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Low-Temperature Interface Reaction between Titanium and the Eutectic Silver-Copper Brazing Alloy

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Abstract

Reaction zones formed at 790 °C between solid titanium and liquid Ag-Cu eutectic alloys (pure and Ti-saturated) have been characterized. When pure Ag-Cu eutectic alloy with 40 at.% Cu is used, the interface reaction layer sequence is: αTi / Ti_2Cu / TiCu / Ti_3Cu_4 / TiCu_4 / L. Because of the fast dissolution rate of Ti in the alloy, the reaction zone remains very thin (3-6 μm) whatever the reaction time. When the Ag-Cu eutectic alloy is saturated in titanium, dissolution no longer proceeds and a thicker reaction zone with a more complex layer sequence grows as the reaction time increases. Four elementary chemical interaction processes have been identified in addition to Ti dissolution in the liquid alloy. These are growth of reaction layers on Ti by solid state diffusion, nucleation and growth from the liquid of TiCu_4 , isothermal solidification of silver and, finally, chemical conversion of the Cu-Ti compounds by reaction-diffusion in the solid state. A mechanism combining these processes is proposed to account for the constitution of Ti/ Ag-Cu/ Ti joints brazed at 780-800 °C.

Keywords: metals; intermetallics; diffusion paths; chemical potential gradients; ternary system

1. Introduction

The Ag-Cu eutectic alloy with 40 at.% Cu (28 wt.% Cu) has already shown good wetting and bonding characteristics with regard to conventional brazing of titanium parts at temperatures higher than 850 °C [1]. This behaviour is explained by the formation of binary Ti-Cu compounds that promote reactive wetting and spreading at the liquid/solid interface [1-4]. Surprisingly, data are very scarce about brazing of titanium parts at temperatures lower than 850 °C, although promising observations have been made [3]. In fact, operating at temperatures closer to the melting point of the alloy (which is of 780 °C) should be favourable to the preservation of the microstructure and composition of the titanium base metal. Moreover, formation of copper-rich Ti-Cu solid compounds should render possible isothermal solidification of the Ag-Cu brazing alloy. In other words, the development of a process for brazing titanium or titanium alloys by transient liquid phase bonding at low temperature should be very attractive from an applied perspective [5, 6]. For these reasons, it was decided to further investigate the chemical interaction between titanium and the eutectic Ag-Cu alloy at temperatures down to 780 °C, the temperature of the eutectic transformation.

In the first approach at investigating the kinetics of compound formation in the Ag-Cu-Ti system, cold-pressed mixtures of Ag, Cu and Ti powders were heated at 700-860 °C and characterized [7]. In the present work, additional experiments have been carried out at 780-800 °C on Ti/Ag-Cu semi infinite couples and Ti/Ag-Cu/Ti sandwiches in order to determine the extent and constitution of the interface reaction zone formed between solid Ti and liquid Ag-Cu eutectic alloy.

2. Experimental

Experiments on Ti/Ag-Cu couples were performed in the sessile drop configuration. On the one hand, a pure binary Ag-Cu eutectic alloy (40 at.% Cu) without Ti was used; on the other hand, 1.88 at.% of Ti (1 wt.%) was added so that the Ag-Cu alloy was slightly oversaturated in Ti at 790 °C according to [8]. In both cases, the quantities used were such that the composition of the liquid remained as constant as possible. For that purpose, small blocks of Ag-Cu or Ag-Cu-Ti alloy (5 mm x 3 mm x 4-5.5 mm, 0.6-0.82 g) were prepared by cold-pressing (270 MPa) commercial powders of silver (99.99 wt.% pure, Goodfellow), copper (99 wt.% pure, Goodfellow) and titanium (purity higher than 98 wt.%, grain size after sieving $d < 100 \mu\text{m}$, Merck). The blocks were put on a freshly polished and degreased titanium plate (10 mm x 5 mm x 2 mm) that was entirely coated with a Y_2O_3 -based oxide liner (Stopyt, Morgan), except for a square area of 2 mm x 2 mm at its upper face that remained uncovered and was thus in direct contact with the Ag-Cu(-Ti) alloy. The samples were put in an alumina boat and placed inside a silica reaction tube evacuated under a dynamic primary vacuum of ~ 1 Pa. Another boat filled with titanium powder was also placed in the hot zone of the reaction tube to act as a getter protecting the samples from oxidation, nitridation or carburization. The reaction tube was heated using a horizontal tubular furnace regulated to better than ± 1 °C. The temperature was first raised in less than 30 min from 25 °C to 790 °C and then held at that value for durations varying from 2 to 50 min. At the end of the isothermal heat-treatment, the samples were cooled to room temperature by pulling the silica reaction tube out of the furnace. The mean cooling rate during the first 100 °C drop was faster than 10 °C s^{-1} .

The heat-treated samples were diamond sawn, polished and examined by optical metallography (OM) and field-emission gun scanning electron microscopy (FEG-SEM, Hitachi S-800). Analyses were carried out by electron probe microanalysis (EPMA, Cameca Camebax) with an accelerating voltage of 10 kV and a beam current of 9 nA: under these conditions the lateral resolution was of $\pm 0.7 \mu\text{m}$. After background subtraction, the counting rates obtained for Ag, Cu and Ti in at least ten different points of the same layer or type of crystals 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 were obtained with an accuracy better than ± 0.5 at%. It had been previously verified by X-ray powder diffraction [7] that the crystalline phases for which each interface reaction layer or crystal analysed were effectively obtained under the same heat-treatment conditions.

3. Results

Depending on whether the Ag-Cu alloy was saturated in titanium or not, the reaction zones formed between solid titanium and the liquid alloy varied in thickness, morphology and composition.

3. 1. Ag-40 at.% Cu liquid saturated in Ti

When titanium reacted at 790 °C with Ti-saturated Ag-Cu eutectic alloy, a thick reaction zone rapidly developed at the liquid/solid interface. After 2 min at 790 °C, the reaction zone had a total thickness of about $15 \mu\text{m}$. After 15 and 50 min at that temperature, the reaction zone thickness attained $\sim 100 \mu\text{m}$ and $\sim 150 \mu\text{m}$, respectively. For the latter two reaction times, the reaction zone morphology was the same. As shown in Fig. 1, five successive layers can be distinguished between the unconverted titanium substrate and the solidified Ag-Cu liquid saturated in Ti.

Fig. 1. Thick reaction zone formed between solid Ti and liquid Ag-40 at.% Cu alloy saturated in Ti (1.88 at.% Ti) after 50 min of heating at 790 °C: (a) general view; (b) zoom near the Ti surface

In direct contact with titanium, a first thin layer (less than 2 μm thick) with a single-phased appearance has formed. According to its EPMA analysis (Table 1), this first layer consists of the phase Ti_2Cu with some silver in solid solution. A second layer (less than 3 μm thick) surrounding the first one also exhibits a single-phased appearance: it analyzes by EPMA (Table 1) for the compound TiCu with some silver in solid solution. A third layer which is thicker than the two previous ones (about 10 μm thick) and which clearly consists of two different phases can then be observed: in that layer, the dark phase analyzes for Ti_3Cu_4 whereas the bright inclusions are made of metallic silver with about 9 at% of copper and 5 at% of titanium dissolved (Table 1). The fourth layer rapidly contains more bright phase than the third so that the bright phase becomes a matrix which embeds dark elongated crystals. According to EPMA (Table 1), the bright phase consists of metallic silver with 9-14 at.% of copper and 5-1 at.% of titanium dissolved and the dark phase is made of TiCu_4 . Finally, a thick transition zone with non-defined borders can be seen between the fourth $\text{TiCu}_4 + \text{Ag}_s$ layer and the free solidified Ag-Cu(Ti) alloy. According to SEM, OM and EPMA, three phases were present at 790 °C in this transition zone: nearly eutectic Ag-Cu(Ti) alloy, a solid silver-rich phase and globular TiCu_4 crystals. The reaction layer sequence taking all these features into account can be expressed as:

where L designates a $\text{Ag}_s + \text{Cu}_s$ nearly eutectic mixture resulting from the solidification of the liquid Ag-Cu(Ti) alloy (Cu_s and TiCu_4 phases cannot be distinguished by SEM in Fig. 1 but are easily identifiable by their colour when observed by OM). It is to note that in the Ag-Cu-Ti system, no ternary eutectic transformation exists involving the four phases Ag_s , Cu_s , TiCu_4 and L. Instead, the liquid L reacts with TiCu_4 below 783 °C (transitory ternary peritectic reaction) to give solid copper and solid silver. This is the reason why although the liquid L is saturated in Ti, no TiCu_4 crystal precipitates up to complete solidification at 780 °C.

Table 1. Ag, Cu and Ti contents found by EPMA in the reaction layers formed after 50 min at 790 °C between solid titanium and Ti-saturated Ag-40at.% Cu liquid alloy

	Ag (at.%)	Cu (at.%)	Ti (at.%)	Phase attribution
1 st layer	0 - 2	34.0 – 32.0	66.0	Ti ₂ Cu
2 nd layer	2.0 – 3.3	48.0 – 46.7	50.0	TiCu
3 rd layer	dark phase 1.3 – 1.9	55.2-54.6	43.5	Ti ₃ Cu ₄
	bright phase ~ 86	~ 9	~ 5	Ag
4 th layer	dark phase 1.5 – 2.0	75- 74.5	23.5	TiCu ₄
	bright phase ~ 86	~ 14	-	Ag

3. 2. Ag-40 at.% Cu liquid without Ti

When no titanium was initially present in the Ag-Cu alloy, the major phenomenon seen was the dissolution of that element in the liquid alloy. After 50 min of heating at 790 °C, a depression with a depth attaining 60 µm was observable at the surface of the titanium plate, where a direct contact with the liquid alloy was established. Taking into account the area of the exposed surface (2 mm x 2 mm) and the volume of the liquid (~80 mm³), the increase of the Ti content in the drop was estimated to be about 0.2 at.%, which is only a tenth of the saturation value at 790 °C. Regardless of the heat-treatment time (from 2 min to 50 min), the reaction zone formed under these conditions at the liquid/solid interface remained very thin: its total thickness was in the range 3-6 µm. Fig. 2 shows that this zone consists of four different layers. Each of them is dense, continuous and exhibits a single-phased appearance, apart from some rare places in the outer layer where silver-rich inclusions are observable. The counting rates obtained for Ag, Cu and Ti by EPMA in the thickest parts of each layer were characteristic for single-phased compounds arranged according to the reaction layer sequence:

$$\alpha\text{Ti} / \text{Ti}_2\text{Cu} / \text{TiCu} / \text{Ti}_3\text{Cu}_4 / \text{TiCu}_4 / \text{L}',$$

where L' designates a Ag_s + Cu_s mixture resulting from the solidification of the liquid alloy.

Fig. 2. Thin reaction zone formed between solid Ti and titanium-free Ag-40 at.% Cu liquid alloy after 50 min of heating at 790 °C

3. 3. Reaction layer sequences and phase equilibria

Fig. 3 shows the isothermal section of the Ag-Cu-Ti phase diagram at 790 °C, calculated with the Thermo-calc software by using the already developed thermodynamic descriptions of the Ag-Cu [9], Ag-Ti [10] and Cu-Ti [11] binaries. Extension to the third-order Ag-Cu-Ti system was made by using the assessment by Arroyave [12]. In this section, which is in good agreement with previous literature data [8, 13-15], two reaction paths have been drawn to represent each of the two layer sequences. Both reaction paths comply with the mass balance, provided that the liquid is slightly enriched in Ag near the liquid/solid interface. For both sequences, it has moreover been verified by using the Thermo-Calc software that the activities of Ti and Cu regularly decrease and increase, respectively, when moving through the reaction zone from Ti to the liquid alloy as shown in Fig. 4. Accordingly, Ti and Cu atoms can intrinsically diffuse in opposite directions down their activity gradient [16]. Finally, local phase equilibria are established at all interfaces [17], except at the $\text{Ti}_3\text{Cu}_4/\text{TiCu}_4$ interface where the stable compound Ti_2Cu_3 should be present. In fact, it has been shown in previous work that in the solid state, Ti_2Cu_3 grows at a much slower rate than TiCu_4 and Ti_3Cu_4 [7]. The two reaction paths drawn in Fig. 3 can thus be considered as diffusion paths, it being understood that due to a very slow rate of growth, the compound Ti_2Cu_3 is transiently "missing".

Fig. 3. The Ag-Cu-Ti ternary phase diagram as calculated at 790 °C. Two diffusion paths have been drawn corresponding to the reaction zones formed in Ag-40 at.% Cu alloys saturated in Ti (path A) and without Ti (path B)

4. Discussion

Formation of the Ti/Ag-Cu reaction zones of the second type (Fig. 2) can be described as follows. As soon as the eutectic Ag-Cu alloy melts (M.P. 780 °C), the Ti base metal begins to dissolve in the liquid. When the Ti activity in the liquid is sufficiently high near the Ti surface, the compound TiCu_4 nucleates on Ti and rapidly forms a continuous reaction layer of small crystals that isolates Ti from the liquid as previously reported [7]. Other Ti-Cu compounds can then nucleate and grow by solid state reaction-diffusion between Ti and the TiCu_4 layer. A reaction zone is thus formed (Fig. 4a), consisting of four dense and single-phased layers of compounds arranged according to the diffusion path B in the Ag-Cu-Ti phase diagram (Fig. 3). Obviously, the four layers tend to grow by solid state volume diffusion.

Fig. 4. Chemical activities of fcc-Cu and cph-Ti in the intermetallic compound layers formed by reaction at 790 °C of solid titanium with (a) pure and (b) Ti-saturated Ag-40 at.% Cu liquid alloy

However, at the same time, titanium is dissolved in the liquid Ag-Cu alloy which is far from being saturated in titanium. In such an instance where growth by solid state diffusion and dissolution are competing, the reaction zone rapidly attains a constant thickness, as described in detail by Dibkov [18]. This explains why, although growing by solid state diffusion, the reaction zone does not increase in thickness. As a consequence, the Ti and Cu chemical activity gradients through the reaction zone remain steep (Fig. 4a), which might be the key for keeping up nearly planar interfaces.

When the Ag-Cu liquid is fully saturated in titanium, dissolution of this element does not proceed and the different layers of the interface reaction zone can grow according to two main processes: solid state diffusion of Ti and Cu atoms for all layers and precipitation from a liquid locally over-saturated in Ti for the TiCu_4 crystals of the outer layer. As TiCu_4 precipitation proceeds at a fast rate, the liquid in contact with the outer layer is depleted in copper. This gives rise to the formation of some solid silver grains. Then, new TiCu_4 crystals precipitate on these grains from the liquid and new silver grains appear. Finally, a thick outer layer consisting of TiCu_4 crystals embedded in a solid silver-based matrix is formed after a few minutes of reaction at 790 °C. At this point, further precipitation of TiCu_4 and of silver-rich grains implies the solid state diffusion of titanium through the growing reaction layers. Accordingly, as the thickness of the reaction layers increases, the rates of precipitation of TiCu_4 and Ag decrease. This would explain why the size and shape of the TiCu_4 crystals (and also of the silver-rich grains) gradually change from small and elongated to larger and more globular. As the thickness of the reaction zone continues to increase, another process, implying long-range crossed diffusion of Cu and Ti in the solid state, takes place. This process is the chemical conversion of the oldest TiCu_4 particles present in the inner part of the reaction zone into Ti_3Cu_4 . Development of these different processes gives the liquid-solid

reaction zone the morphological features schemed in Fig. 4b. It should be noted that, because of the saturation of the liquid in Ti and also of the large thickness of the two outer layers, the chemical activity gradients for Ti and Cu at the solid-liquid interface tend to be flat (Fig. 4b). This might be a reason why the solid/liquid boundary is not well-defined.

Let us now consider the formation of joints when Ti plates are brazed at 780-800 °C with Ag-40 at.% Cu alloy. For that purpose, 50-100 µm thick Ag-Cu ribbons are generally used, which means that solid titanium in excess reacts with a limited amount of Ag-Cu. The liquid alloy is thus rapidly saturated in Ti and the Ti/alloy reaction zone rapidly changes from type 2 to type 1. Fig. 5 shows a Ti/Ag-40 at.% Cu /Ti joint brazed at 790 °C for a short period of time (3 min) with an Ag-Cu ribbon. The particular morphology of this joint is the result of a time sequence of four of the above-described processes, namely Ti dissolution, growth by solid state interdiffusion, fast rate precipitation of TiCu_4 , and isothermal solidification of Ag. It is worth emphasizing that the four processes develop at a fast rate. Indeed, isothermal solidification of the braze alloy is completed after only 3 min of brazing. This implies fast rate migration of titanium and copper through solid silver. For lattice diffusion of Ti in solid Ag at 790 °C, a diffusivity of the order of $1.5 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ is reported [19, 20]. This value is too low to account for an isothermal solidification of the joint in less than 3 min. On the other hand, a diffusivity of the order of $5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ is reported for grain boundary diffusion of Ti in Ag at 790 °C [20]. Such a high grain boundary diffusivity is consistent with the fast rate isothermal solidification observed, and this all the more than silver grains tend to grow in the form of joining columns (Fig. 5). The fact that a silver-rich zone without TiCu_4 crystals exists in the central part of the joint would indicate that Cu diffuses slightly faster than Ti. Upon further annealing (up to 15 hours) at 790 °C, the crystals of TiCu_4 embedded in the Ag-based matrix will be slowly converted by solid state reaction-diffusion first into Ti_3Cu_4 and then into TiCu . This will increase the re-melting temperature of the brazed joint step by step from 780 to about 910 °C [21].

Fig. 5. Ti/Ag-40 at.% Cu / Ti sandwich joint after 3 min of brazing at 790 °C

5. Conclusion

Interface reaction zones of two different types are formed by chemical interaction at 780-800 °C between solid titanium and liquid Ag-40 at.% Cu eutectic alloy:

- as long as titanium is in contact with a pure Ag-Cu alloy, a thin reaction zone (3-6 µm in thickness) is present at the liquid/ solid interface. This zone consists of four continuous layers arranged according to the sequence $\alpha\text{Ti} / \text{Ti}_2\text{Cu} / \text{TiCu} / \text{Ti}_3\text{Cu}_4 / \text{TiCu}_4 / \text{L}$. The layer sequence is consistent with a solid state growth process, with Ti and Cu diffusing down their

activity gradients. The fact that the reaction zone thickness does not change when the reaction time increases is explained by the fast dissolution rate of titanium in the liquid alloy;

- when the Ag-Cu alloy is saturated in titanium (about 1.88 at.% Ti at 790 °C), dissolution no longer proceeds and a reaction zone is formed with a thickness increasing with the reaction time. In that case, the reaction layer sequence is: αTi / Ti_2Cu / TiCu / $\text{Ti}_3\text{Cu}_4 + \text{Ag}_s$ / $\text{TiCu}_4 + \text{Ag}_s$ / $\text{TiCu}_4 + \text{Ag}_s + \text{L}$ / L . In addition to Ti dissolution and Ti-Cu solid state interdiffusion, three other elementary reaction processes are identified. These are the nucleation and growth from the liquid of TiCu_4 particles, the isothermal solidification of silver, and the chemical conversion of Cu-Ti compounds by reaction-diffusion in the solid state. A time sequence of these five elementary reaction processes is finally proposed to account for the morphology and composition of Ti/ Ag-Cu/ Ti joints brazed at 780-800 °C.

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