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Details on the formation of Ti_2Cu_3 in the Ag-Cu-Ti system in the temperature range 790-860 °C

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Abstract

Silver-copper-titanium ternary alloys are often used as active braze alloys for joining ceramics to metals at temperatures ranging from 780 °C (the melting point of the Ag-Cu eutectic) up to 900 °C. When Ti/Ag-Cu joints are brazed at low temperature (near 800 °C), the intermetallic compound Ti_2Cu_3 (tetragonal, P4/nmm, a = 0.313nm, c = 1.395nm) is systematically missing from the interface reaction layer sequence. An experimental investigation based on isothermal diffusion experiments in the Ag-Cu-Ti ternary system has then been undertaken in order to clarify the issues of thermal stability and formation kinetics of this compound. Evidences have been brought for the stability of Ti_2Cu_3 at temperatures ranging from 790 to at least 860 °C. By heat-treating Ag-Cu-Ti powder mixtures at 790 °C for increasing times, it has moreover been shown that Ti_2Cu_3 forms at a much slower rate than the two adjacent Ti-Cu compounds: $TiCu_4$, the first phase to form, and Ti_3Cu_4. This explains why although thermodynamically stable, Ti_2Cu_3 is not obtained when temperature is too low or reaction time too short.

Keywords: intermetallics, stability, ternary phase diagram, experimental study

1. Introduction

Alloys of the Ag-Cu-Ti ternary system are often used for brazing ceramics to metals in the temperature range 800-900 °C [1]. Some alloy compositions containing 40 at% of copper (28 wt%Cu, binary eutectic alloy with a melting point at 780 °C) and a few percents of titanium are commercially available in the form of pre-alloyed powders, ribbons or plates. To develop high performance metal/ceramic brazed joints, more especially when the metal is a titanium base alloy [2, 3], a thorough knowledge of the phase diagram of the Ag-Cu-Ti system is needed.

Thermodynamic data on the binary Cu-Ti system and the ternary Ag-Cu-Ti system are available from different sources [4-14] and assessments have recently been made [15, 16]. The 800 °C section reported in Fig. 1 and the partial projection drawn in Fig. 2 show the most probable phase equilibria in the Ag-Cu-Ti system at temperatures ranging from 780 to 860 °C. It is to note that the reaction scheme given in [16] is drawn in dotted line for that temperature range because of uncertainty on the stability of Ti_2Cu_3 in the binary Cu-Ti and the ternary Ag-Cu-Ti systems. For Eremenko et al. who conducted extensive experimental investigations on both systems, Ti_2Cu_3 is stable only at temperatures ranging from 805 to 890 ± 4 °C in the Cu-Ti binary system and from 803 to 890 °C in the ternary Ag-Cu-Ti system [6-7]. For other authors who achieved thermodynamic modelling, Ti_2Cu_3 is stable at any temperature lower than 875 ± 10 °C [13] or 885 °C [14]. Enthalpies of formation and crystallization of the Ti-Cu compounds were experimentally determined [17] but the values thus obtained do not remove the uncertainty on the stability of Ti_2Cu_3.

In the course of a recent investigation on the chemical reactivity near 800 °C of liquid Ag-Cu eutectic alloy with solid titanium [4], the question arose why the intermetallic compound

Ti_2Cu_3 was systematically missing from the reaction layer sequence that was observed to develop at the liquid/solid interface [4]. To provide a response to that simple but practical issue, more detailed information had to be acquired on the thermal stability and formation kinetics of the intermetallic compound Ti_2Cu_3. It is with this aim in view that isothermal diffusion experiments were undertaken in the Ag-Cu-Ti system between 700 and 860°C.

2. Experimental

For isothermal diffusion experiments, mixtures of commercial powders of silver (99.99 wt%, grain size d ~ 100 µm, Goodfellow) copper (99 wt%, grain size d ~ 50 µm, Goodfellow) and titanium (98.5 wt%, grain size $3 < d < 300$ µm, Fluka) were ball-homogenized and cold-pressed under 200 MPa into small rods (3 mm x6 mm x30 mm). The titanium powder was previously sifted two times so that the diameter of the biggest particles was lower than 100µm. Each rod was then placed in an alumina boat lined with yttria (STOPYT 62A, Morgan Wesgo) and heated in a silica reaction tube for up to 500 h under pure argon (3-5 10^4 Pa) in the presence of titanium powder as gas getter. It is to note that at 850 °C and above, heat treatments were realized under dynamic primary vacuum and the annealing time was reduced down to 50 min to avoid spreading of the Ag-Cu-Ti liquid on the alumina boat through the yttria liner. The horizontal furnace was regulated to better than ± 1 °C. The exact treatment temperature was controlled by putting the hot junction of a K type thermoelectric couple inside the alumina boat in place of the rods. At the end of the isothermal treatment, the reaction tube was pulled out of the furnace and allowed to cool in ambient air. Starting from a heating temperature in the range 790-860 °C, the cooling rate measured during the first 100 °C drop was faster than 10 $°C.s^{-1}$.

Two samples were analysed by differential thermal analysis (TGA/SDTA 851, Mettler-Toledo) in Al_2O_3 crucibles (sample weight: 1-100 mg) under 10^5 Pa argon. The other samples were characterized after heat treatment by X-ray diffraction (XRD), optical metallography (OM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The XRD spectra were recorded on grossly polished sections, using standard diffraction equipment (Panalytical MPD-Pro diffractometer equipped with a back monochromator and a X'celerator detector, Cu Kα radiation). OM and SEM observations were made on diamond polished sections. SEM observations and EPMA analyses were carried out using a Camebax apparatus (Cameca) equipped with an energy dispersive analyser. The accelerating voltage was of 10 kV and the beam current of 9 nA. After background subtraction, the counting rates obtained for Ag, Cu and Ti in at least eight different points were averaged and referred to the counting rates recorded under the same conditions on pure and freshly polished element standards. After corrections for atomic number, absorption and fluorescence, the atomic contents of Ag, Cu and Ti in the different phases deriving from the Cu-Ti binary system were obtained with accuracy better than ± 0.5 at%.

3. Results and discussion

3. 1 Synthesis and annealing at 815 °C and above

All authors who have reported on the Ag-Cu-Ti system agree that in the temperature range 810-830 °C, Ti_2Cu_3 is in equilibrium with an Ag-Cu-Ti liquid [6-12]. Therefore, first attempts to synthesize the compound Ti_2Cu_3 from the elements in the ternary Ag-Cu-Ti system were carried out in this temperature range. More precisely, three different powder mixtures with compositions F, F' and G (Fig. 1) were prepared and heated at 815 °C or 825 °C (Table 1). In full agreement with the literature data, all the treated samples contained as a major constituent Ti_2Cu_3 (tetragonal, P4/nmm, a = 0.313 nm, c = 1.395 nm [5]). Ti_3Cu_4 (tetragonal, I4/mmm, a = 0.313 nm, c = 1.994 nm) was still present in little amounts in sample F1 heated at 815 °C for 205 h but was no more detected in samples F2, F'1 and G1 heated at higher temperature (825 °C) and for longer durations (350 h or more). Ti_2Cu_3 grown from the liquid during isothermal heating always appeared in the form globular crystals (Fig. 3). These were surrounded by a very thin layer of $TiCu_4$ crystals (orthorhombic, Pnma, a = 0.453 nm, b = 0.4342 nm, c = 1.293 nm) that were formed on cooling near 808 °C, as a product of the incomplete ternary transition reaction (U_9 in Fig. 2):

$$L + Ti_2Cu_3 \rightarrow TiCu_4 + Ag_s \qquad (1)$$

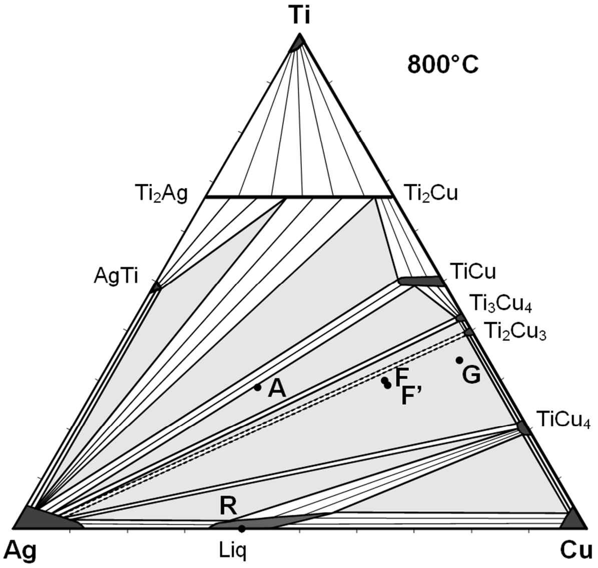


Fig. 1. Ag-Cu-Ti isothermal section at 800 °C, according to experimental data and thermodynamic evaluations [6-16]. The tie lines joining Ag_s to Ti_2Cu_3 have been drawn in dotted lines since for Eremenko et al. [6-8], Ti_2Cu_3 is not stable at 800 °C

Table I. Crystal nature and composition of the phases produced by reacting Ag-Cu-Ti mixtures at 815 or 825 °C

Sample	Initial composition, at%			Reaction duration and temperature	Phases by XRD (decreasing abundance)	Composition by EPMA, at%		
	Ag	Cu	Ti			Ag	Cu	Ti
F1	20	50	30	205 h at 815 °C	Ag	84	16	-
					Ti_2Cu_3	1.3	58.3	40.4
F2	20	50	30	353 h at 825 °C	$TiCu_4$	2.1	75.6	22.3
					Ti_3Cu_4*	-	-	-
F'1	20	51	29	353 h at 825 °C	TiCu(Al,Si)**	-	47	51
					Cu	4.9	91.2	3.9
G1	5	61	34	424 h at 825 °C	Ti_2Cu_3	1.5	58.4	40.1
					$TiCu_4$	1.6	76.2	22.2
					Ag	87	13	-
					TiCu(Al,Si)**	-	48.4	49.6

(*):little amounts detected by XRD only in sample F1, not found by EPMA
(**): small crystals containing Al and Si (~2at%) not characterized by XRD but analysed by EPMA

Once treated at 815 or 825 °C, the samples containing Ti_2Cu_3 were annealed at higher temperatures. Results obtained by XRD for sample F are shown in Fig. 4. On the one hand, no significant modification occurred in the phase composition after annealing at 825 °C (for 353 h), 835 °C (for 237 or 277 h) and 850 °C (for 50 min). Ti_3Cu_4 initially present at 815 °C just disappeared upon subsequent annealing. On the other hand, an important change occurred upon re-heating for 50 min at 854 °C or 860 °C. Effectively, the intensity of the diffraction peak characteristic for Ti_2Cu_3 at $2\theta \approx 43$ ° considerably decreased between 850 and 854 °C whereas a new peak characteristic for Ti_3Cu_4 appeared (it is to note that in the 37-47 ° angular range represented in Fig. 4, the XRD lines characteristic for Ti_2Cu_3 and Ti_3Cu_4 are distinguishable only at $2\theta \approx 43$ °). At the same time, the morphology of the crystals changed from globular to plate-like (Fig. 5). Given that at 850 °C, samples with composition F (or F') are lying inside a tie triangle Ti_2Cu_3-Ag_s-L, such changes mean that upon re-heating at 854 or 860 °C, Ti_2Cu_3 and solid silver have reacted according to the transformation (U_8 in Fig. 2):

$$Ti_2Cu_3 + Ag_s \rightarrow Ti_3Cu_4 + L \qquad (2)$$

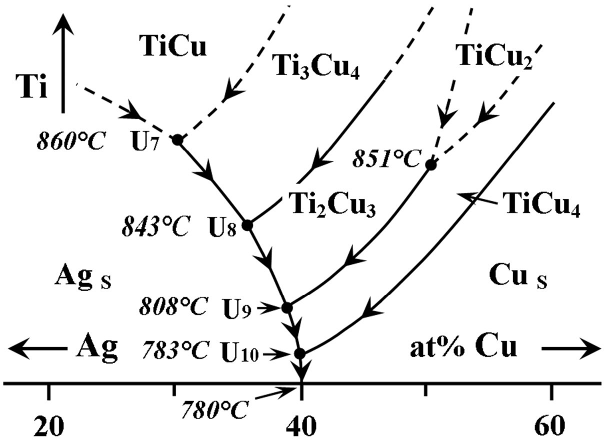


Fig. 2. Partial liquidus projection between 860 and 780 °C of the Ag-Cu-Ti phase diagram, according to [7, 10, 15, 16] (transformations are indexed like in reference [16])

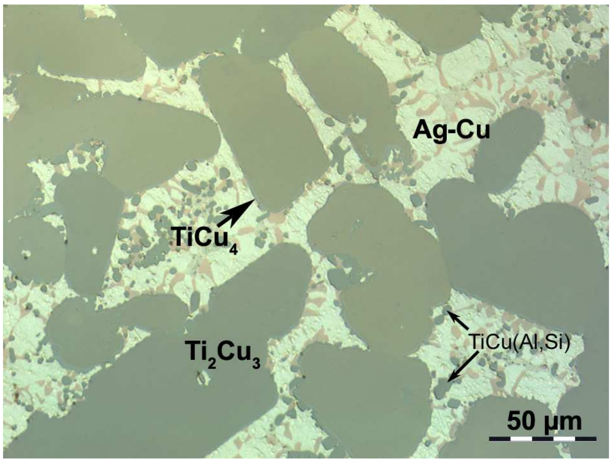


Fig. 3. Ti_2Cu_3 globular crystals in a silver-rich matrix, as synthesized in mixture F after heating at 825 °C for 353 h: small crystals in the matrix analyse for TiCu(Al,Si) whereas $TiCu_4$ crystals are stuck onto Ti_2Cu_3

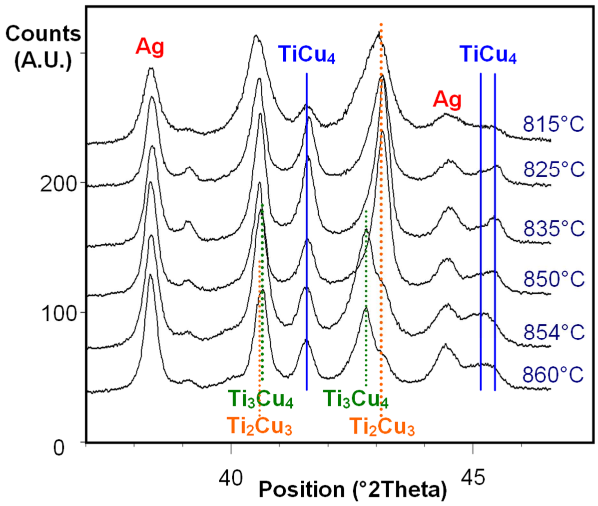


Fig. 4. Evolution of the XRD pattern for mixture F first reacted 205 h at 815 °C (sample F1) and then annealed at higher temperatures: 825, 835, 850, 854 and 860 °C

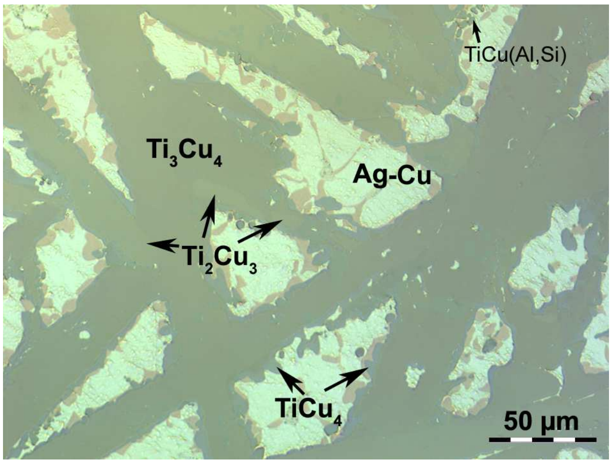


Fig. 5. Ti_3Cu_4 plate-like crystals grown in mixture F first reacted at 825 °C for 353 h and then annealed at 854 °C for 50 min (note the difference with Fig. 3)

According to the foregoing XRD and metallographic observations, the temperature of that invariant transformation is of 852 ± 2 °C.

Conversion of Ti_2Cu_3 into Ti_3Cu_4 was also observed in samples with composition G after 50 min annealing at 860 °C, but Ti_2Cu_3 remained abundant. This can be explained by the fact that mixtures F and G are different in composition. Consequently, only the compound Ti_3Cu_4 is in equilibrium with the liquid L at 854 and 860 °C in samples with composition F or F' whereas in samples with composition G, the three phased equilibrium Ti_2Cu_3-Ti_3Cu_4-L tends to be reached when approaching 860 °C, as shown in Fig. 2.

In the experimental approach by Eremenko et al. [7], the invariant transformation (2) is reported to occur at 843 °C, whereas we find it at 852 ± 2 °C. The slight shift between these two values may have different origins, one of these being the purity of the samples. Indeed, isothermal diffusion needs use of fine powders that cannot be as pure as the massive ingots used by Eremenko's co-workers. An illustration of this purity problem is given in Fig. 3 and Fig. 5 with the presence in the solidified liquid of small well-facetted crystals that analyse as TiCu with extra aluminium and silicon for a total amount of 2-3 at% (Table 1, phase designated as TiCu(Al,Si)). Because of their too low abundance, these crystals could not be characterized by XRD. They might be either of the tetragonal TiCu type (P4/nmm, a = 0.3107 nm, c = 0.5919 nm [13]) stabilized by impurities or of another crystal type like B2 cubic Cu_2AlTi, as evoked for crystals with an approaching composition in a paper by He et al.

[18]. It is to note that the weak reflection at 2θ = 39° in Fig.4 might be a strong X-ray diffraction line coming from the small crystals of TiCu(Al,Si) and that Al and Si were not detected in the other phases constituting the samples.

3. 2 Synthesis and annealing below 815 °C

A part of sample F1 that was first heated for 205 h at 815 °C was placed in an alumina boat along with an untreated cold-pressed mixture of Ag, Cu and Ti powders having the same composition. Both samples were heated at 790 °C for 330 h and characterized (Table 2, samples F3 and F4). In sample F3 first heated at 815 °C and annealed at 790 °C, Ti_2Cu_3 was still the major constituent. The only change concerned the compound Ti_3Cu_4 that disappeared upon annealing at 790 °C. The cold-pressed mixture directly heated at 790 °C (sample F4) also contained Ti_2Cu_3 as major constituent but some Ti_3Cu_4 was present, like in sample F1 before annealing at 790 °C.

Table 2. Phases characterized in Ag-Cu-Ti mixtures after reaction or annealing at 790 and 700 °C

Sample	Initial composition, at%			Heat treatment	Phases by XRD (decreasing abundance)	Composition by EPMA, at%		
	Ag	Cu	Ti			Ag	Cu	Ti
F3	20	50	30	205 h at 815 °C	Ag	84.3	15.7	-
				+	Ti_2Cu_3	1.5	58.7	39.9
				330 h at 790 °C	$TiCu_4$	1.3	76.2	22.5
					TiCu(Al,Si)*	-	47.5	49.3
F4	20	50	30	330 h at 790 °C	Ag	85.1	14.9	-
					Ti_2Cu_3	1.4	58.0	40.6
					$TiCu_4$	1.2	76.4	22.4
					Ti_3Cu_4**	-	-	-
G2	5	61	34	424 h at 825 °C	Ti_2Cu_3	0.9	59.3	39.8
				+	$TiCu_4$	1.2	76.6	22.2
				512 h at 700 °C	Ag	91.3	8.7	-
					TiCu(Al,Si)*	-	48	50
G3	5	61	34	512 h at 700 °C	Ti_3Cu_4	0.7	55.7	43.6
					$TiCu_4$	0.9	76.6	22.5
					Ag	90.9	9.1	-

(*): small crystals containing Al and Si (~2at%) not characterized by XRD but analysed by EPMA
(**): still present in little amounts by XRD, not found by EPMA

The same type of experiment was reproduced at 700 °C on samples with composition G. After 512 h annealing at 700 °C, only small changes occurred in the sample previously treated at 825 °C (Table 2, samples G2): Ti_2Cu_3, $TiCu_4$ and Ag were still the major constituents. As to the cold -pressed mixture directly reacted in the solid state at 700 °C (Table 2, sample G3), it only contained Ti_3Cu_4 and $TiCu_4$; no trace of Ti_2Cu_3 at all was found.

If there is no ambiguity from the foregoing results about the existence of Ti_2Cu_3 at 790 °C, things are not so simple at 700 °C. Effectively, starting from the same initial composition, a mixture heat-treated for a long time at 700 °C contains either Ti_2Cu_3, $TiCu_4$ and Ag or Ti_3Cu_4, $TiCu_4$ and Ag according as it has previously been heated at a higher temperature (790-850 °C) or not. As a matter of fact, equilibrium has not been reached in one of the two mixtures treated at 700 °C. Complementary experiments have then been carried out at 790 °C to acquire more detailed information on that question.

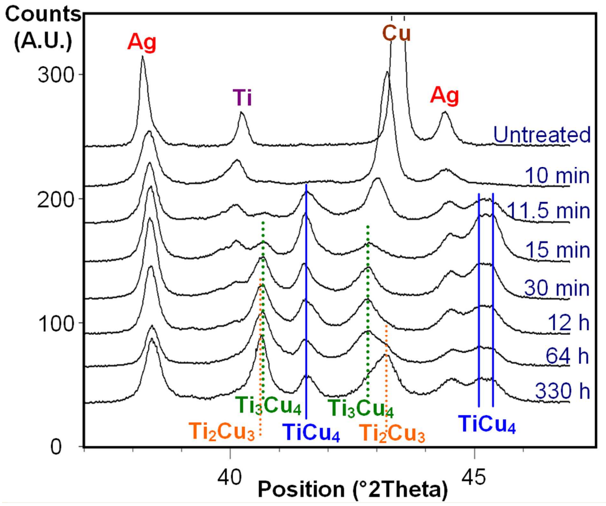


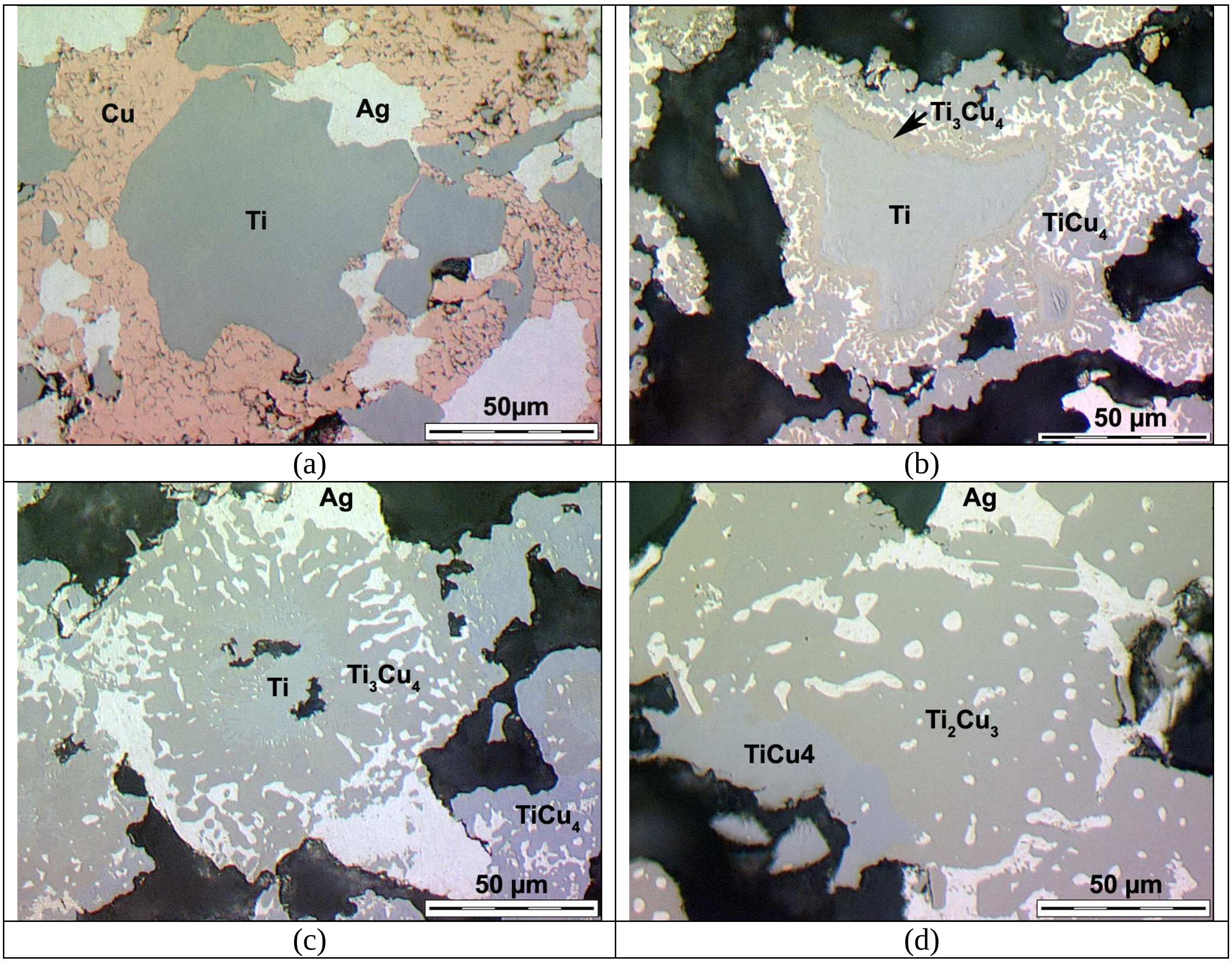
Fig. 6. Evolution of the XRD pattern of mixture F placed for increasing times in a tubular furnace held at the constant temperature of 790 °C

3. 3. Isothermal diffusion at 790 °C

Cold-pressed powders of Ag, Cu and Ti with the atomic composition F (Ag:Cu:Ti = 20:50:30 at%) were placed in the furnace at 790 °C for durations varying from 10 min to 330 h. It will be recalled that according to the phase diagram shown in Fig. 1, the chosen composition lies either inside the tie triangle Ti_2Cu_3-$TiCu_4$-Ag_{sol} or inside the wider triangle Ti_3Cu_4-$TiCu_4$-Ag_{sol}.

Results in terms of phase composition of the treated samples are illustrated by the series of XRD patterns presented in Fig. 6. After 10 min in the furnace, the three starting elements Ag, Cu and Ti are still present. The only noticeable change is an increase in the full width at half maximum and a shift in the angular position of the XRD peaks of these elements (Fig. 6, 10 min). After heating for 1.5 min more, the diffraction lines characteristic for the compound $TiCu_4$ begin to appear ((Fig. 6, 11.5 min). After 15 min in the furnace, these lines have attained their maximum height while Cu has disappeared and Ti_3Cu_4 has become detectable (Fig. 6, 15 min). Then, the diffraction lines characteristic for Ti_3Cu_4 slightly increase while those characteristic for $TiCu_4$ decrease and in the meantime, elemental titanium tends to disappear (Fig 6, 30 min, 12 h and 64 h). Finally, Ti_2Cu_3 develops to the detriment of Ti_3Cu_4 as the heat treatment time increases from 64 h to 330 h (Fig 6, 330 h). It is to note that for a non ambiguous characterization, the unit cell parameters of Ti_2Cu_3 had to be refined. Indeed as indicated by EPMA results (Table 2), 1.4 at% of silver enter (very likely by Ag/Cu substitution) in the framework of Ti_2Cu_3. The refined tetragonal unit cell parameters found for such a phase with Ag/Cu substitution were a = 0.3138(5) nm and c = 1.4064(3) nm, which corresponds to a slight increase compared with the pure Ti_2Cu_3 binary compound (a = 0.313nm, c = 1.395nm).

Combining these XRD results with metallographic examination and EPMA characterization, a reaction scenario can be proposed for the formation of Ti_2Cu_3 from the elements at 790 °C. The series of micrographs presented in Fig. 7 illustrates the four main stages of this reaction scenario:



(a) (b) (c) (d)

Fig. 7. Morphological changes in mixture F after heating for increasing times at 790 °C: (a) untreated cold-pressed mixture: Ag, Cu and Ti grains; (b) after 15 min in the furnace: small $TiCu_4$ crystals around Ti and in the Cu-free solid Ag matrix; (c) after 12h reaction: formation of Ti_3Cu_4 and recrystallization of $TiCu_4$; (d) after 330 h reaction: the stable Ti_2Cu_3-$TiCu_4$-Ag_s three-phased equilibrium tends to be reached

Stage I: the first process that develops during the rise in temperature of the cold-pressed powder mixture (Fig. 7a) is the solid state volume interdiffusion of atoms, more especially by Ag/Cu substitution. Such a solid state interdiffusion is known to modify the unit cell parameters of the two elements and a shift with enlargement of their XRD reflections is effectively observed in Fig. 6 after 10 and 11.5 min heating;

Stage II: when the temperature attains 780 °C, which occurs between 10 and 11.5 min heating, a eutectic reaction proceeds between the grains of Ag and Cu giving a Ag-Cu liquid alloy. As soon as formed, the Ag-Cu eutectic alloy spreads at the surface of the titanium grains by reactive wetting. Comparison between Fig. 7a and 7b clearly shows consumption of copper and spreading of a silver rich phase over the titanium grains. As previously shown by XRD (Fig. 6, 11.5 min and 15 min) and confirmed by EPMA, it is essentially $TiCu_4$ that is produced in that fast rate process. Two simultaneous reactions can then be written:

$$Ag_s + Cu_s \rightarrow L \qquad (3)$$

$$L + Ti \rightarrow TiCu_4 + Ag_{sol} \qquad (4)$$

At the end of this second stage, most of solid elemental copper initially introduced has been first dissolved in the Ag-Cu liquid, L, and then converted into $TiCu_4$ at the Ti grains surface. It is this process that has left the large pores visible in Fig. 7b. As to the nearly eutectic liquid phase, L, it has disappeared. Indeed, formation of $TiCu_4$ by reaction between the (Ag-Cu) liquid, L, and solid Ti according to reaction (4) implies the precipitation of solid Ag from the liquid. Arrived at this point, the Ti grains are surrounded with a $TiCu_4$ reaction layer and embedded in a white Ag base matrix with many small crystals of $TiCu_4$ dispersed in it (Fig. 7b).

Stage III: in a third stage, Ti_3Cu_4 slightly increases, $TiCu_4$ slightly decreases and elemental titanium tends to disappear (Fig 6, 30 min, 12 h and 64 h). This means that $TiCu_4$ reacts in the presence of solid Ag with remaining Ti to form Ti_3Cu_4 according to the reaction:

$$TiCu_4 + 2\,Ti \rightarrow Ti_3Cu_4 \qquad (5)$$

During the course of this reaction that proceeds until titanium is completely consumed, remaining $TiCu_4$ recrystallizes in blocky crystals, as shown in Fig. 7c.

Stage IV: in a last stage, Ti_3Cu_4 and $TiCu_4$ react by solid state diffusion through solid Ag to form round-shaped crystals of Ti_2Cu_3 (Fig. 7d). The reaction can be written:

$$5\,Ti_3Cu_4 + TiCu_4 \rightarrow 8\,Ti_2Cu_3 \quad (6)$$

Ti_2Cu_3 with 1.4 at% of silver substituted for Cu is thus formed as the equilibrium phase for mixture F reacted at 790 °C.

From a kinetics standpoint, it can be said that Stage II proceeds at a very fast rate. Indeed, between the formation of the first liquid droplets after a little more than 10 min of temperature rise and complete isothermal solidification at 790 °C of the liquid by Cu depletion and Ag precipitation, only five minutes have passed. Fast rate formation of $TiCu_4$ as first reaction product is confirmed by the SDTA results reported in Fig. 8. It can effectively be seen that when titanium is added to an eutectic Ag-Cu powder mixture, the endothermic peak corresponding to the formation at 780 °C of a liquid with the eutectic composition completely disappears. In place of it appears an exothermic peak which corresponds to the formation of the compound $TiCu_4$ by reaction of solid titanium with the Ag-Cu eutectic liquid as it is produced. Then, formation of Ti_3Cu_4 during stage III proceeds at a medium rate (within a few tens of hours) whereas conversion of Ti_3Cu_4 into the equilibrium phase Ti_2Cu_3 during stage IV proceeds at a very slow rate. Indeed, it has only begun after 60 hours heating and reaction has not yet gone to completion after 330 h.

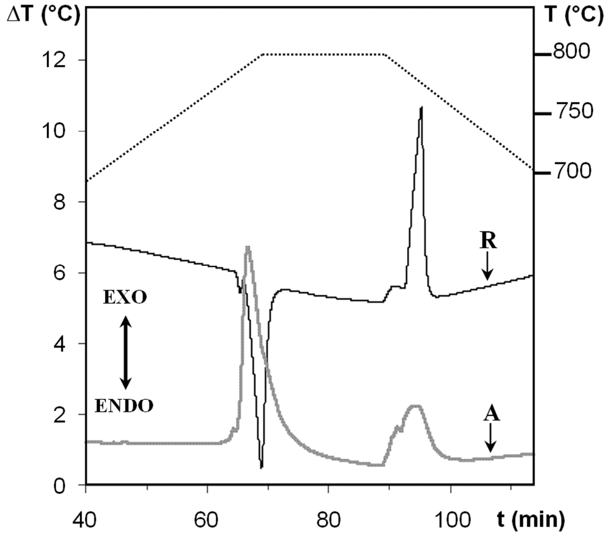


Fig. 8. Thermal behaviour upon first cycle of two cold-pressed powder mixtures analysed by SDTA at 4 $°C.min^{-1}$: mixture R with composition Ag:Cu = 60:40 at% and mixture A with composition Ag:Cu:Ti = 43:28.5:28.5 at% (temperature versus time is drawn in the upper part of the graph)

Of course, the real scenario might be more subtle. First, reactions may progress at different rates depending on the size of Ti grains and on the distance between them. Secondly, because of the detection limit inherent to the characterization techniques used, several minor reactions have not been considered such as for instance the possible formation of TiCu or Ti_2Cu in the solid state at the interface between Ti and Ti_3Cu_4. It remains that although a bit simplistic, the proposed scenario describes the four main processes that successively develop in a Ag-Cu-Ti mixture isothermally heated at 790 °C before attainment of equilibrium. The most striking features are that (i) $TiCu_4$ is the first phase to form by interface reaction at 780 °C between solid Ti and a liquid Ag-Cu eutectic alloy and (ii) when Ti_2Cu_3 and Ti_3Cu_4 are likely to form from the elements, the former develops at a much slower rate than the latter. This explains why $TiCu_4$ and Ti_3Cu_4 can be the major reaction products in a heated mixture whereas Ti_2Cu_3 is actually the equilibrium phase for that mixture. The same explanation remains valid to justify that Ti_2Cu_3 is "missing" from the reaction layer sequence at the interface of Ti/Ag-Cu couples brazed at 800 °C [4].

4. Conclusion

Ti_2Cu_3 has been synthesized by solid-liquid reaction from Ag, Cu and Ti powder mixtures after long time annealing at 790, 815 or 825 °C. No indication for decomposition of Ti_2Cu_3 at 700 °C for 500 h was observed being in line with data described in references [11-16]. At high temperature, Ti_2Cu_3 is stable in the Ag-Cu-Ti system up to at least 860 °C, temperature at which existence of the three-phased equilibrium Ti_2Cu_3-Ti_3Cu_4-L is confirmed. Occurrence of the invariant transformation:

$$Ti_2Cu_3 + Ag_s \rightarrow Ti_3Cu_4 + L \qquad (2)$$

is also confirmed at a temperature that might be slightly higher than 843 °C.

From a kinetics standpoint, it has been shown by SDTA in the range 750-800 °C and by isothermal diffusion at 790 °C that $TiCu_4$ is the first phase to form when a transient Ag-Cu eutectic liquid spreads onto solid titanium between 780 and 790 °C. Then, Ti_3Cu_4 is formed by reaction between $TiCu_4$ and unconverted titanium. Finally, Ti_2Cu_3 slowly appears as a product of the reaction between $TiCu_4$ and Ti_3Cu_4. These features explain why Ti_2Cu_3 is not characterized after reaction at 790 °C for a too short time (less than 60 hours) or after reaction for a long time (more than 500 h) at a too low temperature (700 °C). They also explain why Ti_2Cu_3 can be missing from the reaction layer sequence at Ti/Ag-Cu interfaces after brazing near 800 °C.

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