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A wettability study of Cu/Sn/Ti active braze alloys on alumina

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Active brazing is one of the ideal ways to make metal/ceramic joints. The active braze alloy contains active element(s), such as: Ti, Zr, Cr... etc., reacting and wetting the ceramic surfaces during brazing. Therefore, a strong chemical bonding can be formed after brazing. Cu base active braze alloys are alternatives among active braze alloys. With the aid of additional melting point depressant, Sn, in Cu-Ti alloys, the intermetallic phase in the active braze can be changed. However, its ability to braze structural ceramics, e.g. alumina, needs further study. The purpose of this research is concentrated on the wettability study of the Cu/Sn/Ti alloy on polycrystalline alumina. Based on the experimental results, the minimum Ti content is 6 wt pct in order to effectively wet alumina. Volume fraction of the intermetallic phase in the braze will be greatly increased if the Ti content in the alloy is increased to 12 wt pct. According to sessile drop test results, 70Cu-21Sn-9Ti demonstrates the best wetting ability on alumina. Meanwhile, the Sn content in Cu/Sn/Ti alloy should be less than 21 wt pct in order to maintain proper wettability of the braze. In addition, Cu/Sn/Ti alloys have both lower wetting angle on alumina and lower thermal expansion coefficients than commercial Ticusil® braze.

1. Introduction

With ever increasing both ceramic materials and special purpose alloys in the market place, active brazing is one of good methods to join such materials [1, 2]. Many researchers have been concentrated on reactive brazing for metal-ceramic joining [3–14]. This is because ceramics are not usually wetted by most traditional braze filler metals. Ceramics are chemically very stable with their atoms strongly bonded to one another. Therefore, they will not react with and be wetted by the brazing filler alloys unless the braze contains an active ingredient. Titanium is often used as an active constituent of silver base alloys [5–7, 12]. Meanwhile, it is reported that the active braze containing Ti is effective only if sufficiently high temperatures, typically above 800°C, is reached during brazing [2, 15]. The active element is able to react with the ceramic materials above the critical temperature.

Wettability of the active braze alloy is one of the most important criteria used to choose the proper active braze alloy in joining ceramic materials [16–19]. Practical problems encountered in joining two dissimilar materials are not only the thermal expansion mismatch [20–23], which causes a significant residual thermal stresses at the interface, but the chemical compatibility among the joint components as well as its performance at working temperatures. The active element plays a crucial role in the braze alloy, and has a strong effect on both the chemical compatibility and performance of the braze alloy. The active element must not strongly react with the base metal, or the activity of the active element may be decreased due to the formation of intermetallic compounds in the braze. For instance, Ti is not suitable as an active element in aluminum base braze alloys, because very stable intermetallics will be formed between Ti and Al. The wettability of Al base braze alloys can be enhanced by adding Mg as an active element [24, 25]. Ti is a good active ingredient in copper or silver base brazes [26, 27]. Ticusil®, Ag-Cu eutectic plus 4.5 wt pct Ti made by Wesgo Co., with a solidus of 830°C and a liquidus of 850°C is one of the most popular active silver base braze alloys applied in metal-ceramic joining [28]. However, high silver content in the braze makes high production cost of the alloy. On the other hand, Cu/Sn/Ti active braze alloy is one of the promising alternatives in metal-ceramic joining. The purpose of this investigation is to study the microstructural evolution of Cu/Sn/Ti alloys and their wetting ability to alumina with various Ti contents. In additions, the comparison of the ability to wet high purity polycrystalline alumina is also performed between Cu/Sn/Ti alloys and Ticusil® braze.

2. Experimental procedures

The substrate material was high purity alumina (purity >99.95%). The size of the alumina disk was 12.7 mm in diameter and 2.0 mm in thickness. A commercial active braze alloy, Ticusil®, was used for the purpose of

TABLE I The chemical composition Cu/Sn/Ti used in the experiment

Specimen number	Chemical composition (wt pct)
1	67Cu-21Sn-12Ti
2	70Cu-21Sn-9Ti
3	73Cu-21Sn-6Ti
4	66Cu-28.3Sn-5.7Ti
Ticusil®	68.8Ag-26.7Cu-4.5Ti

comparison. Four copper base active braze alloys with different Ti and Sn contents were used in the experiment as displayed in Table I. Samples of 2.5 g master alloys were prepared from high purity element pellets of 99.9 wt pct by vacuum arc remelting with the operation voltage of 60 V and 150A. At least remelting three times were necessary in order to avoid the inhomogeneity of the braze alloy, and the weight loss of final master alloy was less than 1 wt pct.

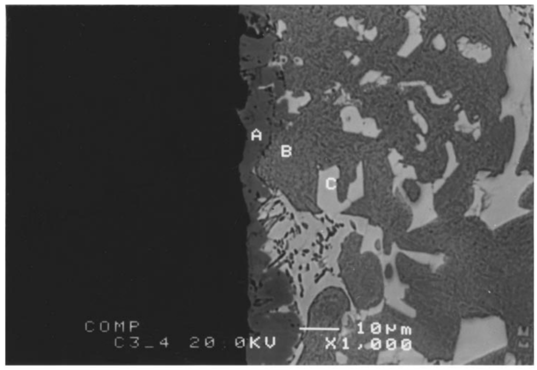
An ultrasonic bath using acetone as the solvent was used to clean samples prior to brazing. Furnace brazing was performed in a vacuum of 5×10^{-3} Pa at temperatures between 880 and 940°C for 10, 20 and 30 minutes, respectively. The heating rate of the furnace was set at 10°C/min throughout the experiment. Dynamic wetting angle measurements were made using a traditional resistance vacuum furnace at the temperature ranges between 880 and 940°C for 0–1800 seconds. 0.15 g master alloy was put on the alumina disk in vacuum furnace for wetting angle experiments. The heating rate of the furnace was set at 10°C/min throughout the experiment.

The brazed specimens were cut by a low speed diamond saw. Its cross section was first polished by SiC paper, and subsequently polished by 1 μm diamond paste. An etching solution of 2g $FeCl_3 + 30$ ml $H_2O + 10$ ml $HCl + 60$ ml C_2H_5OH was used for metallographic examination. The polished cross section of the brazed specimens was examined using a Hitachi 3500H scanning electron microscope (SEM), and quantitative chemical analysis is performed using a JEOL JXL-8800M electron probe microanalyzer (EPMA). All samples were carbon coated before SEM or EPMA examination. Thermal expansion coefficient measurements of various braze alloys were performed by using a SEIKO SSC 500 TMA for temperatures below 600°C.

3. Results and discussion

3.1. Metallographic observations and chemical analysis

Fig. 1 shows the interface between 73Cu-21Sn-6Ti alloy and alumina brazed at 900°C for 30 minutes. Based on the SEM backscattered electron image (BSE), three phases can be found in the braze filler metal including the reaction layer: (A) the reaction layer containing Cu, Sn, Ti, and O, (B) bronze matrix solid solution with 0.1 wt pct titanium, (C) Cu/Sn/Ti intermetallic phase. The reaction layer containing oxygen atoms indicates that the active element, Ti, in the braze reacted with alumina. However, it can not be identified by structural analysis in the experiment. It is also observed that the reaction layer at the interface is continuous, and a continuous reaction layer may deteriorate the bonding strength due to its brittleness. The chemical compo-



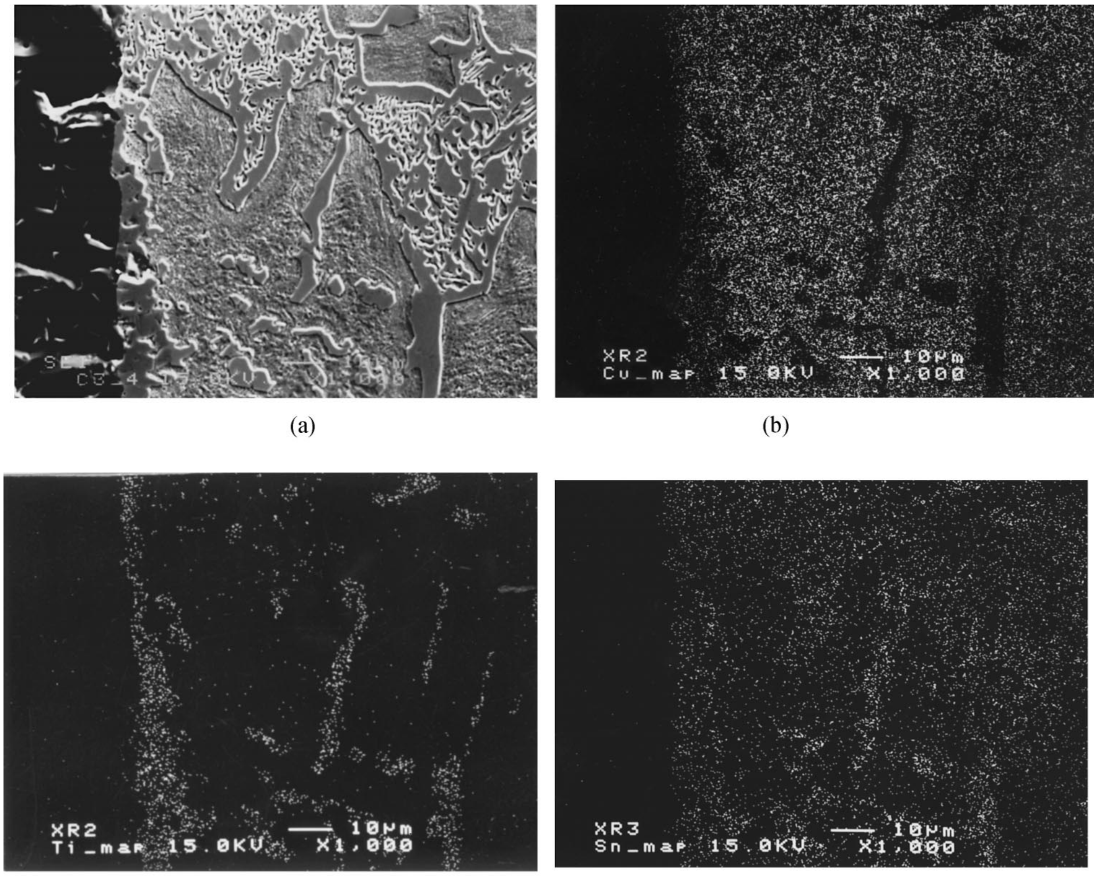
Point	O	Cu	Sn	Ti
A	5.3	33.0	25.2	36.5
B	---	85.3	14.6	0.1
C	---	11.6	52.6	35.8

Figure 1 The SEM backscattered electron image and chemical analysis results of phases at the interface between 73Cu-21Sn-6Ti alloy and alumina brazed at 900°C for 30 minutes.

sition of the matrix after brazing is basically 83.6Cu-14.3Sn with minor Ti. It is consistent with Cu-Ti binary phase diagrams that very limited solubility of Ti in Cu can be observed at low temperature [29]. In addition, Sn is strongly associated with Ti, and forms a Cu/Sn/Ti intermetallic compound in the braze as displayed in both Figs 1 and 2. The chemical composition of the Cu/Sn/Ti intermetallics is not the same as that of reaction layer. Because there is no Cu/Sn/Ti ternary alloy phase diagram available, the structure of this compound needs further study. The association of Sn and Ti consumes lots of Ti in the active braze alloy. It is expected that the Ti content in braze must exceed a certain value in order to improve the wettability of Cu/Sn/Ti alloy.

Fig. 3 is the metallographic observations of three Cu/Sn/Ti alloys with different Ti contents after brazing at 900°C for 10 minutes. It is obvious that the volume fraction of the intermetallic phase in braze is increased as the increase of Ti content in the braze. There should be an optimal content for the active ingredient in the braze. For active braze alloys with little amount of active ingredient, the ability of the braze to wet most ceramic materials is insufficient. On the other hand, the volume fraction of the intermetallic phase is greatly increased for specimens with huge amount of active ingredient. It is well known that most of the intermetallic phases are brittle, so they should be decreased and/or avoided if possible. An active braze alloy with too much active ingredient results in forming intermetallic compound in the braze itself, and there is no contribution to enhance the wettability of the braze alloy on alumina. It will be further studied in the following wetting angle measurements.

Fig. 4 is the effect of brazing time on microstructure of the braze. The morphology of intermetallic phase in the braze has changed with the increment of brazing time. However, the volume fraction of the intermetallic phase is not greatly increased. It is obvious that effect of brazing time is not as important as the content of the active ingredient in the braze alloy.



(a) (b)

(c) (d)

Figure 2 EPMA analysis of 73Cu-21Sn-6Ti (wt pct) brazed at 900°C for 30 minutes: (a) secondary electron image; (b) Cu mapping; (c) Ti mapping; (d) Sn mapping.

3.2. Wetting angle measurements of Cu/Sn/Ti active braze on alumina

Fig. 5 is the dynamic wetting angle measurements of four Cu/Sn/Ti alloys at 900°C. It is important to note that increasing the Ti content in Cu/Sn/Ti braze from 9 to 12 wt pct can not further improve the wettability of the braze on alumina substrate. The wetting angle of 73Cu-21Sn-6Ti braze is larger than that of Cu/Sn/Ti alloys with 9 or 12 wt pct Ti. 15–20 degree difference in wetting angle measurements can be observed between 73Cu-21Sn-6Ti and 70Cu-21Sn-9Ti alloys. Based on the previous discussion, the volume fraction of intermetallic phase in Cu/Sn/Ti is increasing as the Ti addition increased. Ti formed Cu/Sn/Ti intermetallic compound in the braze, and there is no contribution of Ti addition to the reactive wetting of alumina as the Ti content increased from 9 to 12 wt pct. However, 6 wt pct Ti in Cu/Sn/Ti is inferior to both 9 and 12 wt pct Ti of Cu/Sn/Ti alloys in wetting alumina substrate according to the sessile drop experiment. It is concluded that 9 wt pct Ti has the highest ability to wet alumina substrate.

It is found that increasing Sn content in Cu/Sn/Ti alloys from 21 wt pct to 28.3 wt pct results in huge increase of wetting angle between the active braze alloy and alumina as shown in Fig. 5. Fig. 6 displays the wetting angle measurement of 66Cu-28.3Sn-5.7Ti for various brazing temperatures. The final wetting angle at 1800 seconds is kept about the same as the increasing brazing temperature from 920 to 940°C. Its wetting angle even at 940°C for 1800 seconds is 60 degree, which is much greater than that of 73Cu-21Sn-6Ti at 900°C for 1800 seconds. It results from the strong association among Sn, Ti and Cu. Most of Ti content is consumed, so the active ingredient can not contribute to the reactive wetting of alumina. Therefore, increasing Sn content exceeding 28 wt pct will seriously deteriorate the wetting ability of Cu/Sn/Ti braze. For active braze alloys, not only the reaction between active element (Ti) and base metal (Cu) should be avoided, but also reactions between active element and melting point depressant, Sn, in the braze. Fig. 7 shows the microstructure of 66Cu-28.3Sn-5.7Ti alloy brazed at 920°C for 1200 seconds. It is clear that huge amount of second phase in the braze. Consequently, the Sn content in Cu/Sn/Ti alloy should be kept below 28 wt pct in order to maintain the wetting ability of the active braze. Based on the experimental results, Cu/Sn/Ti braze with 21 wt pct demonstrates good performance in sessile drop experiments.

Fig. 8 is the dynamic wetting angle measurements of Ticusil® brazed at 880 and 900°C for 0–1800 seconds, respectively. The wetting behavior between Cu/Sn/Ti and Ticusil® braze is huge in difference. The wetting angle of Ticusil® is decreased rapidly in first 500 seconds, and it becomes stable after 500 seconds. However, the wetting angle of Cu/Sn/Ti alloy is decreased steadily in dynamic sessile drop test. The final wetting angle of Ticusil® at 900°C is 9 degree, which is larger than that of 70Cu-21Sn-9Ti alloy. According to the test

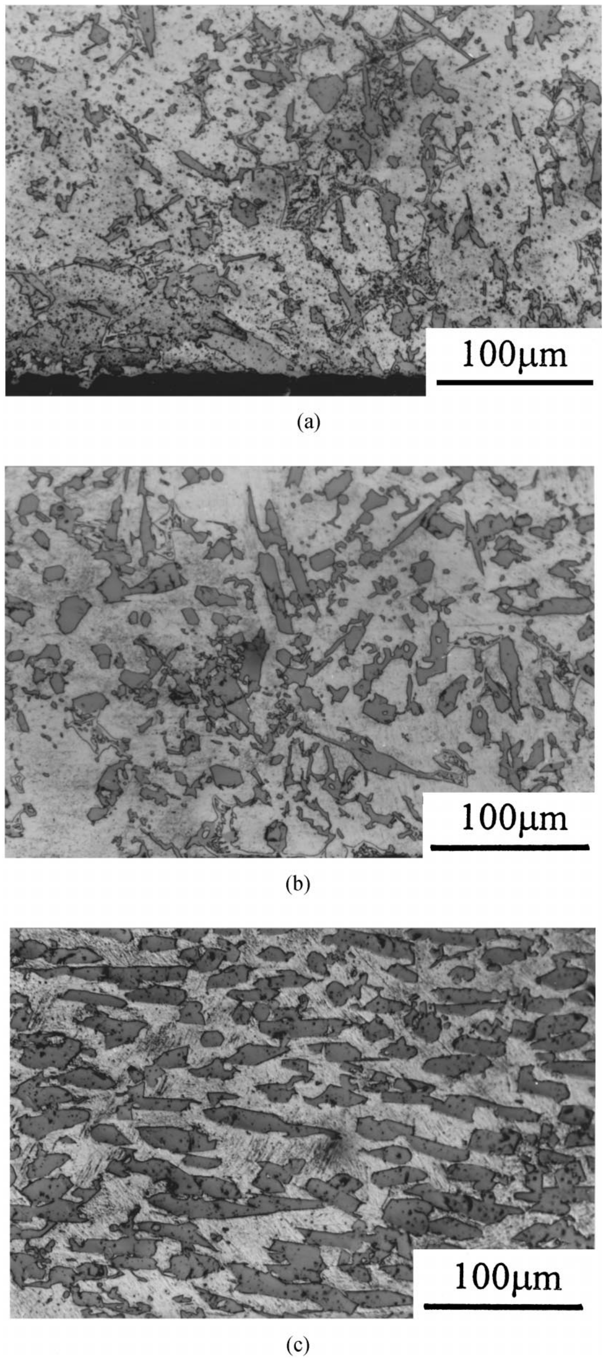


Figure 3 The metallographic observations of Cu/Sn/Ti alloys brazed at 900°C for 10 minutes: (a) 73Cu-21Sn-6Ti; (b) 70Cu-21Sn-9Ti; (c) 67Cu-21Sn-12Ti.

results, 70Cu-21Sn-9Ti demonstrates better ability to wet alumina than Ticusil®.

3.3. Thermal expansion coefficient measurements

Thermal expansion mismatch between ceramics and metals is one of the most important issues in the joining of these materials [30, 31]. When the joints are bonded at elevated temperatures, thermal expansion mismatch produces a large stress concentration in the joints upon cooling cycle. It can cause catastrophic damage to the joint without any applied stress. It is well known that the residual thermal stresses are originated from two ways, temperature gradients in the material and differences in thermal expansion coefficient of the joined materials. Lower thermal expansion mismatch of the joined materials will generate lower thermal stresses. Hence, the thermal expansion coefficient of the braze alloy is a very important factor in engineering applications.

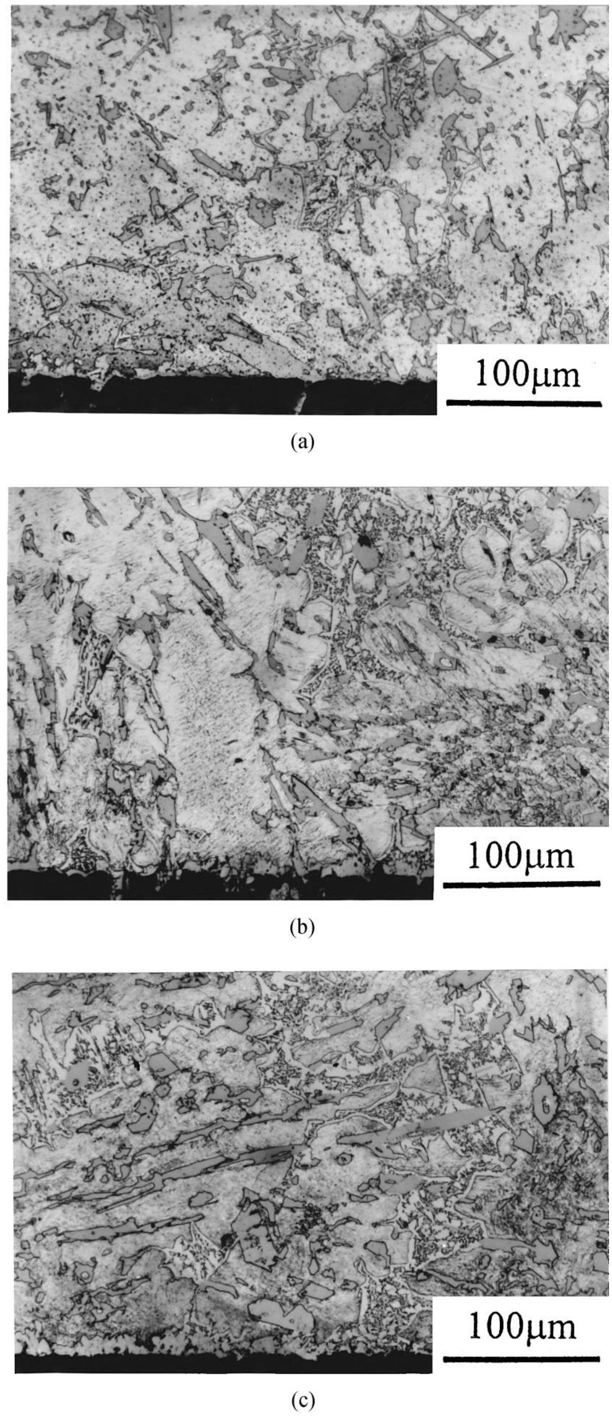


Figure 4 The effect of brazing time on microstructure of 73Cu-21Sn-6Ti alloy brazed at 900°C for (a) 10 minutes; (b) 20 minutes; (c) 30 minutes.

Table II displays the thermal expansion coefficients of various materials in temperatures between 30 and 600°C. It is clear that all thermal expansion coefficients of Cu/Sn/Ti alloys are much lower than that of Ticusil® alloy. For instance, there are about 5 ppm/°K difference in coefficients of thermal expansion between 70Cu-21Sn-9Ti alloy and Ticusil®. Therefore, a much lower residual thermal stress is expected in brazing alumina by using the Cu/Sn/Ti alloy.

TABLE II The thermal expansion coefficients in ppm/°K of various materials in temperatures between 30 and 600°C.

Wt pct	30–100°C	100–200°C	200–300°C	300–400°C	400–500°C	500–600°C	Average
66Cu/28.3Sn/5.7Ti	15.7	17.4	18.0	18.0	19.1	20.7	18.2
73Cu/21Sn/6Ti	15.7	16.9	17.6	17.6	19.2	19.4	17.9
70Cu/21Sn/9Ti	14.2	15.7	16.3	16.3	17.7	18.4	16.5
67Cu/21Sn/12Ti	13.4	14.7	15.1	14.1	15.5	15.9	14.9
Ticusil®	18.7	19.8	19.9	20.4	23.4	26.7	21.4
Al_2O_3	4.5	5.7	6.8	7.4	8.0	8.8	7.0

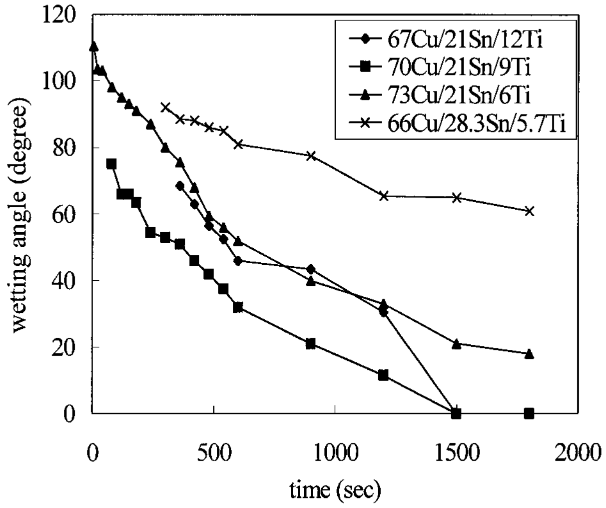


Figure 5 The dynamic wetting angle measurements of four Cu/Sn/Ti alloys at 900°C between 0–1800 seconds.

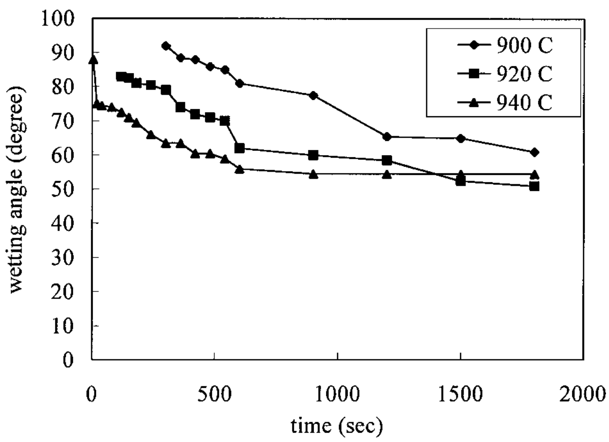


Figure 6 The wetting angle measurement of 66Cu-28.3Sn-5.7Ti for various brazing temperatures.

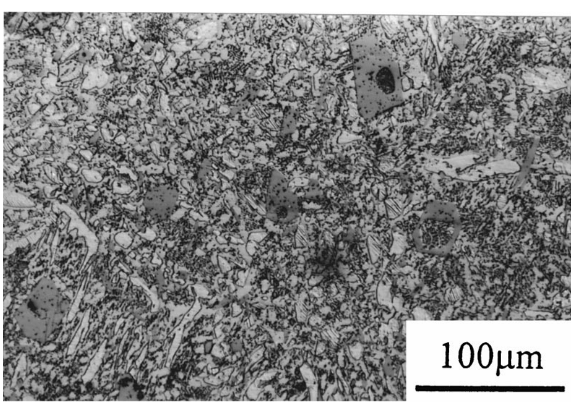


Figure 7 The microstructure of 66Cu-28.3Sn-5.7Ti alloy brazed at 920°C for 1200 seconds.

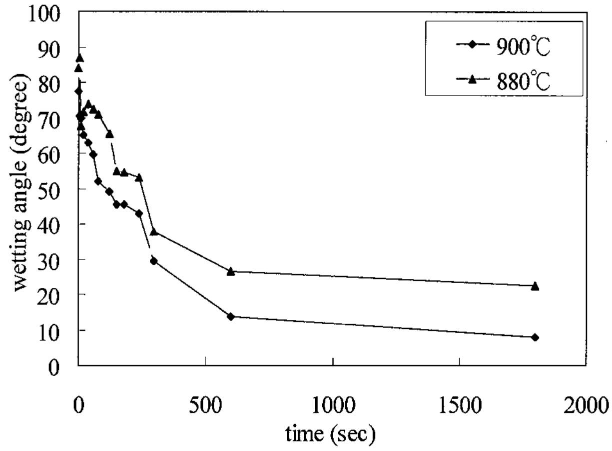


Figure 8 The dynamic wetting angle measurements of Ticusil® brazed at 880 and 900°C for 0–1800 seconds.

4. Conclusion

1. Three phases can be found in the braze filler metal including: the reaction layer containing Cu, Sn, Ti, and O, bronze matrix solid solution with 0.1 wt pct titanium, and Cu/Sn/Ti intermetallic phase. Since Sn is strongly associated with Ti, Sn content should be limited below 21 wt pct in Cu/Sn/Ti braze. Moreover, the volume fraction of the intermetallic phase is rapidly increased if the Ti content in Cu/Sn/Ti braze exceeds 12 wt pct.

2. Increasing the Ti content in Cu/Sn/Ti braze from 9 to 12 wt pct can not further improve the wettability of the active braze on alumina substrate. Based on the experimental results, Cu/Sn/Ti alloy with 9 wt pct Ti brazed at 900°C demonstrates the best wetting ability to alumina substrate.

3. All thermal expansion coefficients of Cu/Sn/Ti alloys in the experiment are much lower than that of Ticusil® alloy. Therefore, a much lower residual thermal stress is expected in brazing alumina by using Cu/Sn/Ti alloys.

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