Communication

Interfacial Reaction and Wettability of 72Ag-28Cu Braze on CP-Ti Substrate Using Infrared Heating

R.K. SHIUE, S.K. WU, F.Y. CHEN, and T.E. YANG

Reactive wetting by infrared heating of a BAg-8 braze on a CP-Ti substrate is achieved at 1073 K (800 °C) for 300 seconds. Increasing the test temperature from 1073 K to 1123 K (800 °C to 850 °C) results in great improvement of the wettability on the CP-Ti substrate due to the lower melt viscosity at higher test temperature and the alloying effect of Cu into the CP-Ti substrate to form the interfacial eutectoid layer.

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Titanium alloys exhibit high specific strength as well as good corrosion resistance, and are particularly suitable for aerospace and medical applications.[1] Titanium exists in two allotropic crystal structures: α phase that has an hexagonal-close-packed (hcp) structure and β phase that has a body-centered-cubic (bcc) structure. Above the β transition temperature, the hexagonal α phase is transformed to the bcc β phase when heating.[2] The β transition temperature is greatly affected by the alloying elements in CP-Ti, *e.g.*, Fe and interstitial elements such as carbon, oxygen, nitrogen, and hydrogen. There are four grades of CP-Ti. This study uses grade 2 CP-Ti, which has transition temperatures for the α and β phases of 1163 K and 1186 K (890 °C and 913 °C), respectively.[2]

Interfacial reactions and wettability of a braze melt on substrate play crucial roles in brazing.[3,4] Traditional furnaces are not well suited to analyzing the initial transient stage of the interfacial reaction due to their slow heating rate. In contrast, an infrared heating furnace is well suited for studying the initial transient reaction kinetics of wetting, having heating rates up to 50 K/s.[5–8]

Ag-based brazed alloys have low brazing temperatures as compared with Cu/Ni-based braze alloys.[3] According to previous studies, Ag-based braze alloys can braze many titanium alloys well.[5–8] The wettability of the molten braze on the substrate and the formation of intermetallic phases at the braze substrate should be considered in detail. This investigation focuses on the infrared heated small BAg-8 (72Ag-28Cu, in wt pct) sphere on a CP-Ti substrate. Mechanisms of interfacial reaction(s) and wettability on CP-Ti are examined and discussed.

Grade 2 CP-Ti plates (3-mm thick) were used as the substrate. BAg-8 foil (50- μm thick) was purchased from Lucas-Milhaupt Inc (Cudahy, WI). The eutectic temperature of BAg-8 is 1053 K (780 °C), which is well below the β transition temperature of grade 2 CP-Ti. All joined surfaces were polished using SiC papers up to grit 1200 and were ultrasonically cleaned with acetone prior to infrared heating. The BAg-8 spheres with the diameter of 3 to 5 mm were fabricated from the foil by vacuum arc remelting. A dynamic wetting angle measurement was performed using an Ulvac Sinko-Riko RHL-816C infrared furnace (ULVAC Taiwan, INC, Hsingchu, Taiwan) with a vacuum of 2×10^{-3} Pa.

Infrared rays were emitted from the infrared lamps, transmitted through the transparent quartz tube, and focused on the specimen's holder. One end of the quartz tube was attached to the specimen's holder, and the other end adopted transmitting infrared rays recorded by an image analysis system. The procedure for measuring the wetting angles and the apparatus used were detailed in a previous article.[8] During the infrared joining, step heating rates were set at 23.3 and 8.3 K/s before and after 973 K (700 °C), respectively. All specimens were preheated at 973 K (700 °C) for 300 seconds to equilibrate the temperature profile of the specimen and were then heated to 1073 K or 1123 K (800 °C or 850 °C) for 300 seconds.

Cross sections of infrared joints were examined using the electron probe microanalyzer (EPMA, JEOL* JXA 8600SX) equipped with wavelength dispersive detectors (WDDs) operated at a voltage of 15 kV and minimum spot size of 1 μm. A transmission electron microscope (TEM) was used for detailed interfacial microstructural observations.

TEM specimens were first sectioned by a diamond saw (Buehler Isomet, Buehler, Irvine, CA) into thin foils and then further thinned by a dimpler and an ion miller (Gatan PIPS, Nippon Gatan, Fukagawa, Koto-ku, Tokyo, Japan). Thin TEM specimens were examined using a PHILIPS** TECNAI 20 operated at 200 kV with an energy dispersive spectroscope (EDS) for chemical analysis of the specific area at the interface.

Figure 1 shows a plot of dynamic wetting angle *vs* time for the BAg-8 braze on a CP-Ti substrate at two different brazing temperatures. The BAg-8 braze wets the CP-Ti substrate at 1073 K (800 °C) with the wetting angle of 38 deg at 300 seconds. The wettability of molten BAg-8 braze on the CP-Ti substrate is greatly improved when increasing the testing temperature to

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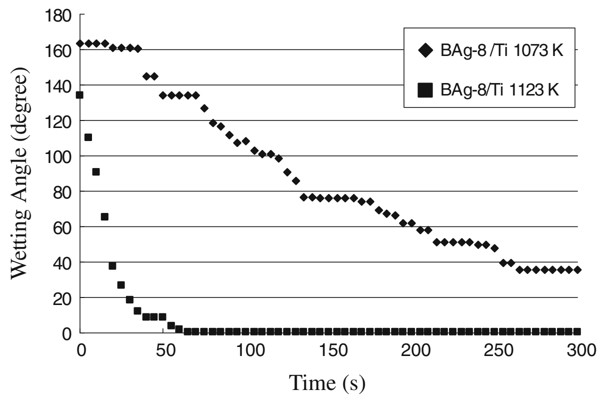
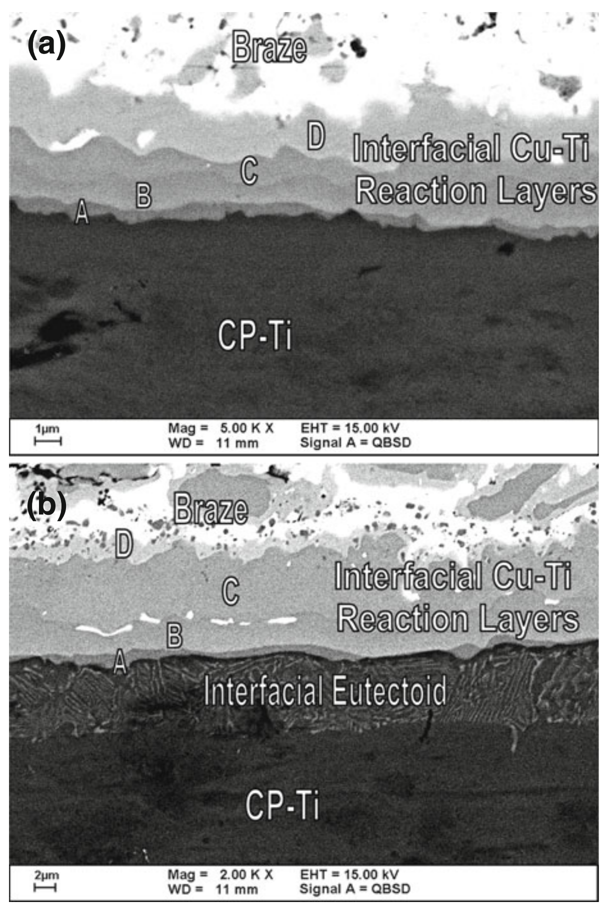


Fig. 1—Dynamic wetting angle measurements of BAg-8 braze on the CP-Ti substrate as a function of time for two different brazing temperatures.

1123 K (850 °C). A wetting angle of 20 deg is readily achieved in 30 seconds, and the wet approaches completely in 60 seconds. The results of Figure 1 indicate that the wetting mechanisms of 1073 K and 1123 K (800 °C and 850 °C) could be different. The abrupt change in wetting angles results from the lower melt viscosity due to higher test temperature. Moreover, both interfacial reactions and lower melt viscosity resulting from higher testing temperature contribute to the wetting between the braze melt and CP-Ti substrate.

Figures 2(a) and (b) show a cross-sectional view of the braze interface, as observed in the EPMA with the WDD chemical analysis results of the BAg-8 braze on the CP-Ti substrate after the wetting angle test at 1073 K and 1123 K (800 °C and 850 °C) for 300 seconds, respectively. From Figure 2(a), four interfacial reaction layers, marked A, B, C, and D, are identified as

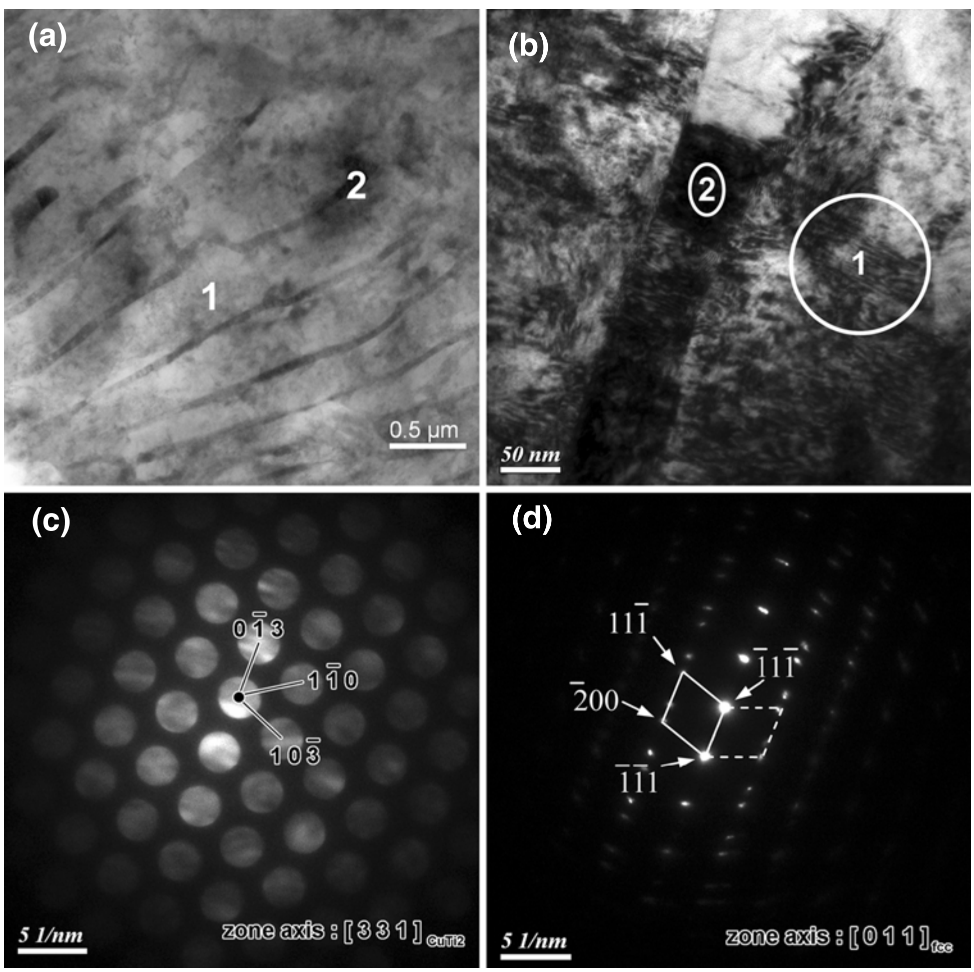


Location (phase)	A ($CuTi_2$)	B (CuTi)	C (Cu_4Ti_3)	D (Cu_4Ti)
Ag	1.1	2.2	2.0	5.2
Ti	77.2	49.2	41.7	19.0
Cu	21.8	48.6	56.3	75.9

Fig. 2—Cross-sectional backscattered images of the braze interface, as observed with an EPMA. Chemical analysis is obtained using WDD chemical analysis (in at. pct) specimens after a wetting angle test using the BAg-8 braze on CP-Ti substrate at (*a*) 1073 K (800 °C) for 300 s and (*b*) 1123 K (850 °C) for 300 s.

$CuTi_2$ CuTi, Cu_4Ti_3, and Cu_4Ti phases, respectively, in accordance with the Cu-Ti binary phase diagram.[9] It has been reported that the dissolution of a CP-Ti substrate into the braze melt results in forming two immiscible liquids: one liquid that is rich in Ag and another liquid that is rich in Cu and Ti.[6,8,10] Based on the experimental observation, the Ag-rich melt has little effect on the wetting of the CP-Ti substrate, but the Cu/Ti-rich melt plays a crucial role in the wettability. Reactions between the Cu/Ti-rich melt and CP-Ti substrate result in the modification of the wetted surface with the formation of interfacial layers. Reactive wetting of the CP-Ti substrate is achieved, and the wetting angle is decreased from 162 to 38 deg at 1073 K (800 °C), as shown in Figure 1.[11,12] Accordingly, the presence of interfacial Cu-Ti reaction layers is beneficial to the reactive wetting of the CP-Ti substrate. The interfacial Cu-Ti reaction layers of B and C shown in Figure 2(b) are remarkably thick compared to those shown in Figure 2(a) due to the higher heating temperature. Different from Figure 2(a), a layer of continuous interfacial eutectoid with approximately 10- μm thickness forms between the interfacial Cu-Ti reaction layers and the CP-Ti substrate, as illustrated in Figure 2(b). The formation of the interfacial eutectoid greatly enhances the wettability of the BAg-8 melt on the CP-Ti substrate at 1123 K (850 °C), as demonstrated in Figure 1.

Figure 3 displays TEM bright-field (BF) images, a convergent beam diffraction pattern (CBDP), a selected area diffraction pattern, and EDS chemical analysis results (at. pct) of the interfacial eutectoid shown in Figure 2(b). From Figure 3(a) and the EDS results, the eutectoid with lamellar spacing of 0.5 μm consists of $CuTi_2$ lamina (dark phase as marked by 2) and Ti-rich matrix (light phase as marked by 1). The Ti-rich matrix is alloyed with minor amounts of Ag and Cu. Figure 3(b) is the enlarged BF image of Figure 3(a) in



Location (phase)	Ag	Cu	Ti
1 (α-Ti)	0.6	1.8	97.6
2 ($CuTi_2$)	0.4	36.0	63.6

Fig. 3—TEM micrographs and electron diffraction analysis, and EDS analysis of the interfacial eutectoid between CP-Ti and BAg-8 braze infrared heated at 1123 K (850 °C) for 300 s: (*a*) and (*b*) BF, (*c*) CBDP of area 2 in (b), and (*d*) SADP of area 1 in (b).

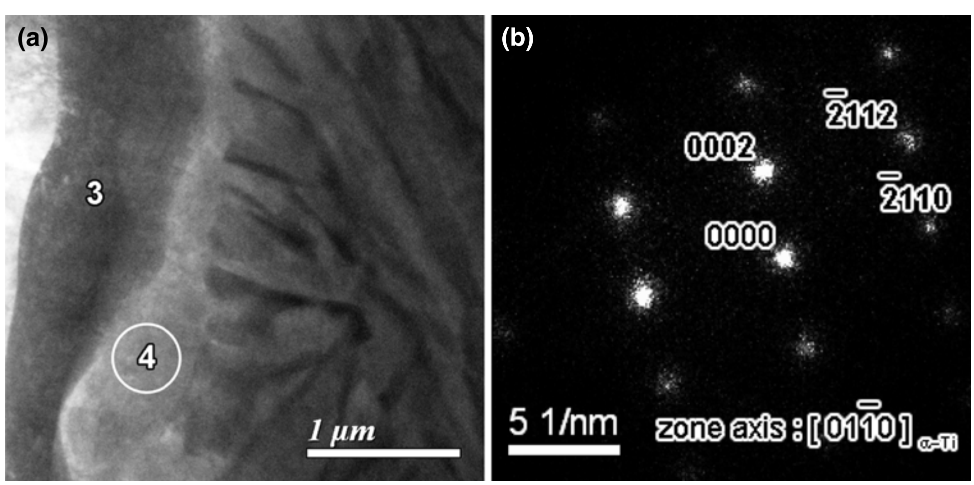
which 1 and 2 represent the Ti-rich matrix and $CuTi_2$ lamina, respectively. Figure 3(c) is the CBDP of area 2 shown in Figure 3(b). From Figure 3(c), the phase is identified as body-centered-tetragonal $CuTi_2$ intermetallic phase with the zone axis of $[331]_{CuTi2}$. Figure 3(d) displays the SADP of the Ti-rich matrix (marked by 1 in Figure 3(b)), and it is identified as the face-centered-cubic (fcc) twin with the zone axis of $[011]_{fcc}$.[13] A dimensionally induced polymorphic phase transition from a hcp to a fcc structure during the preparation of the TEM specimen by using ion miller was reported for Ti layers in Ti/Al, Ti/Ag, Ti/Ni, Ti/Zr, and Ti/Co multilayered structures, but Ti with an fcc structure was not observed in the TEM samples prepared by twin-jet electropolishing.[14,15] Therefore, the occurrence of fcc titanium observed in Figure 3(d) is considered as an artifact resulting from the ion milling of TEM thin foils.

Figure 4(a) shows a TEM BF image of the interface between the BAg-8 braze and the interfacial eutectoid. The EDX results, as shown in Figure 4, indicate that the continuous layer marked by 3 is $CuTi_2$ and that marked by 4 is α-Ti. The SADP taken from area 4 in Figure 4(a), as shown in Figure 4(b), is identified as the $[01\bar{1}0]_{\alpha-Ti}$ zone of the hcp structure. This α-Ti layer cannot be distinguished easily in Figure 2. The morphologies of the interfacial $CuTi_2$ and α-Ti layers are different from those of the interfacial eutectoid due to different forming mechanisms. The $CuTi_2$ and α-Ti layers shown in Figure 4 result from the solidification of the Cu/Ti-rich melt, and the interfacial eutectoid is caused by the solid-state transformation of β-Ti upon cooling of the specimen.

From the results of Figures 2 through 4, the presence of the phase sequence in the CP-Ti/BAg-8 joint heated at 1123 K (850 °C) for 300 seconds is CP-Ti(α-Ti), interfacial α-Ti/$CuTi_2$ eutectoid, α-Ti(Cu), $CuTi_2$, CuTi, Cu_4Ti_3, Cu_4Ti, and Ag-rich matrix. Similar results are obtained for the specimen heated at 1073 K (800 °C) for 300 seconds except for the lack of the interfacial α-Ti/$CuTi_2$ eutectoid.

According to Figure 1, the CP-Ti substrate is completely wetted by BAg-8 joined at 1123 K (850 °C) in 60 seconds. This result is superior to the substrate heated at 1073 K (800 °C). For the specimen tested at 1123 K (850 °C), both interfacial reactions and lower melt viscosity contribute to the wetting between the braze melt and CP-Ti substrate. The reactive wetting of the BAg-8 melt on the CP-Ti substrate results in the formation of the interfacial Cu-Ti reaction layers for both testing temperatures (Figure 2). An eutectoid layer of 10 μm in thickness is observed in the specimen heated at 1123 K (850 °C) (Figure 2(b)), but there is no interfacial eutectoid for the specimen heated at 1073 K (800 °C) (Figure 2(a)). Depletion of Cu content from the molten braze into the CP-Ti results in the formation of the β-Ti phase alloyed with Cu at 1123 K (850 °C), which is much higher than the eutectoid temperature (1063 K (790 °C)) of Ti-Cu_2Ti.[9] The β-Ti is alloyed with a large amount of Cu at 1123 K (850 °C), and the interfacial eutectoid layer is formed once the specimen cools to room temperature. In contrast, insufficient β-Ti is formed for the specimen tested at 1073 K (800 °C), which is slightly higher than the eutectoid temperature of Ti-Cu_2Ti. Limited Cu is dissolved in the α-Ti substrate at 1073 K (800 °C); therefore, there is no interfacial eutectoid layer after cooling the specimen to room temperature.

Because Cu is an eutectoid type of β stabilizer for CP-Ti, β-Ti is stabilized by alloying Cu from molten BAg-8 above 1063 K (790 °C). Diffusion of Cu from the Cu/Ti-rich melt into the CP-Ti substrate stabilizes the β-Ti,



Location (phase)	Ag	Cu	Ti
3 ($CuTi_2$)	5.2	28.5	66.2
4 (α-Ti)	0.0	2.9	97.1

Fig. 4—TEM micrograph, selected-area diffraction pattern, and chemical analyses of the interface between BAg-8 braze and interfacial eutectoid: (*a*) BF and (*b*) SADP of area 4 in (a).

and the wetting of the β-Ti is also significantly enhanced by alloying Cu in the β-Ti substrate at 1123 K (850 °C). Accordingly, the Ti substrate alloyed with the Cu ingredient of the BAg-8 braze contributes to the wetting of CP-Ti. On the other hand, the equilibrium solubility of Cu in α-Ti is about 1.6 at. pct, which is much lower than that of β-Ti, say, 13.5 at. pct.[9] Limited Cu alloyed in α-Ti results in inferior wettability of the BAg-8 braze on the CP-Ti substrate at 1073 K (800 °C), in which the wetting of CP-Ti only depends on the reactive wetting and lacks alloying effect. Therefore, the presence of an interfacial eutectoid layer transformed from β-Ti is a crucial indicator in the wetting of a CP-Ti substrate using the BAg-8 braze.

To summarize, interfacial reactions and the wettability of a BAg-8 braze on a CP-Ti substrate using infrared heating were evaluated and examined. Reactive wetting of the BAg-8 braze on the CP-Ti substrate is achieved at 1073 K (800 °C). The presence of interfacial Cu-Ti intermetallic layers results from the reactive wetting of the BAg-8 braze on the CP-Ti substrate. Increasing the test temperature from 1073 K to 1123 K (800 °C to 850 °C) results in great improvement of the wettability on the CP-Ti substrate. An interfacial eutectoid layer of 10 μm in thickness is observed in the specimen joined at 1123 K (850 °C). Diffusion of Cu from the Cu/Ti-rich melt into the CP-Ti substrate stabilizes the β-Ti at 1123 K (850 °C), and the β-Ti transforms into an interfacial eutectoid upon cooling to room temperature. Interfacial reactions, alloying effect, and lower melt viscosity contribute to the wetting of BAg-8 on the CP-Ti substrate at 1123 K (850 °C).

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