The influence of carbon on the phases in the copper-titanium system and their precipitation

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The influence of carbon on the phases occurring in the copper-titanium system has been experimentally investigated. Samples were fabricated from elemental copper and titanium. Carbon was added in the form of graphite or as titanium carbide. The samples were encapsulated, heat-treated at 1173 or 1373 K for 24 h and subsequently quenched in brine. The phases present at the treatment temperature were identified, as well as the phases occurring during solidification. The microstructure indicates the presence of a miscibility gap. The composition of the phases were determined using EDS-analysis. The composition of the copper phase was found to show a great variation caused by the precipitation sequence during quenching of the melts. The complex precipitation also caused both $TiCu_4$ and the meta-stable $TiCu_3$ to form. The composition of TiCu was found to show a wider compositional interval than earlier found. The variation of its composition with the nominal composition suggests that TiCu can dissolve carbon. The pure Ti phases also showed larger solubility of copper than earlier found. An outline of the precipitation sequence is made.
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1. Introduction
Copper and copper-base alloys are important families of alloys. Their field of application ranges from facade covers and pipes for plumbing to applications in electronics. In electrical connectors and make and break switches it is used together with materials that are stable at high temperatures to increase its service performance. Make and break switches usually consist of a pair if thin slabs, responsible for making, carrying and breaking the current. During making and breaking of the current arcing occurs causing high temperature. The case of make and break switches is one of the oldest and most successful applications of composite materials. Their fabrication is however quite tedious, involving the fabrication of a precursor containing the reinforcement, with a subsequent infiltration process to obtain the switch material.

During the past two decades the research into the field of composite materials have been intense. The traditional composites are normally mixed from powder, laid up using foils or infiltrated with a molten metal. The reinforcement varies from particles to long fibres. These composites have in common that the key problem is the matrix-reinforcement compatibility as well as difficulties when recycling scrap. Their strength is the possibility to have a well-defined orientation of fibres and fairly large fractions of reinforcement. The reinforcement is often a highly stable material with a low solubility in the matrix. Altogether this makes recycling difficult. Using the *in situ* route for fabrication of the composite, the matrix-reinforcement compatibility is in most cases solved. The fact that the reinforcement precipitates in the liquid state and in many cases during solidification suggests a greater opportunity to recycle than using other types of fabrication techniques. In-house re-melting is a definite possibility if clustering and particle growth can be controlled.

The present work treats a possible system for in-situ composites, the Cu-Ti-C system. The binary system Cu-Ti is thoroughly reviewed and the binaries Cu-C and Ti-C presented. The influence of the presence of carbon on the phases occurring in the binary Cu-Ti system is discussed. These matters are necessary to understand both for manufacturing and recycling of the composite.

2. The binary phase diagrams and the phases occurring
2.1. The Cu-Ti system
The binary system Cu-Ti is a complex system in which several different compounds exist [1]. These phases will be described more in detail below after a general outline of the phase diagram, describing the most relevant reactions for the present paper.

The phase diagram compiled by Murray [1] is shown in Fig. 1. Starting at the copper-rich side copper melts at 1358 K [1] and decomposes peritectically at 1158 K under the formation of $TiCu_4$ [1–7]. The solid FCC copper has a fairly large solubility of titanium. The compound $TiCu_4$ forms a eutectic together with $TiCu_2$ [1–6]. The eutectic reaction occurs at 1148 K at 27 at % Ti. $TiCu_2$ undergoes a solid state eutectoid transformation into $TiCu_4$ and Ti_2Cu_3 [1–4, 8, 9]. $TiCu_4$ may thus be formed both from melt and from solid phase. The phases TiCu,
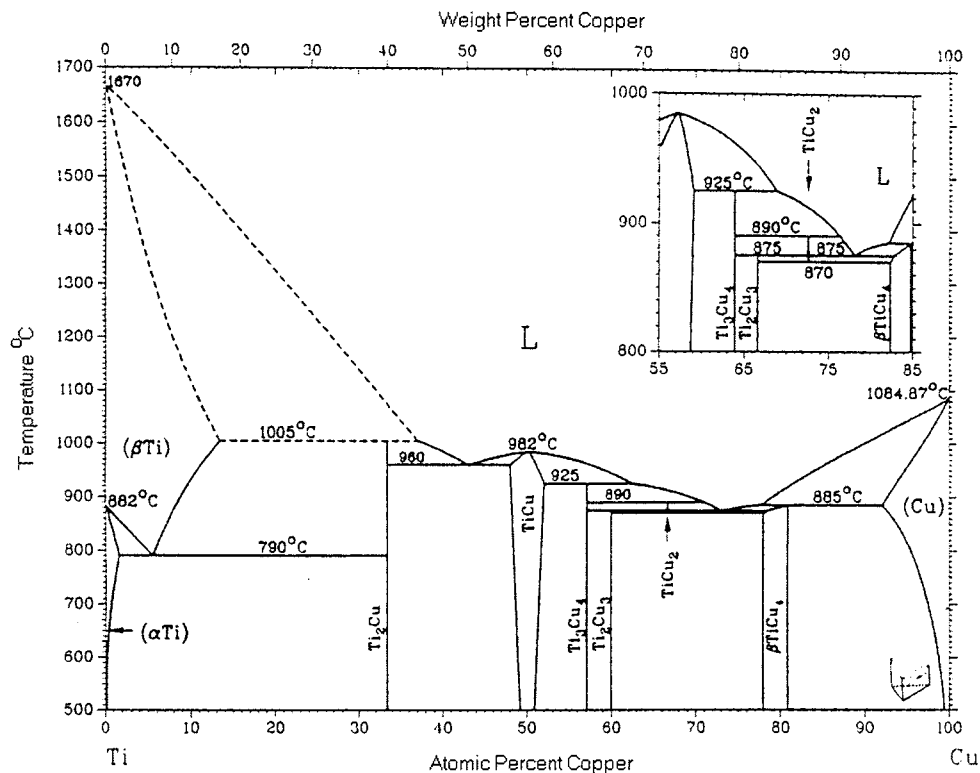
Figure 1 The binary Cu-Ti phase diagram [1, 27].

Ti_3Cu_4, Ti_2Cu_3 and $TiCu_2$ are compounds occurring in a cascade of peritectic reactions [1–5, 9]. It should here be noted that $TiCu_2$ is present only at a narrow temperature range and not at room temperature. This is not the case with the other phases occurring. TiCu represents a local temperature maximum in the system with its congruent melting at 1255 K [1, 2, 4, 5]. Closer to the titanium-rich side of the phase diagram a eutectic point is found in which TiCu and Ti_2Cu precipitates. This occurs at 1233 K at 57 at % Ti. Ti_2Cu is also formed peritectically from β-Ti at roughly 1278 K [1, 4, 5]. Ti_2Cu may also be formed from solid phase when β-Ti decomposes into α-Ti and Ti_2Cu [1, 2, 4, 10, 11].

2.1.1. Cu
Copper may dissolve up to 8 at % Ti at the peritectic temperature [1]. This solubility may increase drastically if oxygen is present [3]. There exists a strong tendency towards ordering in the solid solution at composition higher than 4 at % Ti [1, 12, 13].

2.1.2. TiCu₄
The exact composition of $TiCu_4$ has been under considerable debate. First it was designated $TiCu_3$ [1, 4, 5, 14, 15]. It was however finally concluded that the real formula was $TiCu_4$ and that the composition could vary between 19.1 at % Ti up to 22 at % Ti [1]. It should here be noted that the phase $TiCu_3$ may occur as a metastable phase having compositions between 21 at % Ti up to 25 at % Ti [16]. It should furthermore be noted that the presence of oxygen stabilises $TiCu_4$ [3].

2.1.3. TiCu₂
The phase, $TiCu_2$, is considered to be stoichiometric corresponding to 33.3 at % Ti. An interesting feature is

that Cu, containing Ti may form non-crystalline phase during rapid solidification. Diffraction analysis of the non-crystalline material shows a pre-peak indicating chemical short-range ordering [1, 17–20]. A weak but similar type of peak was found in the liquid state [1, 21]. This short-range structure was suggested to have the same ordered structure as $TiCu_2$ [1, 18]. This is strong evidence for a short-range ordering tendency in the Cu-Ti system in addition to the tendency to form compounds. This short range ordering suggests that the integral enthalpy of mixing, H_m^M, is negative in the liquid.

2.1.4. Ti₂Cu₃
Ti_2Cu_3 is the phase in equilibrium with $TiCu_4$ in the solid state. It is considered to be stoichiometric with a titanium concentration of 40 at % [1]. It should here be noted that Ti_2Cu_3 only forms from a solid state reaction and is thus unlikely to form when quenching from the liquid or mushy state.

2.1.5. Ti₃Cu₄
Ti_3Cu_4 is also a stoichiometric compound with a nominal titanium concentration of 42.9 at % [21]. The slim difference in composition between Ti_3Cu_4 and Ti_2Cu_3 makes it extremely difficult to distinguish between them by composition and thus also by EDS-analysis.

2.1.6. TiCu
TiCu is a congruently melting compound, with a non-stoichiometric composition. Eremenko *et al.* [2] studied the width of the composition range for TiCu and found that it may vary between 48 at % Ti up to 51 at % Ti. Karlsson [15] reported a maximum solubility of 53% Ti. Karlsson [15] also reported a substantially lower solubility on the Cu-rich side but the experiments suffered

from a substantial contamination of oxygen. The experiments of Karlsson [15] are therefore regarded as less reliable.

2.1.7. Ti_2Cu

Ti$_2$Cu form a eutectic with TiCu as mentioned above. The exact composition has been under debate and Ti$_3$Cu have been suggested [15] at which the compositional variations lies between 72.5 at % Ti up to 75 at % Ti. Eremenko *et al.* [2] found the composition range to be between 67 at % Ti up to 70 at % Ti at 1073 K. Mueller *et al.* [21] on the other hand reported almost a single phase composition with variations between 76.2 at % Ti up to 77.2 at % Ti. Ti$_2$Cu may also precipitate by an ordering reaction rather then by a re-dissolution process, indicating a positive heat of mixing in titanium [22, 23].

2.1.8. Ti

A large amount of work has been made to investigate Ti. It is well known that there exist two modifications, α-Ti having a hexagonal structure and β-Ti being cubic. α-Ti may dissolve up to 1.6 at % Cu and β-Ti may dissolve as much as 13.5 at % Cu at 1063 and 1278 K respectively [1].

2.2. The Cu-C system

The Cu-C phase diagram comprises no stoichiometric compounds and only limited solubility in the existing phases, i.e., carbon dissolves only to limited amounts in Cu and vice versa [24–26]. The Cu-C system is shown in Fig. 2 [27]. It is likely that there exists an inflection point on the liquidus line. This would indicate that H_m^M

is positive. This is further supported by the fact that the mutual solubility of copper and carbon is low in combination with the absence of an intermediate compound.

2.3. The Ti-C system

The binary Ti-C phase diagram is shown in Fig. 3 [27]. The Ti-C system is a well-established system of which the work by Jonsson [28] covers most aspects. The Ti-C system has α-Ti and β-Ti at one end at which only a very limited solubility of carbon exists. The situation is similar at the carbon-rich side. The difference compared to the Cu-C system is that TiC$_{(1-y)}$ exists. TiC$_{(1-y)}$ is highly non-stoichiometric and shows ordering tendencies with decreased degree of stoichiometry. TiC$_{(1-y)}$ is a highly stable compound that causes most ternary systems to rapidly lower the solubility of titanium and carbon in a liquid in contact or equilibrium with TiC$_{(1-y)}$. It is interesting to note that there exists a limited solubility of Cu in TiC$_{(1-y)}$ which seems to have a tendency to increase with lower temperature and lower degree of stoichiometry [29].

3. Experimental

The materials used to produce the alloys are listed in Table I, while compositions and temperature conditions are found in Table II. The experimental procedure was identical for all experiments. Each crucible was filled with the appropriate amount of copper, titanium and graphite or titanium carbide. Graphite or titanium carbide, having a lower density was put in the bottom and copper on top to enhance the mixing of species. To protect the samples, the crucibles were encapsulated in quartz tubes. Each quartz tube carried three crucibles.
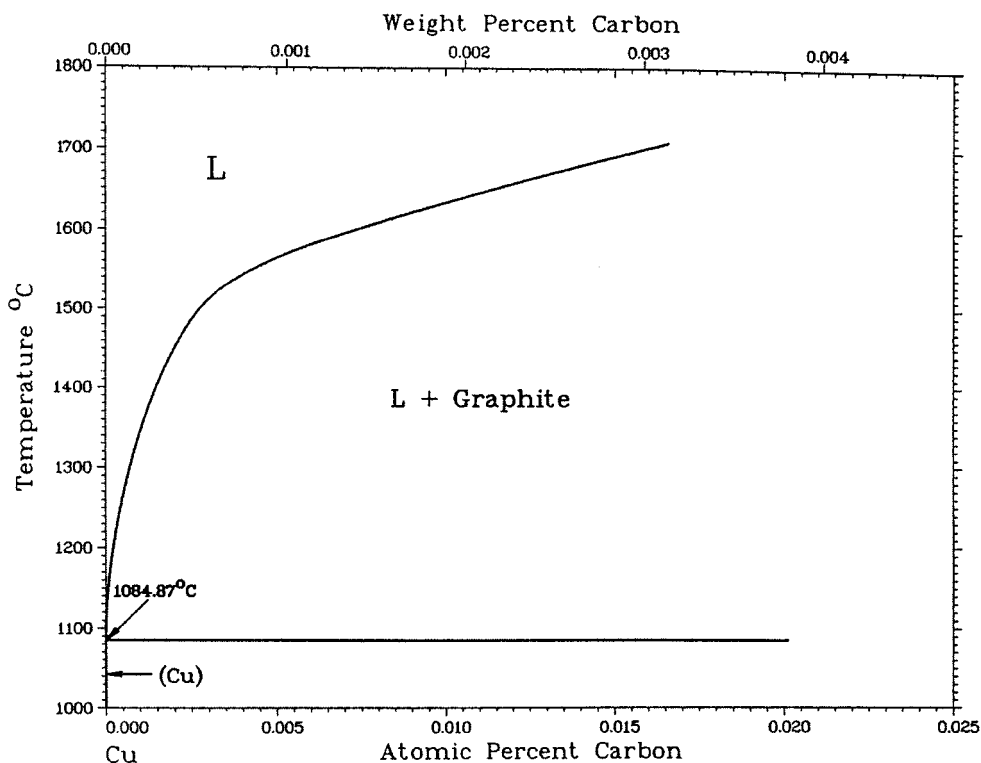

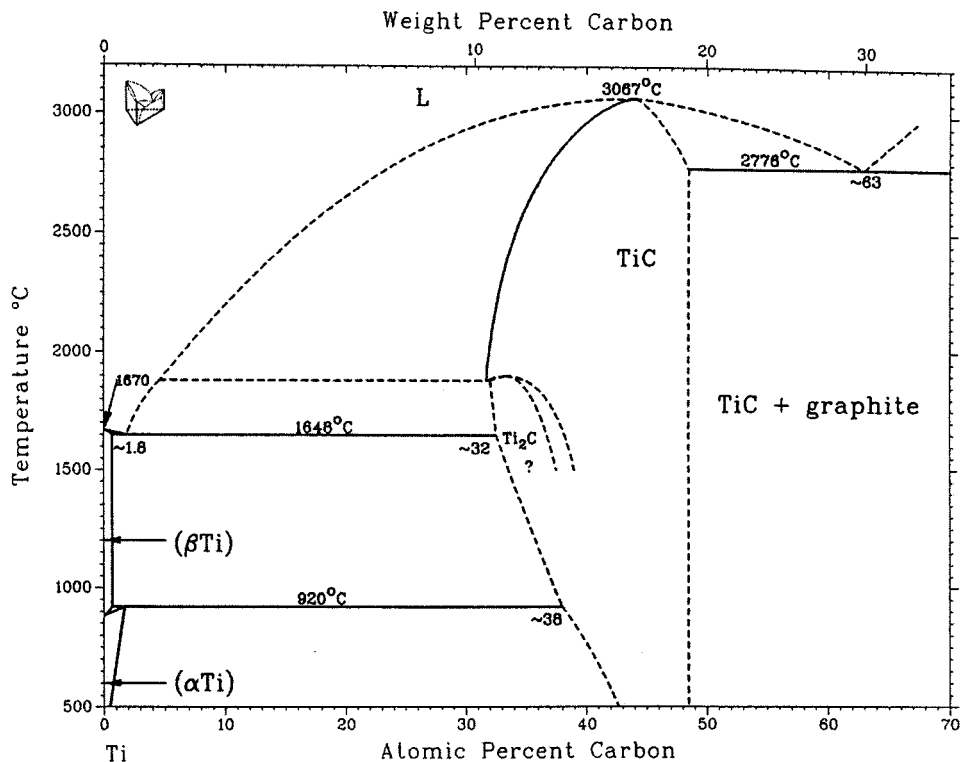*Figure 2* The binary Cu-C phase diagram [27]

Figure 3 The binary Ti-C phase diagram [27]

Before final sealing, the quartz tubes were flushed with argon and evacuated to ensure a low oxygen partial pressure. Several tubes were put into the furnace to ensure an identical thermal history. The furnace used was a resistance furnace. The temperature variation in the region where the samples were located was measured to be less than 10 K. The temperature during heat treatment was only measured at one location. The temperature variation during heat treatment were less than ±2 K. After 24 h the samples were removed from the furnace and quenched by letting the sealed quartz tube fall into brine, in an effort to freeze the state at the treatment temperature. The size of the samples after solidification was typically a cylinder with a height of 0.006 m and a diameter of 0.008 m.

The choices of alloy composition were such that all alloys contained 5 at % carbon. Two different groups of alloys were produced. The first set was made in such a way that stoichiometric titanium carbide was added to the alloy in such an amount that the carbon content corresponded to 5 at % carbon. Additional titanium was added to reach the required titanium content in the different samples. The second set of samples was made from copper, titanium and graphite. Graphite was added to the same concentration as the first set, that is 5 at % carbon and titanium was added to reach the proper composition of the samples. The set of phases present is in principle decided by the average concentration in the alloy. The reason for the choice of two different sets of samples is as follows: When carbon is added in the form of TiC it will go in to solution to the amount dictated by the equilibrium with TiC which is low. If on the other hand carbon is present in the form of graphite, the carbon-activity will be forced towards unity and the solubility of carbon will be higher. This forces the path towards equilibrium to be different than when carbon is added in the form of TiC. The choice of the two different fabrication methods was thus made to double check and to ensure the solution of carbon into the molten copper and to ensure the formation of all compounds possible.

TABLE I Specification of the material used to fabricate the alloys

Material	Purity	Major impurities		
Cu	99.95	—	—	—
Ti (wt %)	99.89	Fe	O	C
		0.050	0.040	<0.01
TiC	98.5	—	—	—
Graphite (ppm)	99.99	Ash	B	S
		20	<2	2

TABLE II Experimental conditions with titanium concentration ranges given as at % titanium

	TiC base ($X_C = 0.05$)			Graphite base ($X_C = 0.05$)		
Temperature (K)	Minimum	Maximum	No. of samples	Minimum	Maximum	No. of samples
1373	0.3	41	11	2	54	11
1173	5	46	11	1	45	10

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4. Results and discussion

The results and discussion section will be divided into three sections. The first part comprises a general outline of the ternary region Cu-Ti-C. The second part will discuss the composition of the individual phases and experimental results in detail. The third parts treats the possible precipitation sequences.

4.1. General outline of the phase diagram

It should first be noted that titanium carbide was found in all samples. It is also clear that it is present in the liquid state during heat treatment.

A typical SEM micrograph, in the back-scattered mode, is shown in Fig. 4. The darkest phase is $TiC_{(1-y)}$ and will not be considered in the discussion below. The microstructures clearly indicates the presence of a miscibility gap showing the typical smooth and adjustable interfaces commonly found in systems with a liquid miscibility gap. That the surrounding phases are found in the interior of the other phases, indicate a secondary precipitation during cooling. This indicates that the miscibility gap is skewed. This is due to the presence of $TiC_{(1-y)}$ at one side of the ternary system, forcing the liquidus surfaces towards higher temperatures in alloys having low copper contents. The Cu-Ti system shows a strong tendency towards chemical ordering and thus the equilibrium occurring will be skewed [1, 17, 18, 21]. As was mentioned above the ordering tendency in the liquid showed similarities to the compound $TiCu_2$.

The thermodynamic description by Murray [1] enables the calculation of the integral heat of mixing in the Cu-Ti system. In general the thermodynamics of a phase, i.e., may be described as

$$^{i}G_{m} = {}^{i}G_{m}^{0} + T{}^{i}S_{m} + {}^{i}G_{m}^{E} \tag{1}$$

where

$$^{i}G_{m}^{0} = \sum_{j} x_{j} G_{j}^{0}$$

$^{i}S_{m}$: Integral entropy of the phase i (J/mol, K)
$^{i}G_{m}^{E}$: Integral Gibbs excess energy (J/mol)
T: Absolute temperature (K)
$^{i}G_{m}^{0}$: Integral Gibbs energy of pure substance in phase i (J/mol)
x_{j}: Molar fraction of element j
G_{j}^{0}: Partial Gibbs energy of the pure substance j (J/mol)

The Gibbs energy of mixing is then defined as

$$^{i}G_{m}^{M} = {}^{i}G_{m} - {}^{i}G_{m}^{0} \tag{2}$$

This results in the following expression for the Gibbs energy of mixing

$$^{i}G_{m}^{M} = RT \sum (x_{i} \ln(x_{i})) + {}^{i}G_{m}^{E} \tag{3}$$

where R: General gas constant (J/mol, K)

In a binary system, using that $x_1 + x_2 = 1$ and Equation 3 yields

$$^{i}G_{m}^{M} = RT(x_1 \ln(x_1) + (1 - x_1) \ln(1 - x_1)) + {}^{i}G_{m}^{E} \tag{4}$$
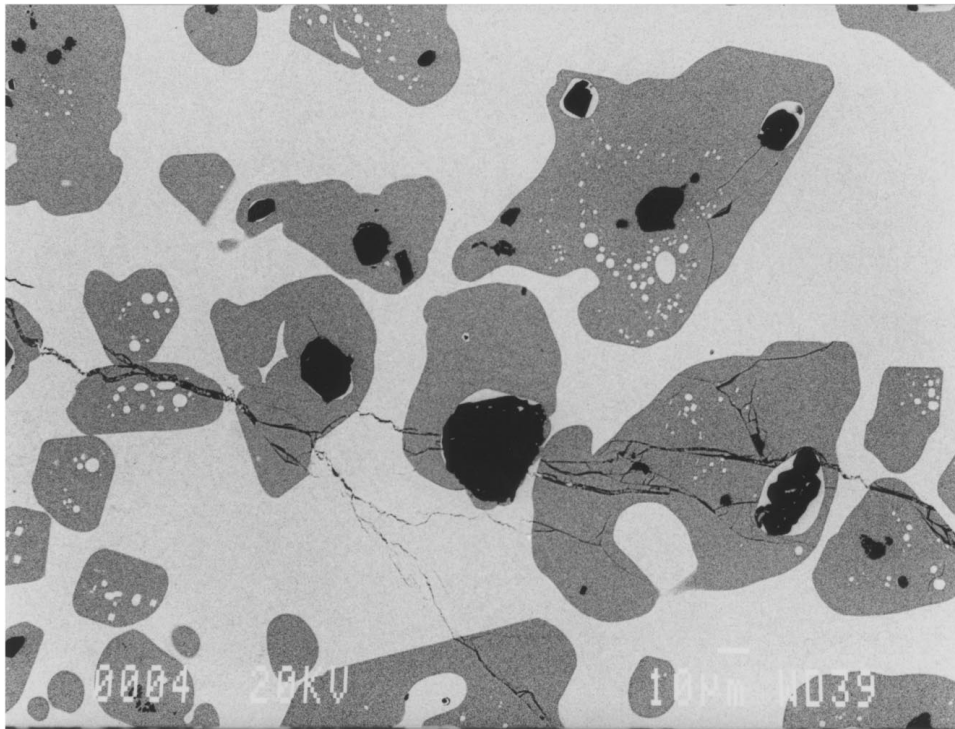

Figure 4 SEM-micrograph (back-scattered mode) showing a microstructure indicating a miscibility gap. The sample having an analyzed nominal concentration of 36.2 at % Ti treated at 1173 K with TiC as carbon source. The black phase is TiC, the dark phase is TiCu and the light phase is $TiCu_2$.

Phase	B (J/mol)	C (J/mol)	D (J/mol)
FCC Cu	4600	0	0
β-Ti	4300	0	0
α-Ti	16500	0	0
Melt	-12000	3539	8278

Murray used Equation 5, below, to describe the Gibbs excess energy

$$^{i}G_{m}^{E} = x_1(1-x_1)\big(^{i}B + {^{i}C}(1-2x_1)$$
$$+ {^{i}D}\big(6x_1^2 - 6x_1 - 1\big)\big) \tag{5}$$

In the work of Murray the coefficient ^{i}B, ^{i}C, ^{i}D are independent of temperature why the following can be stated

$$^{i}H_{m}^{M} = \frac{^{i}G_{m}^{E}}{x_1(1-x_1)} \tag{6}$$

This provides better understanding of the clustering behaviour of the material. If $H_{m}^{M} < 0$ then short-range ordering of copper and titanium atoms occur while if $H_{m}^{M} > 0$ separation of the atoms will be dominant. Studying the values for some the phases present the following is found. In the melt $H_{m}^{M} < 0$, indicating that a tendency for clustering in the melt is possible. For the FCC-copper phase $H_{m}^{M} > 0$, indicating a tendency for separation of the atoms is found. The same is valid for both α-Ti and β-Ti. The values for the coefficients used in the calculations where given by Murray and are collated in Table III.

It is now possible to calculate the spinodal for the separation. The equation of the spinodal is the given by the condition that

$$\left(\frac{\partial^{2i}G_{m}^{M}}{\partial x_1^2}\right) = 0 \tag{7}$$

The derivative is given by

$$\big(\partial^{2i}G_{m}^{M}/\partial x_1^2\big) = -\big[RT + 2x_1(x_1-1)\big(^{i}B + 3^{i}C$$
$$+ 5^{i}D - (6^{i}C + 36^{i}D)x_1$$
$$+ 36^{i}Dx_1^2\big)\big]/x_1(x_1-1) \tag{8}$$

The condition for the spinodal, Equation 7 and the second order derivative of Gibbs energy of mixing, Equation 8 yields the following expression for the spinodal.

$$T_{\text{spinodal}} = -\big[2x_1(x_1-1)\big(B + 3C + 5D$$
$$- (6C + 36D)x_1 + 36^{i}Dx_1^2\big)\big]/R \tag{9}$$

The results from the calculation are shown in Fig. 5a and b. None of the spinodals exceeds the liquidus lines in the binary diagram, Figs 5a and 1. Interesting to note is that the minimum for the calculated spinodal temperature of the melt is located just around TiCu$_2$,
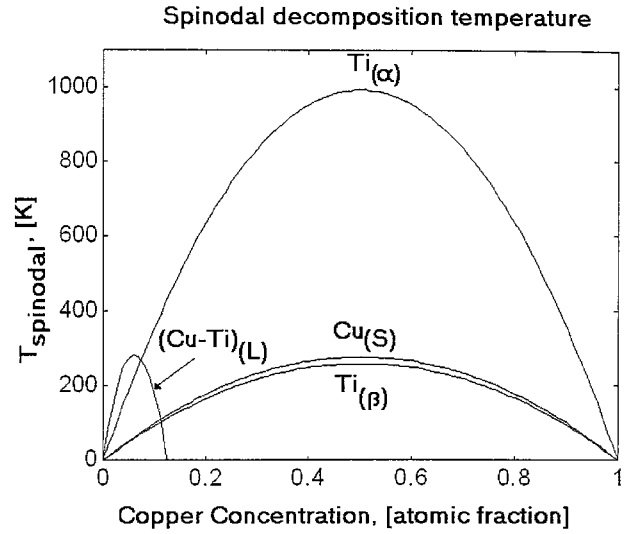

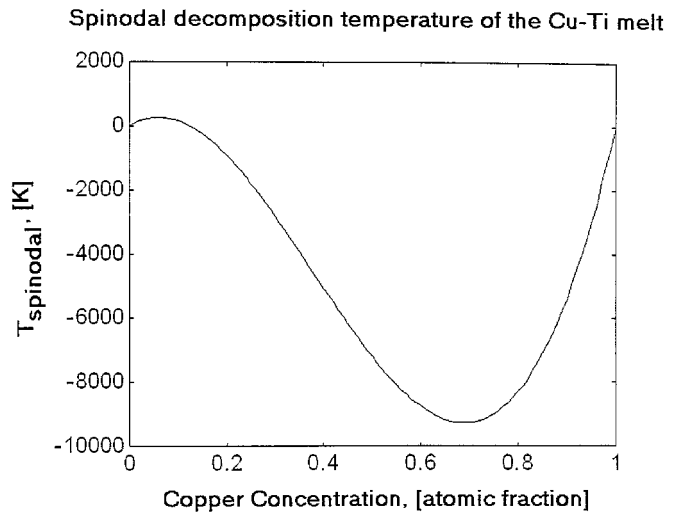*Figure 5a* Spinodal decomposition temperatures for liquid Cu-Ti, FCC Cu, α-Ti and β-Ti.

Figure 5b Full view of the decomposition temperature in the Cu-Ti melt.

Fig. 5b. Since the spinodal decomposition temperature is negative, the location of the minimum should be interpreted as the most likely concentration for a short-range clustering instead of separation. This is consistent with the findings that there exists a clustering in the binary melt around this composition, i.e. TiCu$_2$. It may thus be concluded that the thermodynamic description made by Murray [1] provides a good description of the binary system.

As carbon is added clearly a phase separation occurs, visible from Fig. 4. This indicates that the presence of carbon has a strongly positive contribution to the heat of mixing in the ternary system. Any miscibility gap in the system must be located towards the Cu-C side of the system. Since the short-range order near TiCu$_2$ is, from a phase separation point of view, the most difficult point to overcome, this is a critical point for the miscibility gap. As carbon is added, the heat of mixing is increased. Any point near this concentration will have a more positive value for the heat of mixing and thus a greater tendency for phase separation. As phase separation occurs the liquid will thus separate into one liquid having lower titanium concentration and
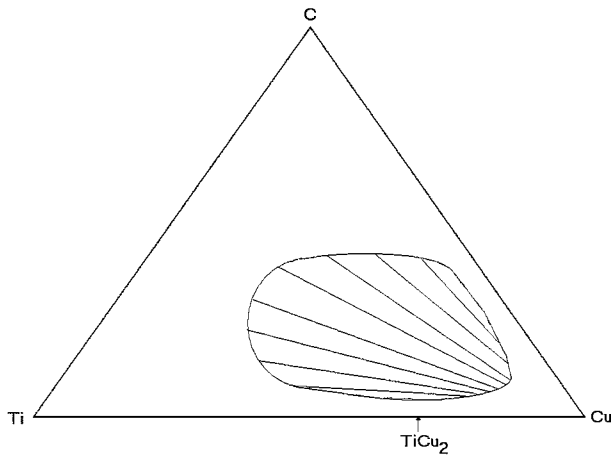
Figure 6 Schematic representation of the miscibility gap indicating the direction of the tie-lines and indication of the critical point at the Cu-Ti side of the phase diagram.

one having a higher titanium concentration than the critical concentration close to TiCu$_2$. This suggest that the tie-lines primarily are located along the Cu-Ti side of the phase diagram and that the shortest tie-lines are close to TiCu$_2$ in concentration. This is schematically illustrated in Fig. 6.

Another interesting feature is that the most dominant solid spinodal is that of the α-Ti, which is consistent with earlier findings that Ti$_2$Cu is predominantly formed by a spinodal decomposition rather by the eutectic reaction. The general tendency found in the samples is that Ti$_2$Cu is present at higher temperature while TiCu occurs at lower temperature. TiCu appears again at the higher concentrations at lower temperatures. This suggests that Ti$_2$Cu is mainly formed by a eutectic reaction, but does not exclude the spinodal decomposition.

At 1373 K the only solid phase occurring is TiC$_{(1-y)}$ at the compositions studied. It was impossible to accurately establish the fact whether or not the two liquids are present at 1373 K in an alloy containing 5 at % carbon. It was however clear that after solidification of the samples phase separation had occurred. The fact that is was impossible to positively determine the presence of two liquids at the treatment temperature is due to distortion of the samples during quenching.

The situation is somewhat different at 1173 K, at which the phases listed below are stable in addition to TiC$_{(1-y)}$.

$$Ti_3Cu_4, TiCu, Ti_2Cu, \beta\text{-}Ti$$
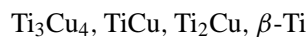
A consequence of the presence of a miscibility gap is that two liquids will form having different compositions. As the molten alloy solidifies each liquid will precipitate phases given by the local composition of the liquid. This causes a large number of different phases to form during solidification making the samples difficult to interpret.

4.2. Composition of the phases

The composition ranges of the occurring phases are collated in Table IV together with the earlier reported

ranges, discussed above. The composition of TiC has been separately treated elsewhere [29].

The FCC copper phase was found in all samples but two. One of these samples was manufactured from graphite and treated at 1373 K. The other sample were made from titanium carbide and treated at 1173 K. The composition of these samples were 41.3 and 36.3 at % Ti respectively. The fact that copper was absent in a sample treated at 1173 K with a composition of 36.3 at % Ti, which is close to TiCu$_2$ supports that the critical point for the spinodal is in this range. The fact that copper is found in all other samples even though it not is stable in the binary phase diagram supports the presence of a miscibility gap in the ternary Cu-Ti-C system.

The analysis of the Ti-concentration in the copper matrix phase is shown in Fig. 7a and b. The leftmost line in the figure correspond to the amount intentionally added, i.e., it has the slope one. The upper and lower bounds were arbitrarily drawn and should not be seen
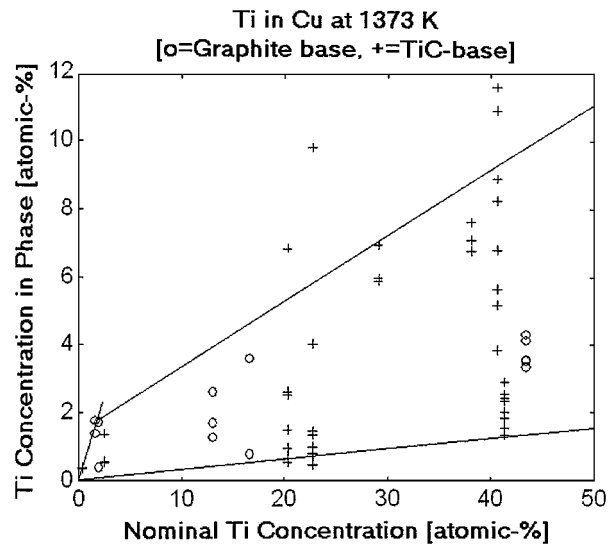

Figure 7a Ti content in Cu quenched from 1373 K where (o) Graphite base and (+) TiC base alloys. Lines indicates upper and lower boundaries of the solubility.
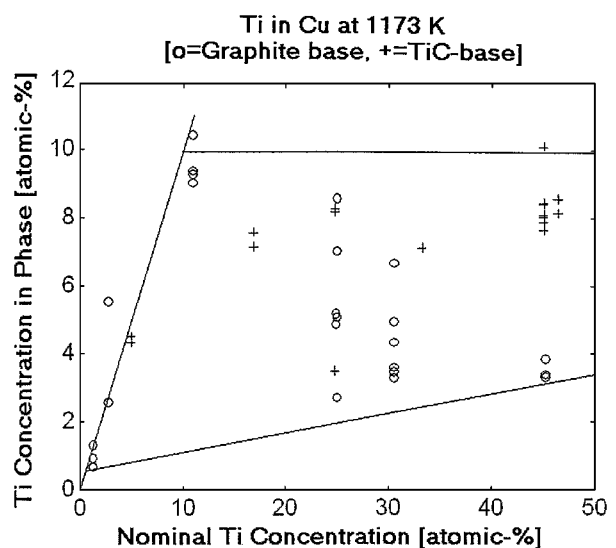

Figure 7b Ti content in Cu quenched from 1173 K where (o) Graphite base and (+) TiC base alloys. Lines indicates the upper and lower bounds of solubility.

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TABLE IV Comparison between reported solubility and experimentally assessed solubility

Phase	Temperature used in experiments	Reported range		Experimentally found range		Remarks
		Min	Max	Min	Max	
Cu	1373			—	11	Only maximum values relevant
		Max 8				
	1173			—	10	Ditto
TiCu$_4$	1373			16.9	21.2	—
		19.1	22			
	1173			15.8	19.0	—
TiCu$_3$	1373			26.8	28.8	—
		21	25			
	1173			22.5	27.2	—
TiCu$_2$	1373			32.9	35.5	Only found in TiC-base specimen with nominal concentrations below 22.7 at % Ti
		33.33				
	1173			29.2	30.9	Only found in the range of nominal concentrations between 30.6 and 36.2 at % Ti
Ti$_2$Cu$_3$	1373			37.8	39.3	Only found in specimens with a nominal concentration below 22.7 at % Ti
		40				
	1173			—	—	No Ti$_2$Cu$_3$ found at this temperature
Ti$_3$Cu$_4$	1373			43.2	44.0	Only found in two samples having nominal concentrations of 1.6 and 41.3 at % Ti
		42.9				
	1173			43.0		Only found in one sample having a nominal concentration of 1.6 at % Ti
TiCu	1373			48.9	59.6	Concentrations mainly within a 4 at % Ti window with upper en lower bounds increasing with nominal Ti content. Present in graphite base samples between nominal concentration between 1.9–45.3 at % Ti. In TiC base samples the range was 29–54.3 at % Ti
		48	53			
	1173			48.8	60.0	Increasing window range with increasing nominal Ti concentration. Present in graphite base samples between nominal concentration between 1.25–45.3 at % Ti. In TiC base samples the range was 16.9–45 at % Ti
Ti$_2$Cu	1373			63.6	75.2	Present in the range of nominal concentrations between 16.6 and 43.5 at % Ti
		67	77.2			
	1173			60.8	77	Present in the range of nominal concentrations between 1.25 to 30.6 at % Ti
Ti	1373			80.3	98.4	Present in the range of nominal concentrations between 2.6 to 41.3 at % Ti
		Min 86.5 (α-Ti)				
	1173	Min 98.4 (α-Ti)		80.5	90.3	Present in the range of nominal concentrations between 1.6 to 25 at % Ti in graphite base samples

as exact. It is clear that the samples made from graphite base alloys shows a lower solubility of titanium than the samples made from titanium carbide base alloys due to the increase carbon activity. The spread, in the measured composition, is caused by phase separation and the re-precipitation occurring during cooling. The analyses will not give the exact composition of the liquid phases. At 1373 K the upper bound concentration of the liquid is increasing constantly from value of 1.8 at % Ti up to 11 at % Ti, if the average nominal concentration is on the order of 40 at %. The lower bound concentrations ranges from around 0.4 at % Ti up to 1.6 at % Ti. At 1173 K, the upper bound increases from roughly 6.5 at % Ti (extrapolated value) up to roughly 10 at % Ti. The lower bound starts around 0.4 at % Ti increasing to 3.6 at % Ti. The lower bound corresponds to the first precipitated solid phase while the upper bound corresponds to the last solidified material from the melt with

a low titanium concentration. Interesting to note is that the maximum solubility in the FCC copper phase tends to be slightly increased in the ternary system, indicating a direction for the phase boundary, as well as a limited solubility of carbon in FCC copper.

Additionally it is worth noting that in the range fairly close to the composition of $TiCu_2$ the spread in titanium concentration seems to be lower. This may be due to that the difference between the two liquids is small, supporting the statement that this concentration is a critical point for the miscibility gap.

$TiCu_4$ was not found extensively in the samples indicating that little or no oxygen was present in the samples since this phase was stabilised by the presence of oxygen [3]. The composition of this phase is more similar to $TiCu_3$ that may form as a meta-stable phase. Thus it may be concluded that when carbon is present and the cooling rate is rapid $TiCu_3$ is favoured instead of $TiCu_4$. This may be seen in Fig. 8a and b. The lines in
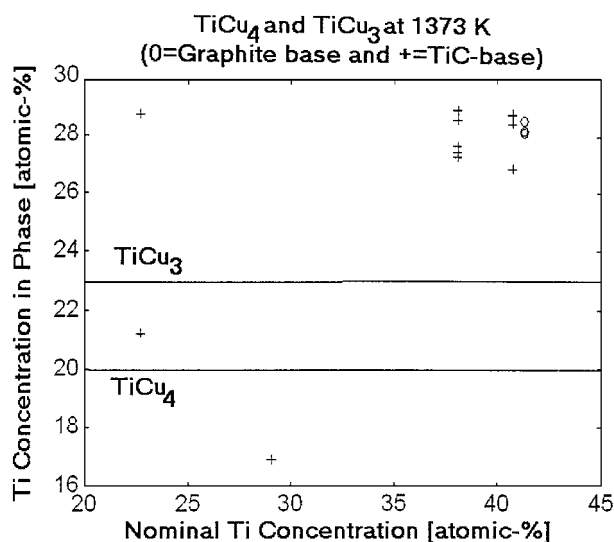

Figure 8a Ti content in $TiCu_4$ and $TiCu_3$ quenched from 1373 K where (o) Graphite base and (+) TiC base alloys. Lines indicating the stoichimetric composition of $TiCu_3$ and $TiCu_4$.
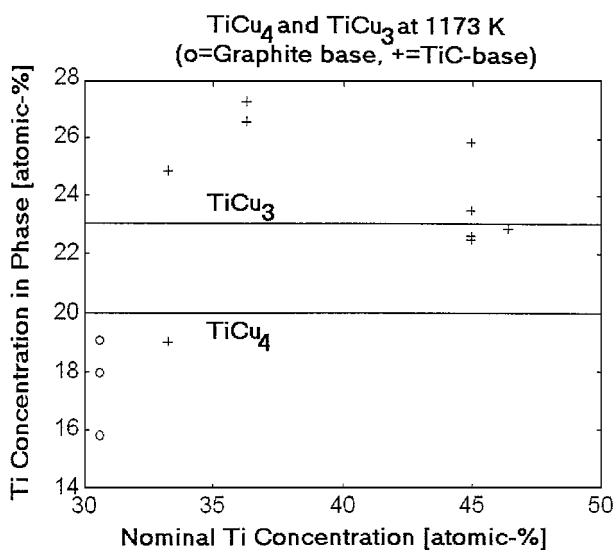

Figure 8b Ti content in $TiCu_4$ and $TiCu_3$ quenched from 1173 K where (o) Graphite base and (+) TiC base alloys. Lines indicating the stoichimetric composition of $TiCu_3$ and $TiCu_4$.

the figures indicates the position of the stoichiometric $TiCu_4$ and $TiCu_3$.

From the figure it can be seen that the $TiCu_4$ is present in the samples having nominal compositions in the interval 22 at % Ti up to 33 at % Ti. $TiCu_4$ tends to be slightly depleted in titanium compared to the earlier reported compositions. The composition of $TiCu_3$ is on the other hand somewhat rich in Ti instead. The increased range of existence suggests that there exists a limited solubility of carbon in both these phase, but this was presently not possible to confirm. Interesting is that $TiCu_3$ is predominantly formed above 35 at % Ti. A possible explanation to the precipitation of $TiCu_3$ instead of $TiCu_4$ may be the following. As the temperature is decreased the titanium-rich liquid will precipitate the copper-rich liquid. As the copper-rich liquid cools, it will precipitate solid copper and should finally precipitate $TiCu_4$. This may be the case if the nominal titanium content is low. On the other hand if the titanium content is increased the driving force for the precipitation of the copper-rich liquid from the titanium-rich liquid is much higher. This will occur at lower temperature from a liquid containing a fair amount of titanium. It is likely that this liquid will precipitate the meta-stable $TiCu_3$ due to the decreased temperatures and increased driving force for precipitation.

The composition of $TiCu_2$ were found to vary between 33 and 35.5 at % Ti at 1373 K and to be around 31 at % Ti at 1173 K, indicating that deviation from stoichiometry is possible. At 1373 K $TiCu_2$ was found in samples having nominal compositions below 22.7 at % Ti, while it only was found in the range between 30.6 and 36.2 at % Ti at 1173 K. At 1373 K it is formed from the titanium-rich liquid during cooling. At 1173 K it is formed by both liquids. This is further support that the critical point of the miscibility gap is located near the composition of $TiCu_2$. Ti_2Cu_3 were only found in the samples treated at 1373 K in samples having a nominal concentration lower than 22.7 at % Ti, supporting the formation of a titanium rich liquid. The composition was slightly hypo-stoichiometric but the number of points measured were not sufficient to draw any decisive conclusion.

The compositions of Ti_3Cu_4 were approximately independent of nominal composition and of treatment temperature. The variation where between 43.2 at % Ti up to 44 at % Ti indicating that it is close to stoichiometric.

TiCu is non-stoichiometric as indicated above and earlier results had found that the concentration had varied between 49 and 53 at % Ti even though Karlsson [15] reported substantially lower solubility on the copper-rich side. In the present study no strong evidence of contamination from oxygen have been found in the evaluated samples. In the present study the concentration of TiCu varies from just typically 48.9 at % Ti up to 59.6 at % Ti, Fig. 9a, in the samples treated at 1373 K. This supports the earlier found solubility on the copper-rich side. In the present investigation TiCu seems to continuously increase its composition with increasing composition showing a window of approximately constant range of about 4 at % Ti. In the samples
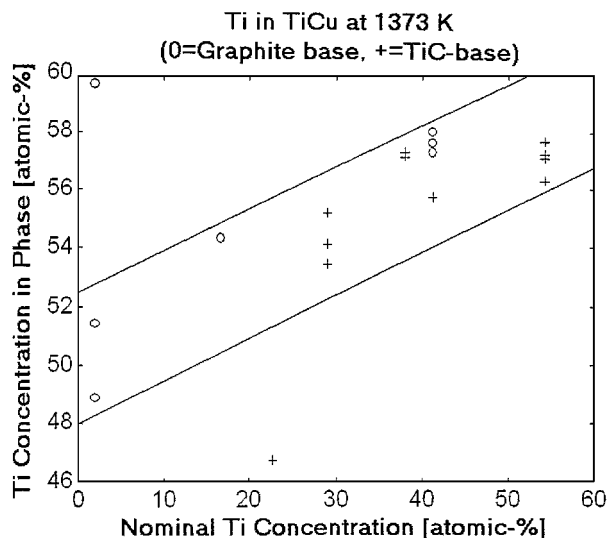
Figure 9a Ti content in TiCu quenched from 1373 K where (o) Graphite base and (+) TiC base alloys. Lines indicating upper and lower bounds of the concentration of Ti in TiCu.
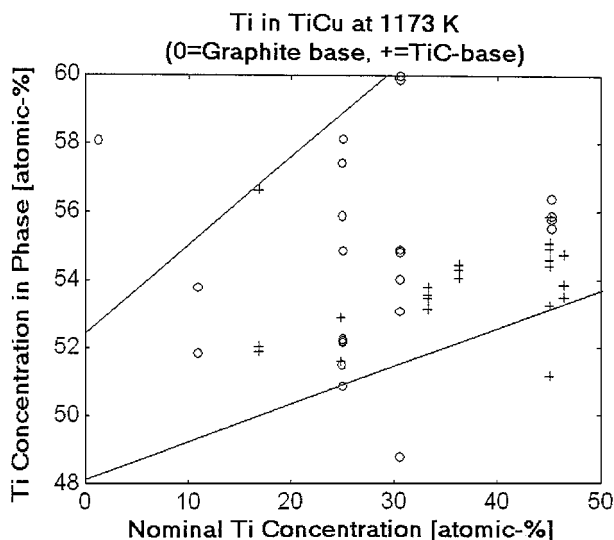

Figure 9b Ti content in TiCu quenched from 1173 K where (o) Graphite base and (+) TiC base alloys. Lines indicating upper and lower bounds of the concentration of Ti in TiCu.

treated at 1173 K this range of variation was from 49 at % Ti up to 60 at % Ti, Fig. 9b. This is a wider range than earlier accepted in the binary system [2, 15]. The only possible explanation for this is that carbon can dissolve in to TiCu. This was again not possible to confirm.

Ti$_2$Cu were found at both 1373 and 1173 K. At 1373 K it was found in two different regions, between 16 and 21 at % Ti and above 40 at % Ti. The variation in concentration of Ti$_2$Cu was, at 1373 K, in between 63.6 and 75.2 at % Ti. This range is slightly shifted toward lower titanium contents than earlier reported. At 1173 K Ti$_2$Cu were found at several different concentrations below 32 at % Ti and even down to 1.25 at % Ti.

Ti as a solid phase were found at both 1173 and 1373 K. At 1173 K evidence of Ti were found below nominal concentrations of 25 at % Ti. The reason for the presence of a Ti-phase with dissolved copper is again the fact that a Ti-rich liquid is formed. The presence of

both Ti and Ti$_2$Cu at low nominal concentrations indicates that the tie-lines are tilted towards the Ti-C side of the ternary phase diagram, as shown in Fig. 6.

An interesting fact is that when measuring the titanium content of the Ti phase it was found to be somewhat lower than reported earlier [1]. At a nominal concentration of 15 at % Ti a saturation limit seemed to be reached and this was roughly 80 at % Ti as compared to the 86.5 at % Ti reported earlier in β-Ti. Similar concentrations were found at 1173 K. At 1373 K the maximum titanium concentration in the Ti phase was identical to the maximum concentration of the β-Ti, i.e. 98.4 at % Ti. α-Ti can according to the Cu-Ti phase diagram contain down to 86.5 at % Ti. In the present study this value was found to be just above 80 at % Ti. This indicates that Ti-phases and then especially α-Ti is precipitated during cooling.

4.3. Precipitation of the phases
The precipitation is best made using a Scheil type of diagram outlining possible sequences. Such a diagram is shown in Fig. 10a and b. At 1373 K the samples consisted of molten Cu-Ti-C and TiC$_{(1-y)}$. It was not possible to clarify whether or not this alloy consisted of two liquids at treatment temperature. As the sample is quenched two liquids will precipitated if not already present. The copper-rich liquid precipitates more or less according to the binary Cu-Ti phase diagram for compositions close to the copper-rich side. Thus FCC copper and TiCu$_4$ is formed as well as the eutectic between TiCu$_4$ and TiCu$_2$. This may occur for alloys of a nominal concentration below typically 23 at % Ti. The copper-rich liquid will also precipitate a titanium-rich liquid. This titanium-rich liquid act identical to that already present due to the phase separation. The titanium-rich liquid formed this way can precipitate α-Ti or β-Ti under the subsequent formation of Ti$_2$Cu and the eutectic between Ti$_2$Cu and TiCu. The lower the nominal titanium content is the more likely it is for α-Ti or β-Ti to precipitate. This is a result of the tilted tie-lines. On the other hand, the titanium rich liquid will precipitate a copper rich liquid. This copper-rich liquid will also precipitate FCC copper and TiCu$_4$ or TiCu$_3$. If the nominal concentration of titanium is high the precipitated copper-rich liquid will predominantly precipitate TiCu$_3$. This occurs for concentrations typically above 37 at % Ti.

In the range of nominal concentrations between 30 and 37 at % Ti the precipitation is somewhat obscure since the difference between the two liquids is small. It is however likely that the titanium rich liquid will basically precipitate TiCu and follow the cascade of peritectic reactions. The behaviour of the copper rich liquid is not clear. It was impossible to clarify whether the originally present copper rich liquid or the copper rich liquid precipitated by the titanium rich liquid precipitates the FCC copper. It is also possible that the copper-rich liquid will follow cascade of peritectic reactions from TiCu$_2$ and down. However, at 1373 K in this range both TiCu$_4$ and TiCu$_3$ tends to be absent.

At 1173 K the phases present originally is different from those present at 1373 K giving a different

```
                          ┌─────────┐
                          │    L    │
                          │    ↔    │
                          │  L1+L2  │
                          └─────────┘

┌─────────┐   ┌─────────┐   ┌──────────┐   ┌──────────┐
│  L1↔Cu  │ → │  L2↔L1  │   │ L2↔TiCu  │   │ L2 ↔ Ti  │
└─────────┘   └─────────┘   └──────────┘   └──────────┘

┌─────────┐   ┌─────────┐   ┌──────────┐   ┌──────────┐
│  L1+Cu  │   │  L1↔Cu  │   │ L2+TiCu  │   │  L2+Ti   │
│    ↔    │   │         │   │    ↔     │   │    ↔     │
│  TiCu4  │   │         │   │  Ti3Cu4  │   │  Ti2Cu   │
└─────────┘   └─────────┘   └──────────┘   └──────────┘

┌──────────────┐  ┌─────────┐  ┌───────────┐  ┌──────────┐
│      L1      │  │   L1    │  │  L2+Ti3Cu4│  │    L2    │
│      ↔       │  │    ↔    │  │     ↔     │  │    ↔     │
│ TiCu4+TiCu2  │  │ Cu+TiCu3│  │   TiCu2   │  │Ti2Cu+TiCu│
└──────────────┘  └─────────┘  └───────────┘  └──────────┘

                            ┌───────────┐   ┌──────────┐
                            │    L2     │   │ Ordering │
                            │    ↔      │   │  Ti(Cu)  │
                            │TiCu2+TiCu4│   │    ↔     │
                            └───────────┘   │  Ti2Cu   │
                                            └──────────┘
```
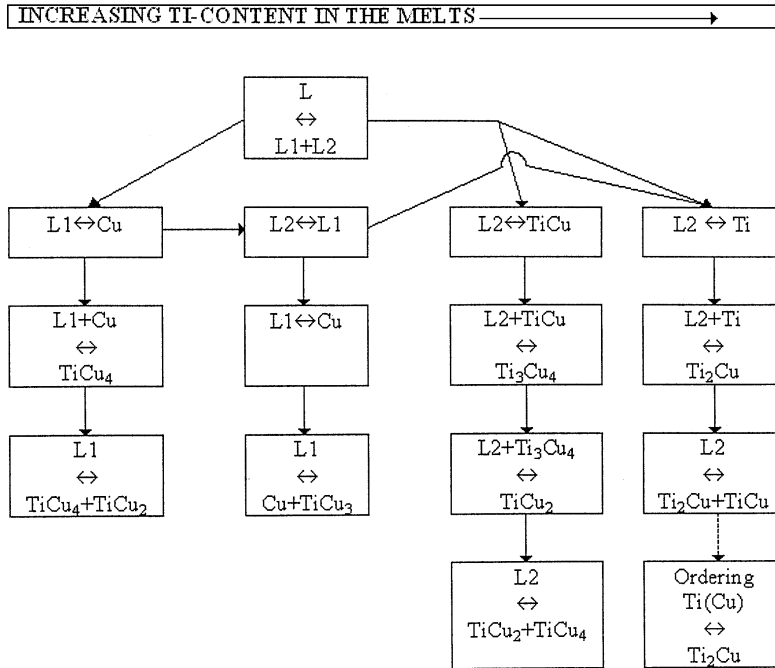
Figure 10a Scheil type of schematic representation of the possible reactions occurring from 1373 K. Note that equilibrium not is prevailing during solidification and thus Gibbs phase rule is not applicable.

INCREASING TI-CONTENT IN THE MELTS ⟶		
$X^L < 30$ [at.-% Ti]	$30 < X^L < 37$ [at.-% Ti]	$X^L < 37$ [at.-% Ti]

```
┌─────────┐   ┌────────────┐   ┌─────────┐   ┌─────────┐
│  Cu+L1  │   │ L2+Ti3Cu4  │   │ L2+TiCu │   │  L2+Ti  │
└─────────┘   └────────────┘   └─────────┘   └─────────┘

┌─────────┐   ┌────────────┐                 ┌──────────┐
│  L1↔Cu  │   │ L2+Ti3Cu4  │                 │    L2    │
│         │   │     ↔      │                 │    ↔     │
│         │   │   TiCu2    │                 │Ti2Cu+TiCu│
└─────────┘   └────────────┘                 └──────────┘

┌─────────┐                   ┌──────────┐
│  L1+Cu  │                   │ L2+TiCu  │
│ ↔TiCu4  │                   │    ↔     │
└─────────┘                   │  Ti3Cu4  │
                              └──────────┘

                              ┌──────────┐
                              │ L2+Ti3Cu4│
                              │    ↔     │
                              │  TiCu2   │
                              └──────────┘

┌──────────────┐              ┌──────────┐   ┌──────────┐
│      L1      │              │    L2    │   │ Ordering │
│      ↔       │              │    ↔     │   │  Ti(Cu)  │
│ TiCu4+Ti3Cu4 │              │  TiCu2+  │   │    ↔     │
└──────────────┘              │  TiCu4   │   │  Ti2Cu   │
                              └──────────┘   └──────────┘
```

In addition the following reactions occur during cooling (Compare to the reactions occurring from 1373 K)

```
        ┌─────────┐           ┌─────────┐
        │  L2↔L1  │           │  L1↔L2  │
        └─────────┘           └─────────┘

        ┌─────────┐           ┌─────────┐
        │  L1↔Cu  │           │ L2↔TiCu │
        └─────────┘           └─────────┘

    ┌──────────────┐      ┌─────────────────┐
    │ L1+Cu↔TiCu3  │      │ L2↔TiCu+Ti2Cu   │
    └──────────────┘      └─────────────────┘
```
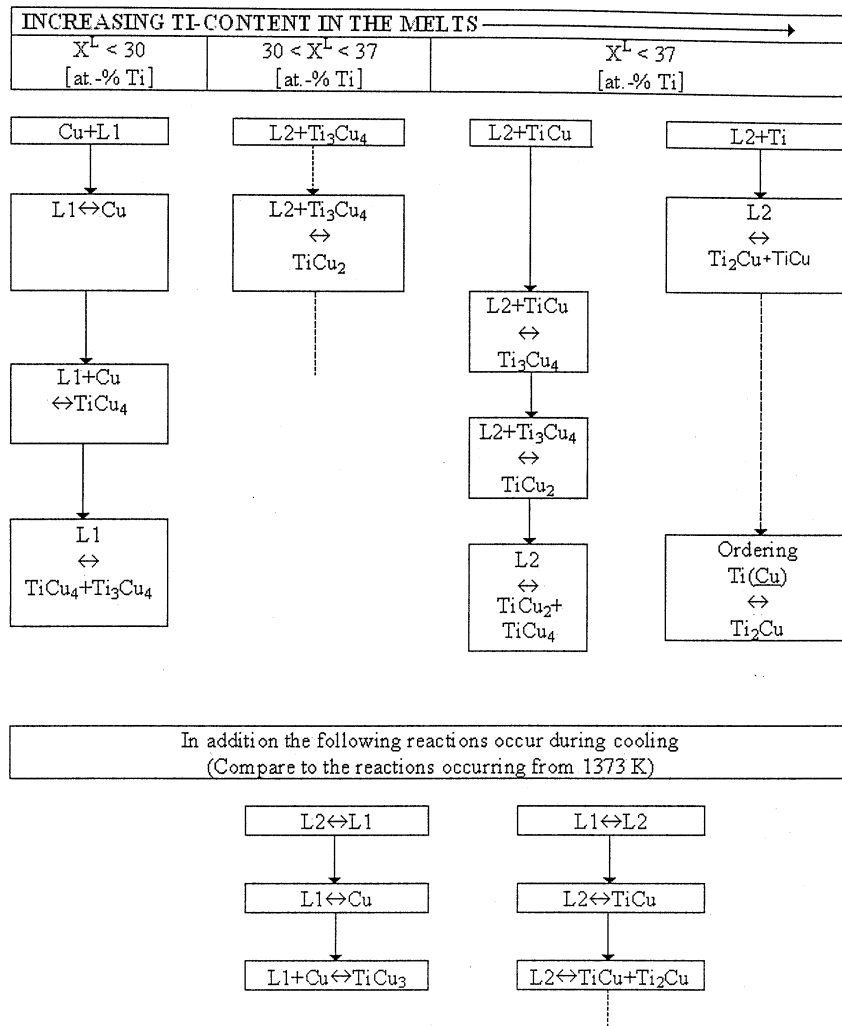
Figure 10b Scheil type of schematic representation of the reactions occurring from 1173 K. Note that equilibrium is not prevailing during solidification and thus Gibbs phase rule is not applicable.

precipitation sequence. At concentrations below approximately 30 at % Ti the phases possible at 1173 K is the copper- and titanium-rich liquids, $TiC_{(1-y)}$ and solid FCC copper. It is interesting to note that TiCu does not appear below a nominal composition of 17 at % Ti if TiC is added, while it is present in the whole experimental range if graphite is added. This implies that titanium rich liquid does not appear before a nominal concentration of 17 at % Ti under true equilibrium conditions, since graphite is forcing the carbon activity toward unity and the fact that residual graphite could be found. Otherwise the precipitation is similar to that at 1373 K. At 1173 K Ti as a phase was only found in samples below a nominal concentration of 25 at % Ti made from graphite. This indicates that the titanium-rich liquid under near equilibrium condition cannot precipitate α-Ti, but will instead precipitate TiCu and subsequently Ti_2Cu as a eutectic. TiCu appear above a nominal concentration of 17 at % Ti. At 1173 K the originally present titanium-rich liquid will not precipitate other phases that TiCu. This is evident from the samples made from TiC-base. In the range between 30.6 and 36.2 at % Ti $TiCu_2$ is found indicating the concentration window in between the two different liquids at 1173 K.

5. Conclusion

It has clearly been established that a phase separation occurs in the ternary Cu-Ti-C system. The critical point on the Cu-Ti-side is approximately at 33 at % Ti. Due to the presence of TiC the miscibility gap is skewed causing the two liquids formed precipitate each other. This caused a complex precipitation sequence in the system. This caused FCC copper to be present at almost all concentrations investigated. This copper phase can dissolve up to 10 at % Ti.

At 1373 K a tentative reaction scheme is proposed. Here the copper rich liquid precipitates according to the binary phase diagram and a titanium rich liquid. At 1373 K this precipitated may precipitate α-T or β-Ti. The precipitated titanium phase may dissolve up to 20 at % Cu. The titanium-rich liquid present will precipitate TiCu and follow the cascade of peritectics towards the eutectic between $TiCu_2$ and $TiCu_4$. The copper-rich liquid precipitated from the titanium-rich liquid will precipitate Cu and predominantly the meta-stable phase $TiCu_3$.

At 1173 K the copper-rich liquid appears as it does at 1373 K. In the concentration range between 30 and 37 at % Ti it is unclear how the system appears. Above 37 at % Ti the liquid is in equilibrium with TiCu. Depending on the liquid concentration it may follow the cascade of peritectics towards the eutectic between $TiCu_2$ and $TiCu_4$ or the titanium content is sufficient it may form the eutectic between TiCu and Ti_2Cu. This last route is also the precipitation sequence of the titanium rich liquid formed by the copper-rich liquid. As at 1373 K the copper-rich liquid precipitated by the titanium rich liquid will precipitate Cu and then predominantly $TiCu_3$.

An interesting feature is that the titanium content of the TiCu phase increases with the nominal concentration of titanium. At 1373 K the concentration window approximately 4 at % Ti, while at 1173 K the window increases.

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