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Combining thermodynamics and DSC to characterize the melting and wetting behavior of a composite powder used for joining ceramics

M. BROCHU, R. A. L. DREW*
Mining, Metals and Materials Engineering Department, McGill University,
3610 University Street, Montreal, Quebec, Canada, H3A 2B2
E-mail: robin.drew@mcgill.ca

The diffusion-assisted melting behavior of a Cu-coated Ti-powder was characterized as a function of the intermetallic formation and corresponding melting temperature using DSC. The endothermic and exothermic events were identified using the respective binary phase diagram. The results demonstrated that initial melting is independent of the heating rate; however complete melting occurred at 900°C when heated at 10°C/min as oppose to 915°C for a heating rate of 40°C/min. The wetting results of the brazing alloy on Si_3N_4 ceramic show that the brazing alloy maintains its initial shape until the complete melting is achieved. Equilibrium contact angle measurements obtained are similar to results previously published but the wetting kinetics observed are different.

1. Introduction

There are many different example of the application of ceramic/metal joints. In low stress/low temperature applications, adhesives have been used extensively [1]. For example, a hip implant is composed of an alumina ball (selected for its high wear resistance and biocompatibility) and a stainless steel (or titanium) stem, glued together and implanted into the femur [2]. Another example is the copper/graphite couple used extensively in the nuclear industry. These materials are brazed together with an Ag-Cu-Ti brazing alloy [2]. Silicon nitride has not escaped from the joining technology craze because Si_3N_4 represents a candidate possessing outstanding potential for high temperature structural applications. This ceramic exhibits properties such as high wear resistance, high strength at low and high temperatures, low thermal expansion coefficient and high resistance to aggressive chemical environments. Moreover, silicon nitride has already found applications in automotive engine components [3, 4].

However, before a metal-ceramic joint can be used industrially, several research steps should be successfully completed. These includes thermodynamic analysis, studies of energy of reaction and joint simulation. This paper presents a feasibility study on the behavior of Ti-containing composite powder, used for active brazing Si_3N_4. Correlation between thermodynamic analysis, DSC, wettability and actual joint microstructure are described.

2. Experimental procedure

2.1. Starting materials

The active brazing alloy (ABA) used was a composite powder, where the core was composed of titanium covered by a copper shell, giving a final composition of 25 wt%Ti. The powder was −325 mesh and 99% purity. The Cu shell of the composite powder was produce by successive electroless plating deposition performed in a $CuSO_4$-based bath. A more complete description of the procedure is presented in [5]. Additive-free alpha-silicon nitride powder (Toshiba) with an average particle size of 2 microns was used for DSC experiments. Plates of 2 cm × 2 cm and bars of 8 mm diameter of commercial sintered silicon nitride (Ceralloy 147-31N®, Ceradyne, California) containing 7–8 wt% of yttria/alumina as sintering additive were used for the wettability tests and joints, respectively.

2.2. DSC experiments

The thermal analysis of the melting events of the composite powder was performed in a DSC (Netzsch, DSC 404C). The powder was heated up to the testing temperature at a heating rate of 10 and 40°C/min respectively, under ultra high- purity argon. As Ti-containing alloys are commonly used for brazing ceramics, the powders were initially placed inside a folded Nb foil in the crucible, to prevent contact and reaction between the molten alloy and ceramic crucible. The reaction between Si_3N_4 powder and the ABA were studied using

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*Author to whom all correspondence should be addressed.

a weight ratio of 85%ABA-15%Si_3N_4 (70–30 vol%). The mixture was heated between 925 and 1025°C in ultra high purity argon and soaked for 6 min in each case. This soaking time was used to ensure temperature equilibrium of the sample between the heating and cooling stages.

2.3. Wettability tests

The wettability of the ABA on Si_3N_4 substrate was evaluated using the sessile drop technique in a horizontal tube furnace. The wetting behavior was tested at 935°C. In each case, the sample was inserted in the center of the hot zone prior to heating in order to take into account the heating stage in a typical ceramic brazing process. Photographs were taken at different intervals to evaluate the change of wetting angle with time. Prior to heating, a vacuum of 5×10^{-5} Torr was applied followed by back filling with high purity argon, which was used as a static atmosphere during the experiment.

2.4. Brazing cycle and microstructure characterisation

The joining cycle was carried out in a graphite furnace. The sample was embedded in a powder bed of boron nitride inside a graphite die. A static pressure of 35 kPa was applied to the top of the jig to keep the samples aligned. The bonding temperatures were varied between 975 and 1075°C for different joining times ranging between 1 and 12 min. The heating cycle was as follows: heating at 10°C/min up to the brazing temperature and cooled down at a rate of 5°C/min to 300°C. Flowing argon was maintained during the cycle. The joints were cut, mounted, polished and characterized using low voltage FE-SEM (Hitachi S-4700).

3. Results and discussion

3.1. Themodynamic evaluation

The chemical reaction between Ti dissolved in Cu and Si_3N_4 will produce titanium nitride and titanium silicide [6]. The reaction products were evaluated previously by several researchers and a general agreement is that the main reaction products formed are TiN and Ti_3Si_5, as describe in Equation 1:

$$((\mathrm{Ti}))\mathrm{Cu} + \langle \mathrm{Si3N4} \rangle \rightarrow \langle \mathrm{Ti5Si3} \rangle + 4\langle \mathrm{TiN} \rangle$$

$$\text{with } \Delta G_1 = \Delta G_1^{\mathrm{o}} - RT \ln a_{\mathrm{Ti}} \quad (1)$$

where $\Delta G_1^{\mathrm{o}} = -1924.06 + 364.35T$ is the standard Gibbs energy of reaction (1) and can be calculated from ΔG_2^{o} and ΔG_3^{o}:

$$2\mathrm{Ti} + \mathrm{N_2} = 2\mathrm{TiN}$$

$$\Delta G_2 = -672.50 + 186.04T(\mathrm{kJ/mol\ K})\ [7] \quad (2)$$

$$5\mathrm{Ti} + 3\mathrm{Si} = \mathrm{Ti_5Si_3}$$

$$\Delta G_3^{\mathrm{o}} = -579.06 - 7.73T(\mathrm{kJ/mol\ K})\ [8] \quad (3)$$

This reaction described in Equation 1 is strongly exothermic in the solid state but is even more exothermic in the presence of a Ti-containing liquid [7]. The activity coefficient of Ti in Cu is approximated to unity in the composition range used in this work [9]. This high activity makes titanium attractive as the active element in copper-based filler metals for joining ceramics.

3.2. DSC joint simulations

3.2.1. Determination of melting sequence of composite ABA

Diffusion is critical in the melting sequence of such coated powder, as several intermetallics formed through diffusion and hence, possess different melting characteristics. The diffusion in turn, depends on heating rate as diffusion is a thermally activated process. The effect of the heating rate on the heat flow is presented in Fig. 1 for the composite ABA heated at 10 and 40°C/min, respectively. A small exothermic peak with an onset temperature of 870°C appears in the 40°C/min sample. A somewhat broader peak also occurs in the 10°C/min sample at lower temperature (i.e. ≈855°C). Following the exotherm, it can be observed that the onset of the large melting peak occurs in both samples at 886°C and 885°C, respectively. However, the end point of melting is different: 900°C for the powder heated at 10°C/min, as opposed to 915°C for the powder heated at 40°C/min. A single melting event was observed for the samples

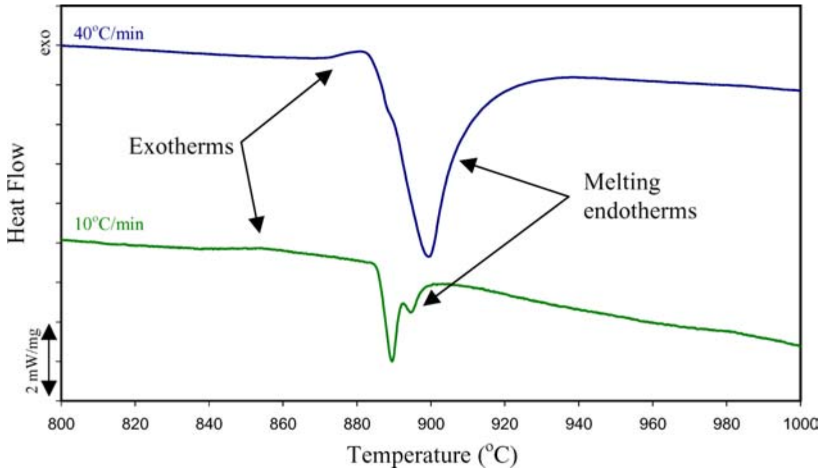

Figure 1 DSC traces of powder heated at 10 and 40°C/min respectively.

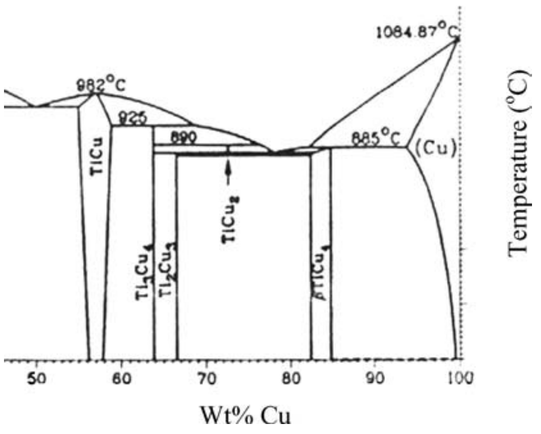

Figure 2 Cu-rich portion of Cu-Ti phase diagram [10].

heated at 40°C/min as opposed to two stages melting for the powder heated at 10°C/min. The onset temperature for this second melting event has been determined as 890°C. After consulting the Cu-Ti phase diagram presented in Fig. 2 [10], this event appears to be associated with the peritectic reaction $TiCu_2 \rightarrow Ti_3Cu_4 +$ liquid as well as initiation of melting of Ti_3Cu_4. The latent heats of fusion determined for the powder heated at 40 and 10°C/min are 113 and 103 J/g, respectively, and are similar to that obtained for pure Cu.

The presence of the very small exothermic peak at about 870°C suggests that only trace amounts of Ti_2Cu_3 were developed in the diffusion couple during heating and so available for transformation to $TiCu_2$. In addition, the lack of a strong melting endotherm at 875°C indicates that very little bi-phase structure was developed during heating. This lack of low temperature melting is correlated to the very little quantity of $TiCu_2$ developed in the diffusion couple. A large melting endotherm with an onset at 885°C indicates a strong peritectic reaction (i.e. $TiCu_4 \rightarrow (Cu) + L$) followed by progressive melting of the remaining (Cu) solid solution as the principal melting mechanism of the composite powder. This in turn would indicate that a large portion of the powder remains as a (Cu) solid solution but includes a measurable amount of $TiCu_4$.

3.2.2. Simulation of Si_3N_4/active brazing alloy joints

The previous results have shown that the active brazing alloy starts melting at 886°C and that the first liquid is created inside the Cu shell through the peritectic reaction. Experiments were carried out in which the composite powder was mixed with Si_3N_4 powder and the resultant DSC traces heated at 40°C/min are presented in Fig. 3. The corresponding trace of melting of the ABA is included for comparison. The initial endothermic peak shows the start of melting of the powder mixture. A major exothermic peak is observed within 10°C following the appearance of a liquid in the shell. This peak is associated with the formation of TiN and Ti_5Si_3 from reaction between $(Ti)_{Cu}$ and Si_3N_4 (ref Equation 1), once the active liquid reaches the surface. This reaction between the ceramic and the ABA begins at 894°C.

Fig. 4 presents the DSC traces for Si_3N_4/ABA powder mixture held for 6 min at 925, 975 and 1025°C, respectively. The captions H and C represent, the heating and cooling curves, respectively. The melting events are similar in all three cases. The composite powder begins to melt at 886°C and reaction with the ABA starts at 894°C. The traces performed at 975 and 1025°C show that the reaction went to completion as the trace returned to the base line. In both cases, the residual change in melting and reaction energy is the same (−140 J/g), suggesting similar melting and reaction behavior regardless of the test temperature. However at 925°C, the base line was not reached implying that the reaction was not complete at this temperature. No solidification peaks are observed on the cooling traces of the 975 and 1025°C samples, suggesting isothermal solidification due to consumption of the active element through reaction (1). However the cooling stage for the sample heated at 925°C shows a small solidification peak at 868°C (−2.23 J/g) indicating that active brazing liquid was still present during cooling.

3.3. Wettability of Cu-Ti alloy on Si_3N_4 substrates

Fig. 5 shows the wetting curve for the alloy on Si_3N_4 substrate at 935°C. As mentioned earlier, the active

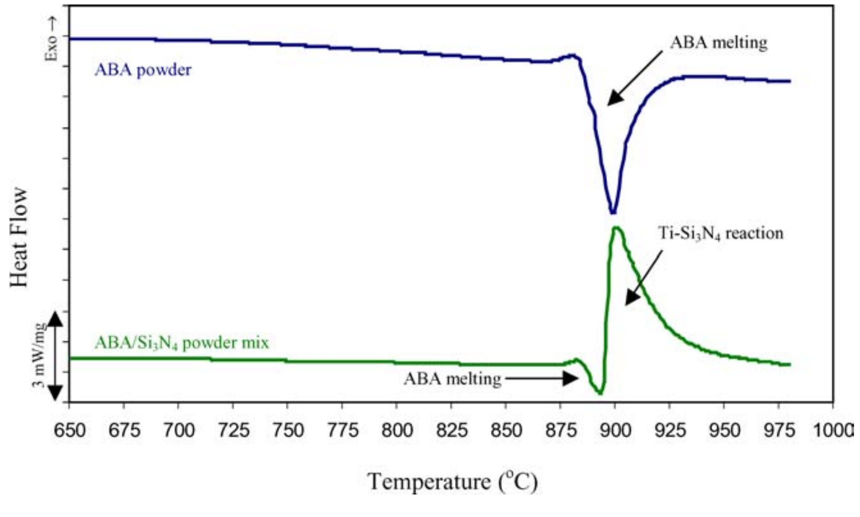

Figure 3 DSC trace of ABA powder and ABA/Si_3N_4 powder mix at 40°C/min in argon.

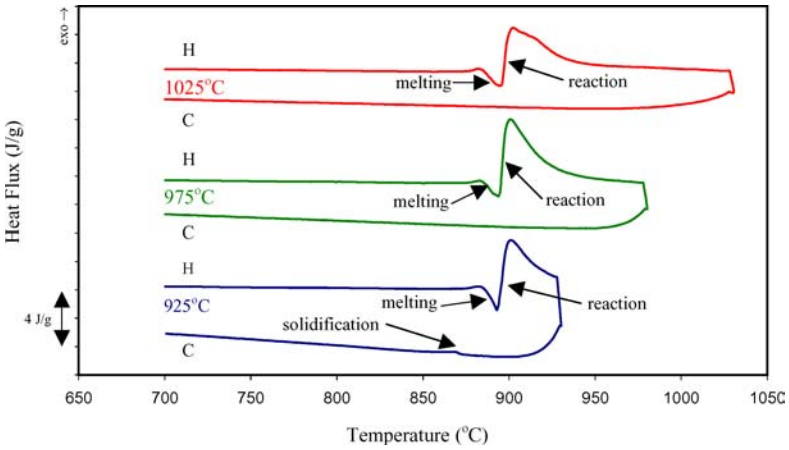

Figure 4 DSC trace of powder mixture soaked for 6 min at 925, 975 and 1025°C, respectively.

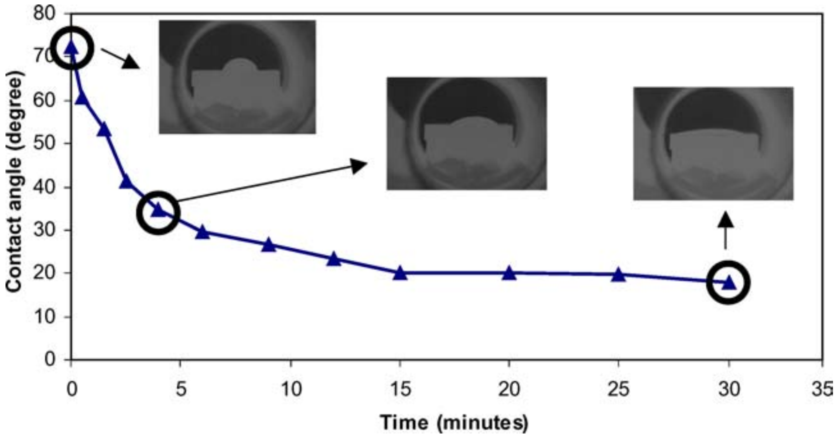

Figure 5 Contact angle of molten composite powder on Si_3N_4 ceramic (935°C).

brazing alloy was molten when the furnace reached the test temperature. From the curve, a rapid decrease in wetting angle can be observed. The wetting angle decreased from 72° to 29° after 6 min. This rapid decline of the contact angle slows down and equilibrium is nearly reached after 15 min giving an equilibrium contact angle of around 20 degrees. The contact angle between 15 and 30 min shows no significant change. Chemical analysis was performed to evaluate the residual titanium content in the drop after solidification and the results shows that the titanium concentration remains approximately similar to the initial concentration (25wt%Ti) which indicates that the drop was still molten during this stable period ($>$15 min). The stable contact angle of the drop is explained by the system approaching reactive equilibrium: establishment of a well-defined alloy/Ti_5Si_3/TiN/Si_3N_4 reactive bi-layer configuration through diffusion-controlled reaction.

3.4. Comparison of previous results with Si_3N_4/Si_3N_4 brazed joints

Fig. 6 presents the back-scattered micrograph showing the microstructure of the reaction layer for the samples joined at 975 and 1025°C for 1 min, respectively. At 975°C, a composite reaction layer is observed, where the darker phase corresponds to a Ti and N-rich phase and the lighter phase is composed of Ti and Si. A substantial thickening of the total reaction layer is observed for the sample brazed at 1025°C, where two distinct layers are clearly illustrated. The darker layer, adjacent to the Si_3N_4 ceramic, is composed of Ti and N and the main reaction layer is composed of Ti and Si. Some Ti/N rich precipitates were observed in the Ti/Si-rich layer and into the Cu/Ti brazing alloy. Cu was also observed in some isolated locations.

At 975°C, the reaction layer contains both intermixed components in the same layer. For these joining conditions, the reaction is near completion, as illustrated on the DSC traces. On raising the brazing temperature to 1025°C, the formation of two distinct layers, as opposed to an intermixed one, is observed. Thermodynamic computations on the stability of TiN during reaction between Ti and Si_3N_4 in low N_2 partial pressure environment have shown that Ti_5Si_3 is more stable than TiN. Therefore, TiN dissociates to form native N at the TiN-Ti_5Si_3 interface resulting in a thicker silicide layer. The combined interactions - reaction between the filler metal and the ceramic (Ti-Si_3N_4) and the dissociation of TiN – allows for the formation of a distinct Ti-silicide layer. This decomposition of TiN at the TiN/Ti_5Si_3 interface releases nitrogen, which in turn goes into solution in the Ti_5Si_3 and diffuses towards the filler metal. This N diffusion, indicates a certain level of solubility in Ti_5Si_3, which, upon super-saturation, results in the growth of TiN precipitates within the reaction layer itself during cooling. In addition, nitrogen will continue to react with free Ti from the filler metal and precipitate

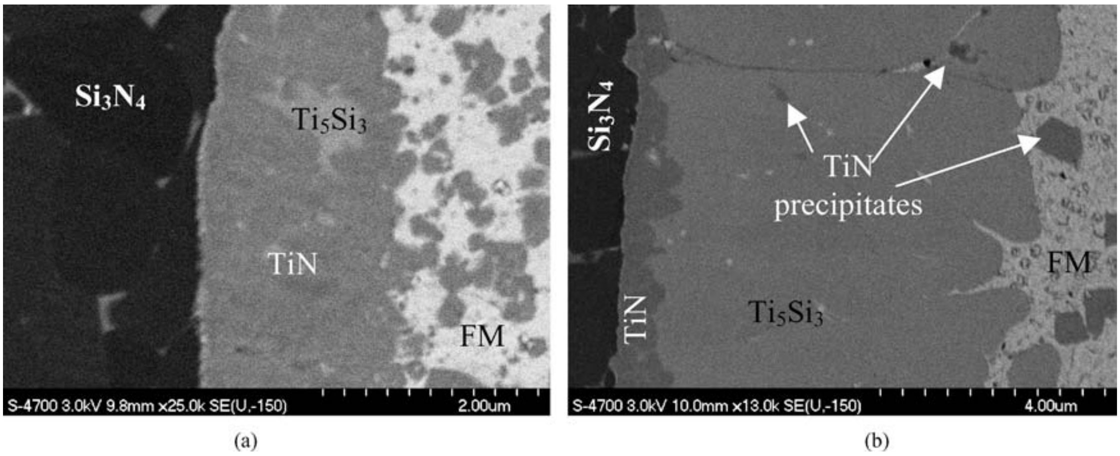

Figure 6 Reaction layer microstructural evolution for joints brazed at (a) 975°C for 1 min and (b) 1025°C for 1 min (FM = filler metal).

TiN outside the reaction layer. This implies that a lower Ti-silicide stoichiometry should be observed around the TiN precipitates present in the Ti_5Si_3 layer.

4. Conclusions

This paper presented an approach to correlate the thermodynamic and thermal analysis, wettability and microstructure for the brazing system Si_3N_4/Cu-Ti (ABA) composite powder. The results demonstrate that the melting of the composite powder occurs through a peritectic reaction as oppose to the lower melting point eutectic. The heat of reaction shows that complete reaction between silicon nitride and the ABA was not obtained at low temperature, which can be correlated to the non-equilibrium microstructure formed in samples joined near the low-end operating window studied.

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