \quad [5]$$

${}^0L_{\text{Ag,Ti:Ag}}^{\text{CuTi}}$	=	23000	[4]
${}^0L_{\text{Ag,Cu:Ag}}^{\text{CuTi}}$	=	50000	This work
${}^0L_{\text{Ag:Ag,Ti}}^{\text{CuTi}}$	=	23000	[4]
${}^0L_{\text{Ag:Ag,Cu}}^{\text{CuTi}}$	=	50000	This work
${}^0L_{\text{Cu,Ti:Ag}}^{\text{CuTi}}$	=	15419	This work
${}^0L_{\text{Cu:Ag,Ti}}^{\text{CuTi}}$	=	23000	This work
${}^0L_{\text{Cu:Ag,Cu}}^{\text{CuTi}}$	=	50000	This work
${}^0L_{\text{Ti:Ag,Ti}}^{\text{CuTi}}$	=	23000	[4]
${}^0L_{\text{Ti:Ag,Cu}}^{\text{CuTi}}$	=	50000	This work
${}^0L_{\text{Ag,Ti:Cu}}^{\text{CuTi}}$	=	23000	This work
${}^0L_{\text{Ag,Cu:Cu}}^{\text{CuTi}}$	=	50000	This work
${}^0L_{\text{Ag:Cu,Ti}}^{\text{CuTi}}$	=	15578	This work
${}^0L_{\text{Cu,Ti:Cu}}^{\text{CuTi}}$	=	15419	[5]
${}^0L_{\text{Cu:Cu,Ti}}^{\text{CuTi}}$	=	15578	[5]
${}^0L_{\text{Ti:Cu,Ti}}^{\text{CuTi}}$	=	15578	[5]
${}^0L_{\text{Ag,Ti:Ti}}^{\text{CuTi}}$	=	23000	[4]
${}^0L_{\text{Ag,Cu:Ti}}^{\text{CuTi}}$	=	21000	This work
${}^1L_{\text{Ag,Cu:Ti}}^{\text{CuTi}}$	=	3500	This work
${}^0L_{\text{Cu,Ti:Ti}}^{\text{CuTi}}$	=	15419	[5]

### **CuTi<sub>2</sub>** (Ag,Cu)<sub>1</sub>(Ti)<sub>2</sub>

${}^\circ G_{\text{Ag:Ti}}^{\text{CuTi}_2} - {}^\circ H_{\text{Ag}}^{\text{FCC-A1}} - 2 {}^\circ H_{\text{Ti}}^{\text{HCP-A3}}$	=	$-8325 + 3.3 T + 2 \text{GHSERTI} + \text{GHSERAG}$	[4]
${}^\circ G_{\text{Cu:Ti}}^{\text{CuTi}_2} - {}^\circ H_{\text{Cu}}^{\text{FCC-A1}} - 2 {}^\circ H_{\text{Ti}}^{\text{HCP-A3}}$	=	$-36393 + 14.064 T + \text{GHSERCU} + 2 \text{GHSERTI}$	[5]
${}^0L_{\text{Ag,Cu:Ti}}^{\text{CuTi}_2}$	=	14500	This work

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