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Phase transformations in Ag70.5Cu26.5Ti3 filler alloy during brazing processes

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Phase transformations that occur in the brazing alloy Ag70.5Cu26.5Ti3 are described. The liquid segregation paths and the liquid composition path are presented. The evolution of the liquid and the concentration of titanium in the liquid are plotted versus temperature. With increasing temperature the activity of titanium in the liquid increases and is sufficient for reactive brazing even before the alloy is completely melted and liquid is segregated. In the liquid, copper suppresses the activity of titanium while silver enhances it. The activities of titanium in both segregated liquids are identical, though the concentrations are very different. Thus, both liquids – Ag-Cu-rich L1 and Cu-Ti-rich L2 – are equally reactive and responsible for wetting and spreading, not just L2, as often believed. The major differences (including gravimetric) between L1 and L2 and the effect of preferential segregation of Ag to the free surface of the liquid on surface tension are discussed.

Silver-copper eutectic / Titanium / Active filler metal / Reactive brazing / Segregation / Phase diagram

Introduction

Ag-Cu near-eutectic alloys modified with such a reactive metal as titanium have been known for some time as filler metals that exhibit high-performance brazing characteristics both for different metals/alloys and for ceramics [1-5]. The bibliography on Ag-Cu-Ti braze alloys is quite extensive but there are still many unanswered questions related to the phase transformations that occur during brazing processes. In our own previous studies involving Ti-modified Ag-Cu near-eutectic braze alloys there were several issues which remained unexplained, like porosity in the joints or the process parameters (time, temperature, vacuum). Having not found any comprehensive thermodynamic or phase analysis of the Ag-Cu-Ti system applicable to brazing processes, we decided to look closer at the phase transformations that occur in the Ag70.5Cu26.5Ti3 alloy (known also as CB4) and address several issues related to brazing processes, like segregation of liquid, the role of titanium, wetability, etc. This analysis, which is based on published phase diagrams and some related experimental and theoretical studies, we hope, clarifies some issues related to the brazing technology and could be useful for other Ag-Cu-Ti alloys or similar systems.

Experimental

Though in this study we do not emphasize on our experimental findings, we still have to give some details of our practical work in order to correctly apply the theory to the experiment. In our studies on joining Y_2O_3–to–Y_2O_3, Y_2O_3–to–Zr, Zr–to–Zr, Si_3N_4–to–(410 type stainless steel) we used the commercially available active filler metal Ag70.5Cu26.5Ti3 (wt.%), known as CB4 [6-9]. Usually, our samples for brazing were made as round sandwiches with a piece of 0.13 mm thick braze alloy foil inserted between the pieces of the brazed materials. These sandwiches were placed in a quartz tube of a vacuum furnace where the pressure was kept within $10^{-1}…10^{-4}$ Pa during the heating-cooling campaign. The maximum temperature for the brazing process was 900 °C, which is right in the middle of the recommended brazing temperature range 850-950 °C for this filler metal [4]. The equilibration time in the different experiments ranged from 6 to 60 min.

The initial microstructure of the braze alloy CB4 (Fig. 1) consists of an Ag-rich matrix, Cu-rich inclusions (both structures are FCC), and copper-titanium intermetallics, usually associated only with a Cu-rich phase, as was reported in the previous works [6-9]. Compositionally, when converted to atomic

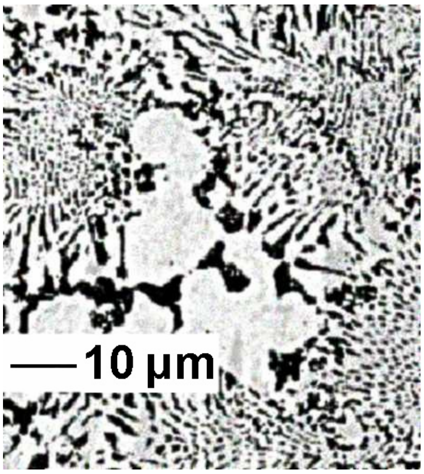

Fig. 1 SEM image of an as-received brazing alloy Ag70.5Cu26.5Ti3 (CB4).

concentrations, this alloy has the stoichiometry $Ag_{57.5}Cu_{37}Ti_{5.5}$, which could be considered as an $Ag_{60}Cu_{40}$ eutectic modified with 5.5 at.% of titanium. With this initial information let's turn to searching and analyzing the available phase diagrams and related structural, thermodynamic and other data.

Selection of the phase diagrams

For the analysis of melting/solidification of CB4, the phase diagrams for Ag-Cu-Ti and for the relevant binary systems have to be located and related information has to be found. The Ag-Cu binary system, having a positive heat of mixing in both the solid and liquid states, is categorized in a group of segregating systems. Being practically immiscible in the solid state at room temperature [10], silver and copper form a single liquid phase due to the large entropic contribution to the free energy of mixing at high temperatures. However, the statistical mechanical modeling of Ag-Cu melts suggests that even in this seemingly homogeneous liquid there is a tendency for homo-coordination, i.e. to a weak demixing, a tendency inversely proportional to the temperature and thus manifested mostly at near-eutectic temperatures [11].

The introduction of titanium into the Ag-Cu eutectic mix changes the energetics of the system. Contrary to the segregating interactions between Ag and Cu, both the Ag-Ti and the Cu-Ti systems exhibit high negative values for the heat of mixing leading to spontaneous heteroatomic coordination, which is reflected in the formation of intermetallic compounds, and thus these systems are classified as compound-forming [12-15].

Titanium has higher affinity to copper than to silver; the Cu-Ti bonds are stronger, i.e. have more negative values of the Gibbs energy of mixing and, consequently, are more preferred than the Ag-Ti ones. This is reflected in the binary phase diagrams, which exhibit only two intermetallic compounds for the Ag-Ti system and six intermetallics for the Cu-Ti system – two phases and four line compounds [10].

In the binary Ag-Ti system there are two intermetallics, AgTi and $AgTi_2$, however, there is discussion on the existence of $AgTi_3$ and some disagreement on the shape of the Ag-Ti phase diagram can be found [10,16-23].

The binary Cu-Ti system appears much more complicated with a long list of published stoichiometries for Cu-Ti intermetallics – $CuTi_3$, $CuTi_2$, CuTi, Cu_4Ti_3, Cu_3Ti_2, Cu_2Ti, Cu_3Ti, Cu_7Ti_2 or $Cu_3Ti{\cdot}Cu_4Ti$, Cu_4Ti – some exhibiting allotropy. A few of them were reported once or twice many years ago and have not been confirmed by experimental studies ever since, like δ-CuTi, Cu_3Ti (any form: α-, β-, or β′-) or Cu_7Ti_2. Others, like $CuTi_3$ and α-Cu_4Ti (LT), were revitalized in a recent review by Okamoto [24]. The former, a suggested tetragonal $CuTi_3$ (*P*4/*mmm*), that appeared in the early 1950-s, was claimed again in 2002 based on DTA studies [24-27]. The latter, initially an unsolved low-temperature modification of Cu_4Ti, published in 1983 and ignored by numerous studies since then, is probably related to α-Cu_4Ti of Ni_4Mo-type structure (*tI*10) mentioned by Okamoto [24,28]. Besides, there are misprints, mistakes and erroneous speculations in the reported thermodynamic and crystallographic data, which could easily be traced [19,24,29].

The relatively low credibility of some physico-chemical parameters stem from the high reactivity of titanium with practically all crucible-making materials and with oxygen and nitrogen in the surrounding, which causes the chemistry and thus the energetics of the studied system to be modified, often significantly. In the case of the silver-containing system (Ag-Ti) the volatility of silver introduces an additional problem [23]. These factors make the experimental studies rather hard and the old experimental works very valuable.

Searching for the most recent publications related to the Cu-Ti phase diagrams, one can assume that the phase relations in this system do not differ much from those published in the early work by Eremenko *et al.* [16,29,30]. Eremenko's Cu-Ti diagram exhibits six intermetallics – $CuTi_2$, CuTi, Cu_4Ti_3, Cu_3Ti_2, Cu_2Ti, and Cu_4Ti. The list was confirmed by a) the popular handbook by Massalski [10], who incorporated the work of Murray [20,21] and the studies of b) Paulasto *et al.* [23], c) Kumar *et al.* [12], d) Arroyave [31,32], and e) Shiue *et al.* [33]. The shape of the diagrams published by Eremenko *et al.* [29,30] remained almost unchanged except for the L ↔ $CuTi_2$ transformation, which was corrected from congruent (Eremenko *et al.* called it *distectic*) to peritectic (Fig. 2). Also, the compositional boundaries for the intermediate phases CuTi and Cu_4Ti and the temperatures for invariant points appeared adjusted first in the handbook by Massalski [10] and lately in several studies based on

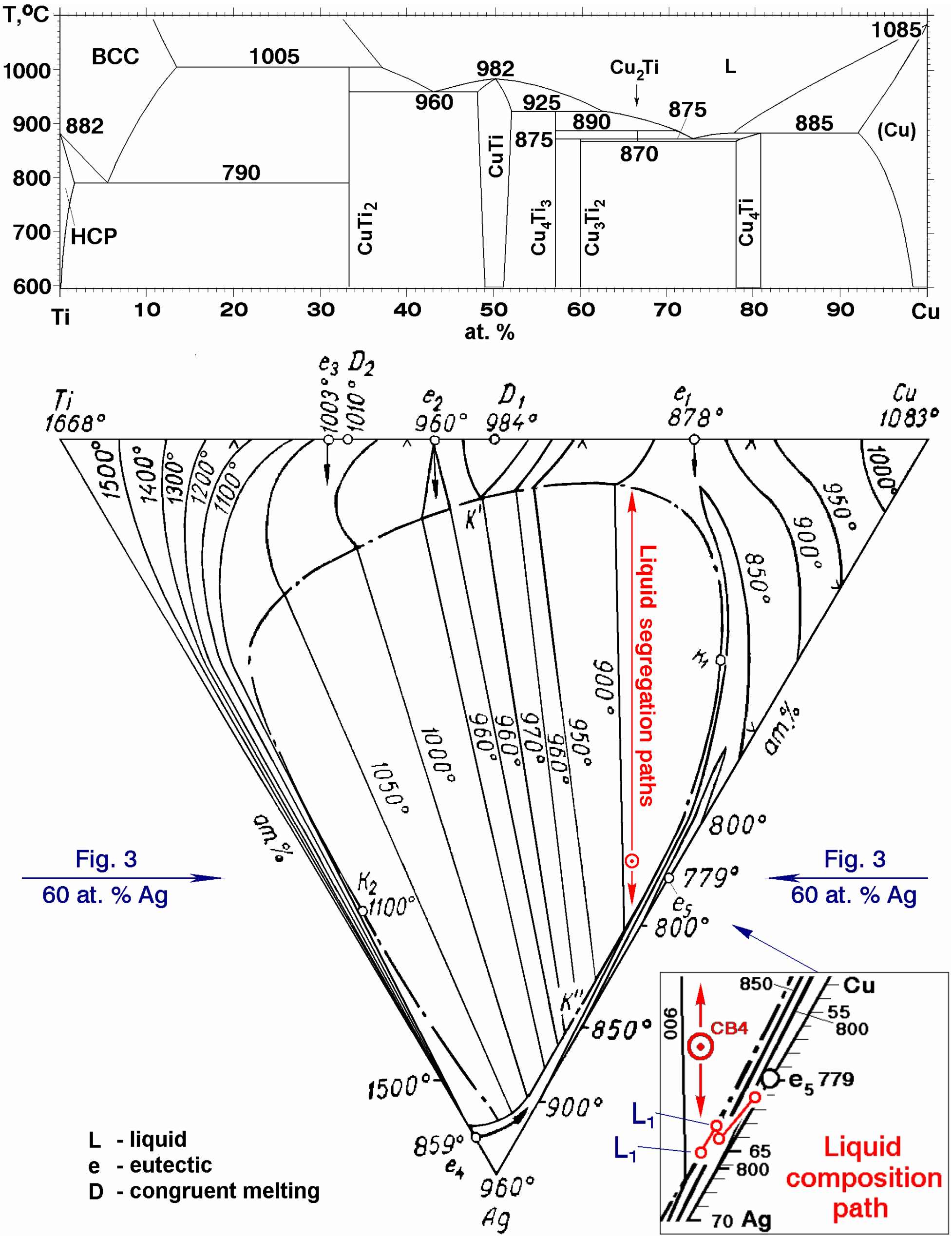

Fig. 2 Liquidus surface projection onto the Ti-Cu-Ag compositional triangle (bottom) [16] and Ti-Cu phase diagram (top) transformed from [10]. Designations: — • — – boundary of the miscibility gap; ← ⊙ → – composition of CB4 and liquid segregation paths.

computer (Calphad) modeling [12,24,31,32]. We transformed the experimentally-based Cu-Ti diagram published by Massalski in order to couple it with the ternary Ag-Cu-Ti diagram (Fig. 2) for better understanding of the phase transformations in the Ag-Cu-Ti system.

The search for ternary Ag-Cu-Ti phase diagrams resulted in finding just a few independent studies. The earliest (1969-1970) most comprehensive experimental investigation was conducted by Eremenko *et al.* [16,30,34,35]. In 1977 Chang *et al.* [19] revised the available data for the ternary Ag-Cu-Ti system and redrew three diagrams from Eremenko *et al.*, missing, however, their major summarizing publication [30] with seven sections of the Ag-Cu-Ti system. The collection of Petzow and Effenberg issued in 1988 reproduced the same three diagrams [36] and only in 1996 the rest of the missed diagrams of Eremenko *et al.* were included in the handbook compiled by Villars *et al.* [37]. A new set of experimental data and two isothermal sections calculated for the Ag-Cu-Ti system were published by Paulasto *et al.* in 1995 [23]. Finally, a thermodynamic model for this ternary system was performed by

Arroyave and Eagar and a calculated 700 °C isothermal section was published in 2004 [38]. These last two sources do not principally change the first published diagrams and it seems justified to use the original diagrams by Eremenko *et al.* For better perception we combined (Fig. 2) the liquidus surface projection of the ternary Ag-Cu-Ti diagram with the binary Ti-Cu diagram converted from the one published in Massalski's handbook [10,16].

The diagram (Fig. 2) exhibits a wide miscibility gap in the ternary liquid phase where the liquid segregates into two liquids:

$$L = L_1 + L_2,$$

L_1 tending towards the Ag-Cu edge with low Ti content and L_2 tending towards the Cu-Ti edge with relatively low Ag content, though it is sometimes thought that the segregating Ag-Cu system have to split into the Ag-Ti and Cu-Ti liquids. Separation into Cu-Ti and Ag-Cu, however, points to the role of copper. Indeed, Cu with its small atomic size must have a crucial role in defining the energetics of the interatomic interactions and, specifically, the entropic terms of the Gibbs free energies, thus defining the coordinating preferences within the Ag-Cu-Ti liquid.

The composition of the braze alloy CB4, $Ag_{57.5}Cu_{37}Ti_{5.5}$, shown as ⊙ (Fig. 2), falls inside the miscibility loop, somewhat lower than the 900 °C isotherm on the liquidus projection, confirming that 900 °C is sufficient for complete melting of the filler metal. We constructed the isotherm that crosses the point corresponding to the composition of CB4 and designated it with two arrows showing the segregation paths. Upon reaching the miscibility boundary line, these arrows point to the compositions of L_1 and L_2 formed by the segregating action.

Estimated from the miscibility gap, the studied braze alloy segregates into $L_1 = Ag_{65.0}Cu_{33.2}Ti_{1.8}$ (87 at.%) and $L_2 = Ag_{6.7}Cu_{62.6}Ti_{30.7}$ (13 at.%). The chemistry of L_1 is close to the Ag-Cu eutectic, while L_2 exhibits apparent Cu_2Ti stoichiometry, which is close to the lowest Cu-Ti eutectic (~870 °C). Note that the intermetallic phase Cu_2Ti exists only in a narrow temperature range between 850-860 and 880-890 °C, *i.e.* just below the liquidus surface.

Now the questions arise: a) how does the temperature affect the stabilities of the phases and their compositions before the braze alloy is completely melted and segregated into L_1 and L_2 and b) how do the phase transformations that occur between the solidus and liquidus points influence wetting/spreading during the brazing process? This and other useful information could be derived from one of Eremenko's vertical sections of the ternary Ag-Cu-Ti system [30]. Since the composition of CB4 is close to the $Ag_{60}Cu_{40}$ eutectic and because the Ti-Cu interactions dominate in this system, a vertical Cu-Ti section of the Ag-Cu-Ti system for fixed 60% Ag could be very useful for an analysis of CB4, especially because this section is almost normal to the isotherms on the liquidus surface. In Fig. 2 this section is designated with two arrows near the Ag-Ti and Ag-Cu lines. Fig. 3 depicts this Ti-Cu-(60% Ag) section within the 700-1100 °C temperature frame.

The CB4 segregation paths (two vertical arrows in Fig. 2) appear exactly normal to the Ti-Cu-(60% Ag) section so we can make a normal projection and obtain a) the position of the liquidus point (marked as ⊙ in Fig. 3) and b) the heating-cooling path for the alloy under equilibrium conditions. This path crosses the Cu-Ti composition axis at 4.25% Ti-35.75% Cu (marked as ⊙ below the axis in Fig. 3). Using the composition of the liquid phase calculated from Fig. 2, we can perform a phase analysis and study the redistribution of the elements among all the phases.

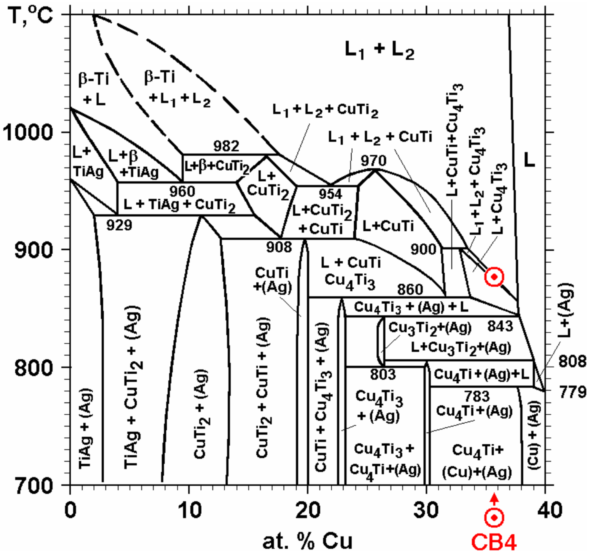

Fig. 3 Vertical Cu-Ti-(60% Ag) section of the Ag-Cu-Ti system [30]. ⊙ – composition of CB4.

Cooling path of the melted CB4

The liquidus temperature of CB4, according to Fig. 3, is 877 °C. The liquid is segregated to 87% L_1 + 13% L_2, the compositions being $Ag_{65.0}Cu_{33.2}Ti_{1.8}$ and $Ag_{6.7}Cu_{62.6}Ti_{30.7}$, respectively. With a decrease of temperature the cooling path enters the ($L_1 + L_2 + Cu_4Ti_3$) domain, which is characterized by precipitation of the first intermetallic compound Cu_4Ti_3 from L_2 (note that L_2 corresponds to Cu_2Ti stoichiometry). With the precipitation of Cu_4Ti_3 several processes can be observed and quantitatively estimated:

a) the amount of L_2 quickly decreases from 13% to 0%,

b) all Ag (L_2) and the excess Cu (L_2) diffuse from L_2 to L_1,

c) the composition of L_1 is modified (Fig. 2) along the miscibility loop, changing from $Ag_{65.0}Cu_{33.2}Ti_{1.8}$ to $Ag_{63.2}Cu_{35.0}Ti_{1.8}$, and

d) the amount of L_1 increases from 87 to 91 at.% and is balanced with 9% of solid Cu_4Ti_3 phase. With the consumption of L_2, the remaining homogeneous liquid L_1 is from now on designated L.

When the temperature drops below 874 °C (Fig. 3) the cooling path enters the (L + Cu_4Ti_3) domain. The direction of the liquid composition path changes abruptly towards enrichment in Ag and depletion in Ti (Fig. 2). The liquid is now balanced only with one phase, Cu_4Ti_3, of which one additional percent precipitates, causing the composition of the liquid phase to change from $Ag_{63.2}Cu_{35.0}Ti_{1.8}$ to $Ag_{63.9}Cu_{34.7}Ti_{1.4}$.

Moving below 852 °C the cooling path enters the (L + Cu_4Ti_3 + Ag[Cu]) domain. Here a second solid phase precipitates: FCC Ag[Cu]. The solubility of copper in Ag at these temperatures is about 8.5 at.%, while the solubility of titanium in this Ag-8.5Cu solid solution is rather low and we ignore it in our approximate calculations. Once again we see an abrupt change in the liquid composition path (Fig. 2) because the precipitation of Ag[Cu] phase causes the composition of the liquid to shift in the direction of the Ag-Cu eutectic. This, in turn, stimulates the precipitation of Cu_4Ti_3. According to our estimates, the amount of the precipitated phases, *i.e.* Ag[Cu] and Cu_4Ti_3, is of the order of 2% with the ratio 3:2 and the final phase composition at 843 °C is: 88% L = $Ag_{64.1}Cu_{34.9}Ti_{1.0}$, 11% Cu_4Ti_3 and 1% Ag[Cu]. The noticeable discrepancy between our calculations (~1%) and Fig. 3 (~2%) for the solubility of titanium in the liquid phase in the 60Ag-Cu alloy at this temperature is probably connected to the precision of the almost 40-year old hand drawings.

At 843 °C, according to Eremenko *et al.* [30], the following reaction takes place:

$$L + Cu_4Ti_3 = Cu_3Ti_2 + Ag[Cu]$$

and the cooling path enters the (L + Cu_3Ti_2 + Ag[Cu]) domain. This reaction at 843 °C a) consumes about 3% of the liquid phase; b) turns all Cu_4Ti_3 into Cu_3Ti_2; c) precipitates about 2% of Ag-8.5Cu phase. Further cooling causes the composition of the liquid to shift towards the Ag-Cu eutectic and thus more Ag[Cu] phase has to precipitate. The solubility of Cu in FCC Ag at the bottom of this domain (808 °C) increases to *ca.* 11.5 at.%. At the same time, the solubility of Ti in the liquid gradually decreases. The estimated phase composition just above the 808 °C boundary line is the following: 78% L = $Ag_{63.2}Cu_{36.2}Ti_{0.6}$, 13% Cu_3Ti_2 and 9% Ag-11.5Cu.

Similarly, at 808 °C, when the cooling path enters the (L + Cu_4Ti + Ag[Cu]) domain, the formation of Cu_4Ti from Cu_3Ti_2 occurs according to:

$$L + Cu_3Ti_2 = Cu_4Ti + Ag[Cu].$$

This reaction turns all Ti contained in Cu_3Ti_2 into Cu_4Ti (in our calculation we take this intermediate phase as a stoichiometric compound) and consumes about 2/3 of the remaining liquid, while precipitating 35% Ag[Cu] phase. This is the most important reaction with respect to the amount of matter involved and the amount of liquid transformed to solid. When this reaction is completed, just below 808 °C, the phase composition is estimated as follows: 29% L = $Ag_{63.2}Cu_{36.2}Ti_{0.6}$, 27% Cu_4Ti and 44% Ag-11.5Cu. Further cooling down to 783 °C is possible only if the composition of the liquid shifts closer to the 60:40 stoichiometry and thus additional Ag[Cu] has to precipitate. The solubility of Cu in Ag further increases from 11.5 to 13.8 at.%. At the same time the solubility of Ti in the liquid decreases. The estimated phase composition just above the 783 °C boundary line is the following: 53 % Ag[Cu], 27% Cu_4Ti and 20% L = $Ag_{60.7}Cu_{39.1}Ti_{0.2}$.

At 783 °C the last portion of liquid phase solidifies according to:

$$L + Cu_4Ti = Cu[Ag,Ti] + Ag[Cu]$$

where Cu[Ag,Ti] is the solid solution in FCC copper. According to the binary Cu-Ti diagram (Fig. 2), at this temperature Cu dissolves 4% Ti. In the ternary Ag-Cu-Ti system this phase accommodates comparable amounts of Ag and Ti, at least according to the published ternary sections for 700 and 900 °C [30,37]. The most recent calculations of the 700 °C ternary section of the Ag-Cu-Ti diagram suggest solubilities of Ag and Ti in Cu of about 3-3.5% for each element [31,38]. At 783 °C the solubilities have to be higher and it seems reasonable to take the composition of this phase to be Cu-4Ag-4Ti. When all these phases are balanced the following numbers are obtained: a) 1.3% of the existent Cu_4Ti is consumed for the reaction; b) 7.5% Cu[Ag,Ti] and additional 13.5% Ag[Cu] are produced; c) below the 783 °C boundary line the phase composition of CB4 is the following:

26% Cu_4Ti + 66.5% Ag[Cu] + 7.5% Cu[Ag,Ti].

Further cooling to room temperature would result in the precipitation of some Cu_4Ti and depletion of solid solutions, *i.e.* Ag[Cu] and Cu[Ag,Ti], from solutes so that the final equilibrium composition of CB4 is

27.5% Cu_4Ti + 57.5 % Ag[Cu] + 15% Cu[Ag,Ti].

However, if we compare the published values for the solidus and liquidus points of commercially available CB4, namely 803 and 857 °C [2], we notice apparent deviation from the values derived in the above phase analysis, *i.e.* 783 and 877 °C. The possible sources for this discrepancy are: a) inaccuracy of the source diagrams; b) Fig. 3 was constructed for 60% Ag, not for 57.5%; c) the as-received alloy is not at equilibrium; and d) the published values for the solidus-liquidus melting range are also non-equilibrium.

Looking at the CB4 heating path (Fig. 3) and at the temperature dependence of the amount of liquid phase (Fig. 4) it could be suggested that the solidus point published for CB4, 803 °C, corresponds to the $Cu_4Ti \leftrightarrow Cu_3Ti_2$ transformation at 808 °C, described above. If one deals with a non-equilibrium alloy and non-equilibrium thermal methods for studying phase transformations it is possible that the solidus stage at 783 °C, involving the $Cu[Ag,Ti] \leftrightarrow Cu_4Ti$, transformation is not detected. The $Cu_4Ti \leftrightarrow Cu_3Ti_2$ transformation at 808 °C could not be ignored,

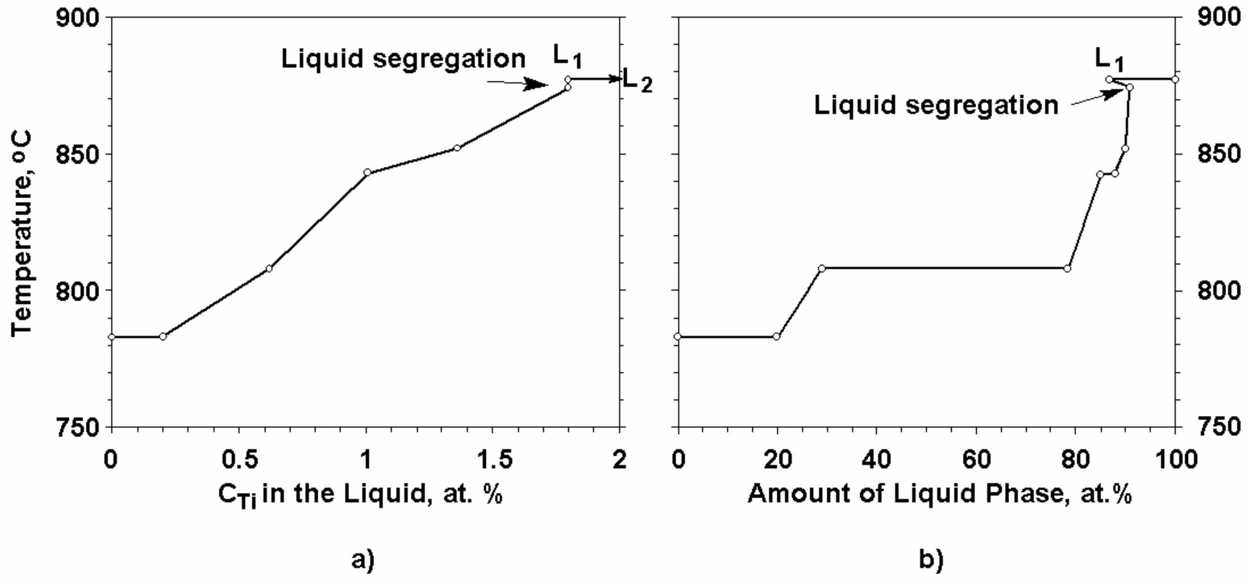

Fig. 4 Temperature dependence of a) the concentration of Ti in the liquid phase and b) the amount of liquid phase.

however, since it is the most prominent transformation in the alloy.

As to the liquidus point published for CB4 (857 °C), it falls into the (L + Cu_4Ti_3) domain. It is hard to blame non-equilibrium conditions for this discrepancy since the temperature is high and the amount of liquid is about 90%. Responsible for this error could be the high reactivity of Ti, poor experimental set-up or a mistake in the diagram (Fig. 3), which, as pointed out above, is not the correct section, but is slightly shifted towards higher Ag values.

The above results conclude the analysis of the cooling path of melted CB4, which could also be read in the opposite direction, *i.e.* as a heating path. Now, knowing the effect of temperature on the phase transformations and compositions, we can look at how this information may be applied in an analysis of the processes that occur during brazing.

Discussion

1. Melting at the solidus point

There are several observations related to the melting of the braze alloy CB4. Firstly, at low temperatures the third equilibrium phase besides the Ag- and Cu-based solid solutions is Cu_4Ti. The presence of Cu_3Ti_2 phase in the analysis of the as-received CB4 alloy reported earlier [7] proves that this alloy was not at equilibrium. Possibly, when the alloy is heated, $Cu_3Ti_2 \rightarrow Cu_4Ti \rightarrow Cu_3Ti_2$ transformations take place at about 808 °C and no detectable $Cu_4Ti \rightarrow Cu \rightarrow Cu_4Ti$ transformations are observed around 783 °C. This could explain the reported solidus point for this alloy.

Secondly, the solidus point is located higher than the AgCu eutectic (779 °C). This is because titanium is present in the FCC copper solid solution. We assume that at this temperature copper dissolves about 4% Ti and 4%Ag. There is also some solubility of titanium in FCC Ag[Cu], though the published experimental works do not give us any significant number. The dissolved titanium causes the AgCu eutectic point to rise.

Thirdly, even under equilibrium conditions the very first portion of liquid should contain some titanium, though a small amount. Estimated from Fig. 3 and verified with Fig. 2 this concentration should be 0.15-0.2%. For a non-equilibrium alloy this number has to be higher.

Fourthly, at 808 °C the major part of the alloy (whether at equilibrium or not) is melted. Only about 20% of the alloy remains solid (Fig. 4). At this point the issue of wetability becomes important.

2. Ti activity in the liquid

At 808 °C there is a significant amount of titanium dissolved in the liquid. Estimations based on Fig. 2 gave 0.6%, while from Fig. 3 we derived about 1% Ti. Based on the above calculations we plotted the temperature dependence of the amount of liquid phase and the Ti concentration in the liquid (Fig. 4) in order to better visualize the role of titanium in the brazing process. It is clear that further increase of the temperature stimulates an increase of the Ti concentration in the liquid. The concentration of Ti in the liquid becomes 1.4% before the last portion of solid (Cu_4Ti_3) is finally melted and the liquid is segregated into two immiscible liquids. According to Fig. 3 this number exceeds 2%. Now a question appears: Is 1-2% Ti enough for reactive-wetting action of the liquid? Since titanium in the liquid has to work as a reactive element, the activity of Ti (a_{Ti}) is a more important parameter than its concentration (X_{Ti}).

Fortunately, there exists a study on the Ti activity coefficients ($\gamma_{Ti} = a_{Ti} / X_{Ti}$) in Ag-Cu liquids based on the experimental work by Pak *et al.* [13]. It was established that the titanium activity in Ag-Cu liquids exhibits a positive deviation from ideal solution behavior. Though the measurements were performed at 1000 °C, the positive deviation should stand true for the lower temperatures of the CB4 melting range. It was calculated that for the $Ag_{59.1}Cu_{39}Ti_{1.9}$ liquid at 1000 °C $\gamma_{Ti} = 4.5$. For the Ag-Cu eutectic the activity of titanium at infinite dilution was extrapolated to be $\gamma_{Ti} = 6.5$ (these numbers are relative to pure solid titanium at 1000 °C). This means that even the very first liquid, which appears above the solidus point of the studied alloy, though it contains only about 0.2% Ti, still has to be reactive. With increasing temperature, when the Ti content in the liquid increases the liquid should become more and more reactive.

The work of Pak *et al.* has demonstrated a very important relationship: the increased Ti activity in the Ag-Cu alloys is directly related to silver. For the $Ag_{99.84}Ti_{0.16}$ liquid the Ti activity coefficient was about 80. What this work did not emphasize was the effect of copper on the titanium activity coefficient. Contrary to silver, which dramatically enhances the activity of titanium, an introduction of copper decreases this parameter. For instance, in an $Ag_{83.57}Cu_{15.76}Ti_{0.67}$ liquid the activity coefficient was 4 times smaller than in $Ag_{99.84}Ti_{0.16}$, *i.e.* $\gamma_{Ti} = 20$, while for $Ag_{59.1}Cu_{39}Ti_{1.9}$ this value was again 4 times lower. The reason for this dramatic decrease of the titanium activity coefficient, 80→20→5, is connected, not so much with the decrease of the silver concentration in the melt, 99.84→83.57→59.1, as emphasized by Pak *et al.*, but rather with the increase of the copper content in the alloy: 0→15.76→39. This effect could easily be explained by the high affinity of Ti to Cu and preferred Cu-Ti pairing in the liquid. Earlier, Paulasto and Kivilahti also pointed out that the strong attractive interaction between Cu and Ti lowers the activity of Ti in Ag-Cu-Ti liquids [39].

Returning to the phase analysis of CB4, we come to the next observation. When we move up in temperature from the solidus point along the liquid composition path (Fig. 2) we observe a tendency towards an increase of the Ag:Cu ratio, *i.e.* a deviation from the near-eutectic composition in the Ag-rich direction. The amount of Ag in the melt increases with the consumption of Ag[Cu] phase until all the Ag[Cu] phase is gone at 852 °C. Since the activity of Ti is stimulated by Ag and depressed with Cu, an increase in temperature would cause the activity coefficient of titanium γ_{Ti} to increase. This process coincides with an increase of the Ti concentration in the liquid (X_{Ti}). The multiplication of these two increasing parameters would produce a quicker increase (or “acceleration”) of the Ti activity: $a_{Ti} = \gamma_{Ti} X_{Ti}$. We would probably not make a big mistake if we assume that $a_{Ti} = 0.08$ at 852 °C. At this point 90% of the alloy is melted and we have to conclude that the activity of titanium is high and thus has to play a crucial role in the brazing process.

Now, let us see how the activity of Ti is influenced by the segregating action in the liquid. At 874 °C a small part of the remaining Cu_4Ti_3 melts, causing an increase of X_{Ti} from 1.4 to 1.8. The Ag:Cu ratio of the liquid decreases, and so does γ_{Ti}. The activity of titanium, $a_{Ti} = \gamma_{Ti} \cdot X_{Ti}$ probably does not decrease, but remains nearly the same or increases insignificantly. At this point the composition of the liquid has reached the edge of the miscibility gap (Fig. 2). Further increase in temperature would melt the remaining Cu_4Ti_3 with the formation of CuTi-rich liquid L_2, which is immiscible with the liquid already present (L→L_1). With the formation of L_2 there has to be some mutual diffusion of elements causing the Ag:Cu ratio in L_1 to increase with temperature (Fig. 2). This, in turn, has to enhance the titanium activity coefficient $\gamma_{Ti}(L_1)$, bringing the activity of Ti to even higher values, for instance to $a_{Ti} = 0.1$.

The second liquid, L_2, is indeed rich in Ti, $X_{Ti}(L_2) = 0.307$ (mole fraction), but this high value does not mean high activity of titanium, as usually considered. L_2 is also very rich in Cu, $X_{Cu}(L_2) = 0.626$, which suppresses the activity of Ti. Also, this liquid is low in the “titanium enhancer”, *i.e.* Ag: $X_{Ag}(L_2) = 0.067$. Thus, the activity of Ti in L_2 and the reactive ability of this liquid have to be lower than expected.

In fact, since these two liquids are in equilibrium with each other, the chemical potential of titanium and its activity in both liquids has to be equal:

$$\mu_{Ti}(L_1) = \mu_{Ti}(L_2),$$
$$a_{Ti}(L_1) = a_{Ti}(L_2),$$
$$\gamma_{Ti}(L_1) \cdot X_{Ti}(L_1) = \gamma_{Ti}(L_2) \cdot X_{Ti}(L_2).$$

From the last relationship it can be deduced that $\gamma_{Ti}(L_2)$ should be about 0.3, which seems a reasonable number.

Consequently, the reactivities of L_1 and L_2, which are based on the activities of titanium, and the wetting/spreading abilities of these liquids during brazing processes, have to be identical, while the concentrations of the elements could be very different. We suppose that the above discussion should be sufficient to disprove the following erroneous beliefs [39-41]:

1) the Ag-rich liquid L_1 does not play an active role in the brazing processes,

2) only the Ti-rich liquid L_2 is responsible for the reactive behavior of Ag-Cu-Ti braze alloys, and

3) the liquid segregation, which produces a Ti-rich phase, is crucial for the reactive abilities of Ag-Cu-Ti braze alloys.

3. *Differences between L_1 and L_2*

The difference between L_1 and L_2 is not in their reactivity but in the ability to sustain this reactivity, should the brazing process be Ti-consuming. Note that titanium is usually needed only for the wetting and spreading. During the cooling procedure any excessive Ti would turn into brittle intermetallics, which are detrimental for the mechanical properties of the braze joint. In this sense L_1 has a great advantage since it is equally surface active, but produces only a small amount of intermetallics. The role of L_2, if there is any, is a buffer storage for Ti in case it is actively consumed by surface reactions, for instance with oxide or nitride ceramics. In case of CB4, the amount of L_2 is low (13 at.%), which means that this liquid alone could not provide the conditions necessary for sound and uniform brazing, since this process is characterized by a high surface-to-volume ratio.

Another significant difference between the segregated L_1 and L_2 is the difference in their densities, which causes a gravimetric effect. The densities of pure solid Ag, Cu and Ti at room temperature are 10.5, 9.0 and 4.5 g/cm^3, respectively, reflecting the differences between their atomic radii (volumes) and atomic weights. We estimate that the density and the volumetric ratios of the segregated liquids L_1 ($Ag_{65.0}Cu_{33.2}Ti_{1.8}$) and L_2 ($Ag_{6.7}Cu_{62.6}Ti_{30.7}$) are about

$$\rho(L_1) : \rho(L_2) \approx 1.35,$$

$$V_1 : V_2 \approx 88:12.$$

The difference in density between L_1 and L_2 was noticed by Paulasto *et al.* in their experiments when they noticed that the lighter liquid L_2 rose to the surface of the melt [23].

4. Driving forces

After the above discussion, it becomes clear that there are two major forces during the brazing processes, which incorporate segregated reactive brazing melts. One Archimedean, which drives the titanium-rich, lighter liquid L_2 upwards and the other Fickian, which tends to equilibrate the chemical potentials of titanium in the different phases. Should titanium be consumed in the reaction layer at the (base metal)-(liquid) interface, as is usually the case in reactive brazing, the chemical (Fickian) driving force would be directed from the bulk to the interfaces, *i.e.* either upwards or downwards. The picture could be distorted and confused with Brownian movement of atoms in the liquids and with surface tension forces that might affect the spatial distribution of the segregated liquids close to the surfaces to be joined. Since the interfaces in the samples are positioned horizontally (to prevent both splitting of the pieces and the loss of brazing alloy) the upper and lower interfaces become asymmetric with respect to the segregated liquids and thus the concentration of titanium (not the activity!) should be shifted towards the upper interface, provided the gravimetric and diffusional factors are dominating.

Now, let us comment on the surface tension, which might affect the redistribution of elements in the liquid since the system, which in our case is a sandwich-like sample, would try to attain the lowest possible surface energy. When the braze alloy wets the surfaces of the brazed parts, the only liquid surface exposed to the furnace atmosphere is the meniscus that circles around near the edges of the coin-like samples. It is expected that the composition of the free surface of the liquid will differ from the stoichiometry of the bulk, like it happens in binary Ag-Cu liquids when silver segregates to the surface [11].

We do not have any data on Ag-Cu-Ti liquids, but the segregating tendencies should be very similar to the Ag-Cu-Zr system analyzed by Novakovic *et al.* [42,43]. The surface tension of the pure elements increases in the row Ag→Cu→Zr(Ti). In the binary alloys Ag-Cu, Ag-Zr and Cu-Zr, the element with lower surface tension will segregate to the surface, thus lowering the surface energy of the system [11,42,43]. It is easy to conclude that in the ternary Ag-Cu-Ti system, the tendency for segregation would be most pronounced for Ag and less for Cu, driving the Cu-Ti-rich L_2 away from the free surface of the liquid and creating a radial force that would keep Ti inside the filler alloy while pushing Ag to the edges.

Note that the melting points of the pure elements increase in the row Ag→Cu→Ti and, consequently, the vapor pressures of the elements will increase in the opposite direction, $p_{Ti} \rightarrow p_{Cu} \rightarrow p_{Ag}$. Under high vacuum conditions, segregation of silver would support its vaporization and loss by the liquid. The loss of Ag-rich liquid L_1 was observed by Shiue *et al.* during brazing studies with Ag-Cu-Ti filler metals [33], but it is hard to say if the loss of L_1 was caused solely by the segregating action, or by another reason like the brazing technique or geometry of the samples. In any case, in the brazing process surface tension is important not only for wetting and spreading, but also for the segregating action on the free liquid surface and should thus be taken into consideration.

Finally, we have to mention that all the above phase analysis was made based on very few experimental studies and thermodynamic estimates considering equilibrium conditions. The brazing process, however, is not an equilibrium one but should be viewed as dynamic since the temperature, the compositions and the densities of the phases, the bond distribution, the activities of the elements and the surface tension between the phases – they all change in time. Still, we hope that some of our conclusions are important in understanding the transformations that occur during the brazing processes involving Ag-Cu-Ti filler alloys.

Conclusions

1. The phase transformations during heating-cooling of the Ag70.5Cu26.5Ti3 filler alloy known as CB4 are described based on the ternary Ag-Cu-Ti phase diagram. The liquid segregation paths and the liquid composition path are constructed for CB4 and the liquid evolution and the concentration of Ti in the liquid are plotted versus temperature. The apparent

discrepancies between the liquidus and solidus points published in the literature and estimated from the phase diagrams are discussed.

2. It is established that at 808 °C the majority of the filler alloy is melted and the Ti activity in this liquid is high.

3. With an increase of temperature the following changes could be noted:

- the composition of the remaining solid Cu-Ti intermetallic phase changes Cu[Ag,Ti]→Cu_4Ti→Cu_3Ti_2→Cu_4Ti_3,
- the amount of Ag[Cu] phase decreases,
- the composition of the liquid shifts towards higher Ag:Cu ratios,
- the concentration of Ti in the liquid increases,
- the Ti activity coefficient also increases,
- the activity of Ti (and its chemical potential) in the liquid accelerates and is sufficient for reactive brazing before the alloy is completely melted and liquid is segregated.

4. In the Ag-Cu-Ti liquid, Cu suppresses the Ti activity, contrary to Ag, which enhances it.

5. The activities of Ti in both segregated liquids are identical, though the concentrations are very different. Both liquids, the Ag-rich L_1 and the Cu-Ti-rich L_2, are equally reactive, not just L_2, as often believed. The segregating action in the liquid is actually not a necessary condition for reactive brazing.

6. The major differences between L_1 and L_2 are the following

- L_2 works as a Ti storage and supplier if Ti is excessively consumed during the reactive brazing process,
- L_2 produces significant amounts of intermetallic compounds, which are brittle and detrimental for the mechanical properties of the braze joints,
- L_1 is heavier than L_2 by ca. 35%, which results in significant Archimedean forces tending to make the two interfaces (upper and lower) asymmetric.

7. The surface tension of the free liquid surface is lowered with preferential segregation of Ag and depletion of Ti. This segregation creates a radial force that for Ti would be centripetal, while for Ag centrifugal, *i.e.* supportive for storing Ti and for losing Ag.

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