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Infrared Heat Treatment of Ti-6Al-4V With Electroplated Cu

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The objective of this study is to investigate an innovative infrared (IR) technique to enhance adhesion of electroplated copper (Cu) on Ti-6Al-4V without dichromate dipping. The ultimate goal is to develop a Cu coating process on Ti-6Al-4V without hazardous hexavalent chromium (Cr) solution treatments. Cu coatings of around 50 μm were electroplated on Ti-6Al-4V specimens at a current density of 0.03 A/cm^2 in an acidic Cu solution. To improve adhesion of coatings, IR heat treatments were performed on the Cu-coated samples at different temperatures and durations: 860 °C for 600 s and 875 °C for 20-120 s. This process was accomplished in an attempt to replace the use of dichromate dipping before electroplating. For samples heat treated at 860 °C, no bonding existed, even after 600 s. It is believed that solid-state diffusion prevailed at 860 °C and that 600 s was not enough for sufficient diffusion to occur. Adhesion was poor when samples were heat treated at 875 °C for 20 s. Excellent adhesion was observed when the heat treatment holding time was increased to 40 s. For 90 s, the surface appearance of coatings partially changed from Cu-colored to a grayish color. There was no Cu left on the surface after a 120 s heat treatment. From optical microscopic observations on sample cross sections, an interlayer between the Cu and Ti-6Al-4V formed when heat treated at 875 °C for 40 s and longer. The interlayer thickness increased as the holding time increased, until depletion of Cu. The sheet resistivity of coated specimens was on the order of pure Cu for samples heat treated at 875 °C and less than 90 s. During the 875 °C heat treatment, the following occurred: solid-state diffusion of Cu in Ti-6Al-4V, formation of eutectic solutions, dissolution of Cu and Ti-6Al-4V into the liquid phase, and the formation of intermetallic compounds. The lowest eutectic temperature of 875 °C played a key role in this innovative process of Cu coating on Ti-6Al-4V.

Keywords infrared processing, intermetallic compounds, sheet resistivity, Ti-6Al-4V

1. Introduction

Titanium (Ti) and Ti alloys are excellent candidates for aerospace applications, owing to their high strength-to-weight ratio and excellent corrosion resistance.[1] Coatings on Ti and Ti alloys are used to improve wear resistance, oxidation resistance, lubricity, or electrical conductivity. However, the thin oxide layer present on the surface of Ti and Ti alloys causes poor adhesion of coatings. Proper surface cleaning and activation before coating or postplating heat treatment are used to improve the adhesion strength. Plating of hard chromium (Cr) or electroless nickel (Ni) on Ti and Ti alloys are most widely used for wear-resistance applications. For these coatings, heat treatment at 700 °C was used to improve the adhesion of hard Cr coatings and Ti substrates,[2] and post-plating heat treatment at 480 °C was reported to improve adhesive strength of Ni coatings on Ti resulting from diffusion of Ni into Ti and vice versa.[3] In another aspect, it has been reported that a thin film of the intermetallic Ti_2Cu compound on Ti alloys provides better corrosion resistance to acids and fluorides and can be used for corrosive protection of Ti equipment.[4] Copper (Cu) coatings on Ti and Ti alloys have also been used to provide lubricity and electric conductivity of Ti wires.[5] It was observed that if the Cu layer is too thick, adhesion is poor. To obtain the adhesive strength, Ti and Ti alloys for Cu electroplating are pickled in a solution of 25% HF and 75% HNO_3 until red fumes are evolved; then the alloys are rinsed and activated at 82-100 °C in a solution of $Na_2Cr_2O_7{\cdot}2H_2O$ (250 g/L) and 4.8% HF for 20 min.[5] Dichromate dipping is used to improve the adhesion of coatings; however, this method is not advisable because Cr (VI) compounds can increase the risk of lung cancer. A post-plating heat treatment can be an alternative to dichromate dipping. In this study, the authors investigate the adhesion and surface electrical conductivity of electroplated Cu without dichromate dipping on Ti-6Al-4V after infrared (IR) heat treatment.

2. Experimental

2.1 Sample Preparation

A Ti-6Al-4V rod, 25.4 mm in diameter, was cut to a thickness of 5 mm. The Ti-6Al-4V disks for Cu electroplating were pickled in a solution of 25% HF and 75% HNO_3, until red fumes were evolved; then the disks were rinsed and ultrasonically cleaned in deionized (DI) water. After cleaning, 50 μm Cu layers were electroplated onto the Ti-6Al-4V disks in a sulfate bath ($CuSO_4{\cdot}5H_2O$, 200-240 g/L; H_2SO_4 45-75 g/L) at a current density of 0.03 A/cm^2, using a pure Cu rod as the

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anode. For comparison, 50 μm Cu foils were cut to 25.4 × 25.4 mm and placed on Ti-6Al-4V samples to replace electroplated Cu for heat treatment.

2.2 Heat Treatment

Figure 1 shows the graphite fixture used for heat treatment. In this fixture, the Ti-6Al-4V disk (with 50 μm electroplated Cu or 50 μm Cu foil) was held with two graphite disks and a chromel-alumel thermocouple was placed between the graphite disks and the specimen. During the entire heat-treatment process, argon (Ar) was purged through the heating chamber at 6 L/min to prevent oxidation. Typically, the temperature of the specimen was brought to the designated heat-treatment temperature in less than 60 s and then the samples were held at that temperature for various lengths of time before the power was terminated. After heat treatment, the specimen was cooled in flowing Ar. The cooling rate was rapid because the furnace wall was cold during infrared (IR) heating and only the assembly was heated to the desired joining temperature. Figure 2 illustrates the typical IR heating cycles. For comparison, typical heating cycles of induction heating and resistance furnace heating were also included. The entire assembly was IR heat treated at 875 °C for 20, 40, 60, 75, 90, and 120 s, and at 865 °C for 10 min.

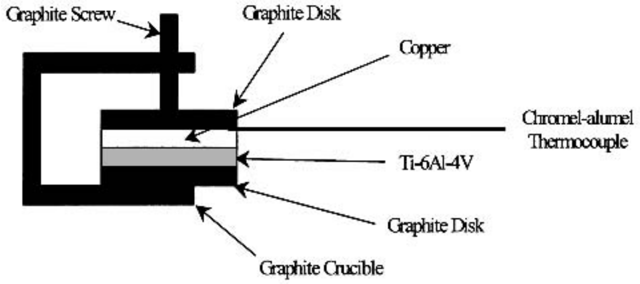

Fig. 1 The graphite fixture used in this study

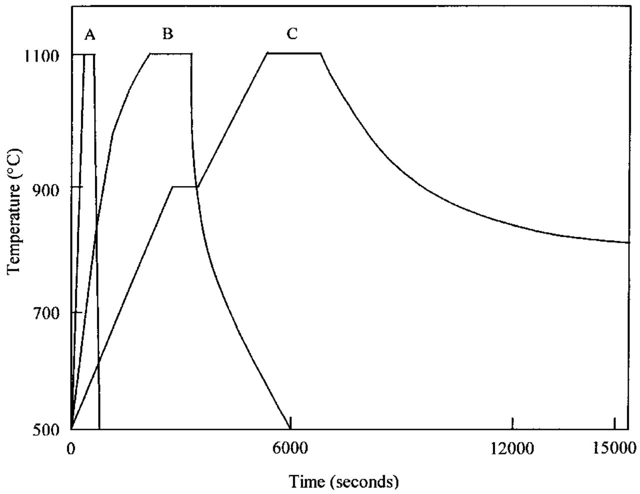

Fig. 2 Heating cycles. A: typical infrared heating cycle; B: induction heating; and C: resistance furnace heating

2.3 Characterizations and Analysis

Heat-treated specimens were cut through the reaction interlayer area, mounted, and polished for cross-sectional area examinations with an optical microscope. Also, the mounted specimens were etched in a solution with 0.1% HF and 0.3% HNO_3 to reveal the microstructure. The sheet resistivity of the Cu films was measured by a Cascade Microtech (Beaverton, OR) C4S-64/5S four-point probe, with a spacing of 0.159 cm between the probes. The sheet resistivity was calculated by

$$\rho = \frac{\pi}{\ln 2} \frac{V}{I} t \tag{Eq 1}$$

where t is the thickness of the film, V is the output voltage, I is the input current, and ρ is the sheet resistivity of films.

Table 1 Appearance and Adhesion of Ti-6Al-4V/Cu Foil and Ti-6Al-4V/Electroplated Cu Layer After Infrared Treatment

Heat Treatment Condition		Ti-6Al-4V With 50-μm Electroplated Cu		Ti-6Al-4V With 50 μm Cu Foil	
Temperature	**Time**	**Appearance**	**Adhesion**	**Appearance**	**Adhesion**
As electroplated		Cu	Very poor	…	…
865 °C	600 s	Cu	Poor (a)	Cu	Poor (a)
875 °C	20 s	Cu	Strong	Cu	Strong
875 °C	40 s	Cu	Strong	Cu	Strong
875 °C	60 s	Cu	Strong	Cu	Strong
875 °C	75 s	Cu	Strong	Cu	Strong
875 °C	90 s	Cu/Gray	Strong	Cu/Gray	Strong
875 °C	120 s	Gray	…	Gray	…

(a) Partially bonded

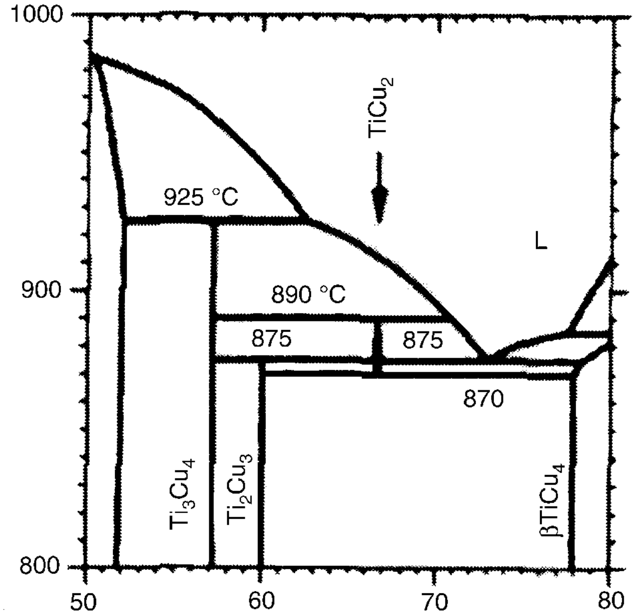

Fig. 3 A portion of the Ti-Cu binary phase diagram near the first eutectic reaction[7]

3. Results and Discussion

3.1 Surface Appearance and Adhesion

Table 1 summarizes the visual examinations of specimens after the IR heat treatment. For specimens with electroplated 50 μm Cu layers, without dichromate dip before electroplating, the adhesion between Cu and Ti-6Al-4V is very strong; thus, Cu coatings could not be peeled off when IR heat treated at 875 °C for 40, 60, and 75 s. The surface retained the Cu color. For the 20 s IR heat treatment, the electroplated Cu is partially bonded to the Ti-6Al-4V disk. The as-peeled Cu and Ti-6Al-4V surfaces showed a color change, indicating that reaction between Cu and Ti-6Al-4V did occur. For 90 s, the surface appearance partially changed to gray. When IR heat treated for 120 s, the entire surface changed to gray, suggesting the depletion of Cu by the eutectic reaction of Ti-Cu at 875 °C (Fig. 3).[7] The heat treatment of Ti-6Al-4V with 50 μm Cu foil showed similar results.

For a few samples with electroplated Cu on Ti-6Al-4V

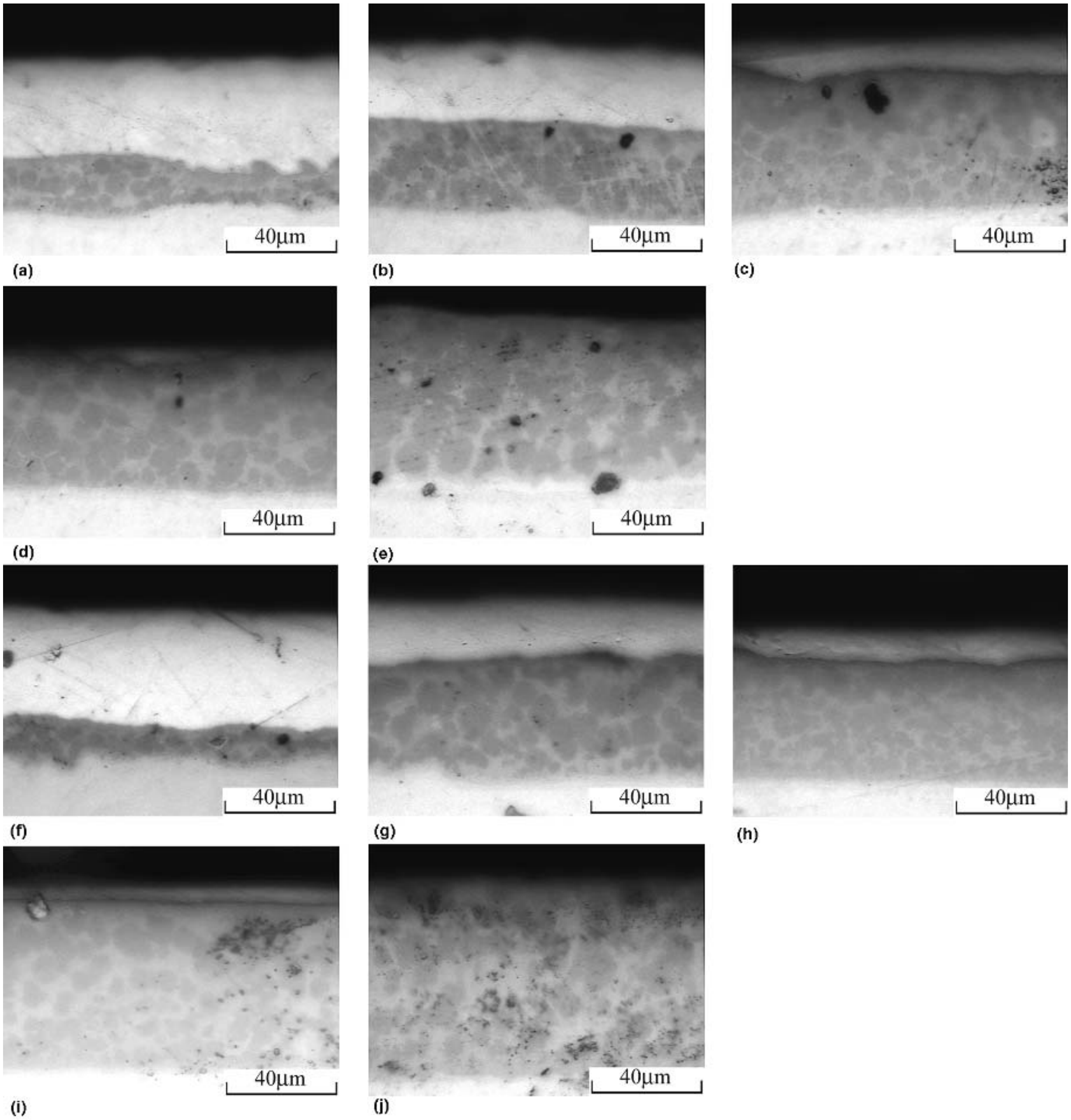

Fig. 4 Optical micrographs of cross section at different heat treatment time. For Ti-6Al-4V with 50 μm electroplated Cu, **(a)** 40, **(b)** 60, **(c)** 75, **(d)** 90, and **(e)** 120. For Ti-6Al-4V with 50 μm Cu foil **(f)** 40, **(g)** 60, **(h)** 75, **(i)** 90, and **(j)** 120. In (a)-(d), the remained copper is on top and the middle is the reaction interlay.

disks, and heat treated without the two graphite disks holding them together ("clipping"), bonding was poor; and Cu spalled off even after IR heat treatment for 120 s at 875 °C. On the other hand, in a previous study, the electroplated Cu coatings with dichromate dipping prior to plating showed excellent adhesion before and after heat treatment at 860 °C.[8] Poor bonding for samples heat treated without clipping indicates limited (or no) reaction between Cu and Ti-6Al-4V due to the improper contact of electroplated Cu and Ti-6Al-4V resulting from the thermal mismatch of the Cu and Ti-6Al-4V. It was reported that the coefficient of thermal expansion (CTE) of Cu and Ti-6Al-4V are 16.5×10^{-6}/°C and 8.5×10^{-6}/°C, respectively.[9] The CTE difference between these two metals is so large that without proper holding, the differential thermal expansion causes misalignment between layers within each sample.

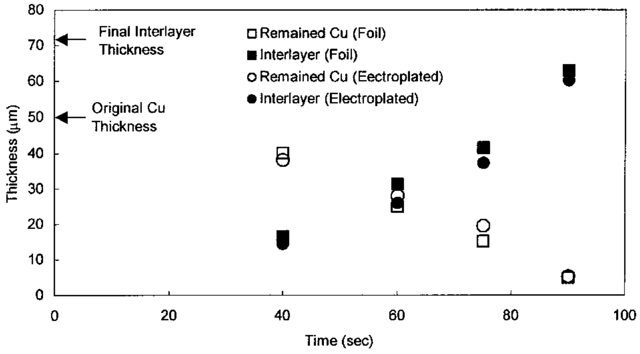

Fig. 5 The remained Cu and interlayer thickness

3.2 Cross-Section Observation

Figure 4 shows the cross-section optical micrographs of coated Ti-6Al-4V IR heat treated at 875 °C for 40, 60, 75, 90, and 120 s. The remaining Cu layer thickness was reduced and the interlayer thickness grew as the heat-treatment time increased. Image analysis carried out by ImagePro (Silver Spring, MD) V4.1.0.0, Media Cybernetics shows the average thickness of remaining Cu and the interlayer thickness varied linearly with the heat-treatment time (Fig. 5). The remaining Cu thicknesses were 38, 28, 19, and 5 µm, while the interlayer thicknesses were 14, 26, 37, and 60 µm for 40, 60, 75, and 90 s, respectively. Copper was completely depleted for samples heat treated at 870 °C for 120 s, and the thickness of the interlayer reached ~71 µm. For comparison, when using 50 µm Cu foils, the heat-treated samples showed similar thicknesses for the remaining Cu and interlayer.

From the cross-section optical micrographs in Fig. 4, there are two distinguishable phases in the joint zone, and it is obvious that the interlayer is the product of solidification of liquid

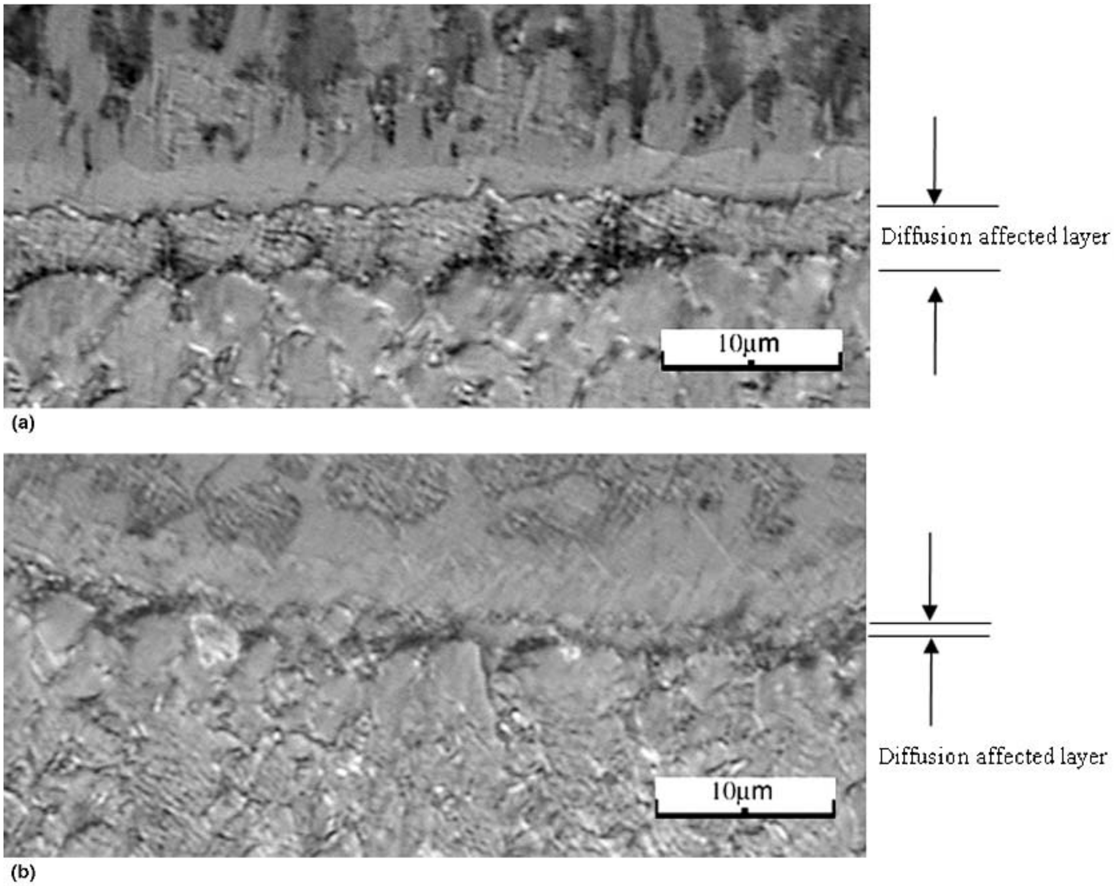

Fig. 6 High-magnification optical micrographs at the interface of reaction interlay and base material. **(a)** 120 and **(b)** 90

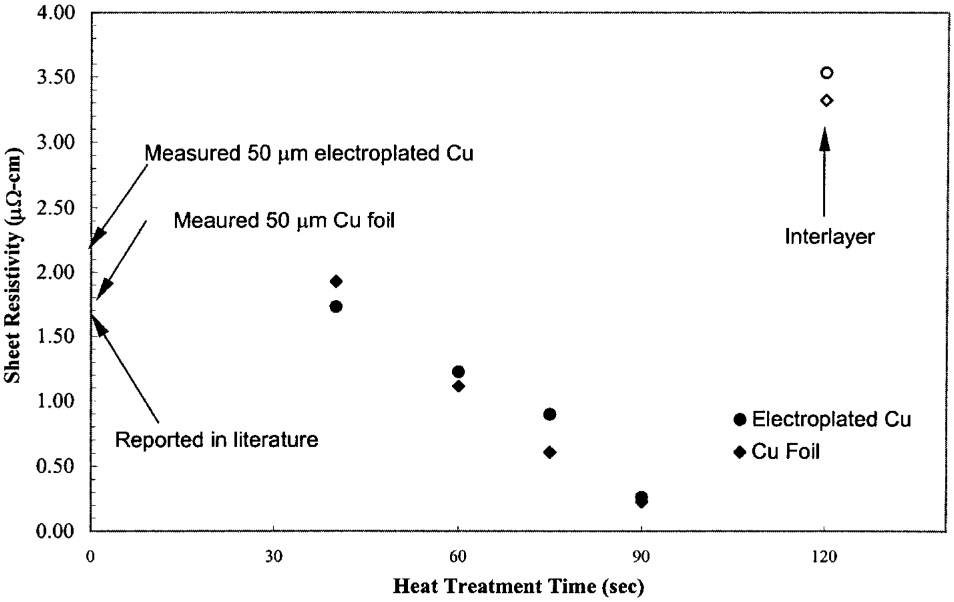

Fig. 7 The sheet resistivity of the remaining Cu and interlayer

after the IR power was turned off. According to the Ti-Cu phase diagram, solidification occurs in the following manner,

$$\text{Liquid} \rightarrow \beta\text{TiCu}_4 + \text{TiCu}_2 \qquad \text{(Eq 2)}$$

This finding suggests that the two phases in the joint zone are βTiCu$_4$ and TiCu$_2$, which may be verified with other analysis techniques.

Figure 6 shows that a distinct diffusion layer of Cu into Ti-6Al-4V is observed with a high-magnification optical microscope for a specimen heated at 875 °C for 120 s. Such diffusion layers are not clear for 90 s samples. This observation indicates that the dissolution rate of Ti-6Al-4V into the liquid phase is much faster than the diffusion of Cu from the liquid into Ti-6Al-4V before the depletion of Cu occurs. That is, the dissolution of solid Ti-6Al-4V or Cu into the liquid was predominant, and the solid-state diffusion was limited at 875 °C before the depletion of Cu.

3.3 Resistivity of Remained Cu

The literature reports sheet resistivities of 1.673 and 167.5 μΩ · cm for Cu and Ti-6Al-4V.[9] The sheet resistivities measured for 50 μm electroplated Cu and 50 μm Cu foil are 2.280 and 1.749 μΩ · cm, respectively. The reason for higher sheet resistivity of electroplated Cu is the residual stress after electroplating. Equation 1 is used for the calculation of sheet resistivity of conducting thin film on a nonconductive substrate. Because the sheet resistivity of Ti-6Al-4V is 100 times greater than that of Cu, Eq 1 was treated as if the Ti-6Al-4V were an insulator. Figure 7 shows the sheet resistivity of the remaining Cu and interlayer. The interlayer has the sheet resistivity of 3.53 μΩ · cm. The sheet resistivity of the remaining Cu decreases as the heat-treatment time increases, due to relaxation of residual stress in Cu from the heat treatment and the effect of interlayer, which has lower resistivity and cannot be treated as an insulator.

3.4 Proposed Reaction Mechanism Between Cu and Ti-6Al-4V

From optical microscope observations, the following mechanism of reaction between Cu and Ti-6Al-4V is proposed.

1. When the IR furnace power is on, the solid-state interdiffusion of Ti and Cu increases as the temperature increases. However, the solid-state diffusion is limited due to the low diffusivity of Ti in Cu or Cu in Ti (6.59×10^{-10} cm^2/s at 875 °C)[9] and the rapid heating rate of IR furnace (less than 60 s from room temperature to 875 °C).
2. A very limited amount of intermetallic, Ti$_2$Cu, TiCu, TiCu$_2$, and βTiCu$_4$, is formed due to the solid-state diffusion.
3. As soon as the TiCu$_2$ and βTiCu$_4$ formed, and the temperature reached 875 °C, the following reaction takes place:

$$\beta\text{TiCu}_4 + \text{TiCu}_2 \rightarrow \text{Liquid} \qquad \text{(Eq 3)}$$

4. After the liquid forms, the dissolution of solid into liquid dominates the process, and it is much faster than solid-state diffusion. The liquid provides strong bonding between Cu and Ti-6Al-4V after the solidification.
5. If the heat-treatment time is too short (20 s), the amount of liquid is not enough to form an interlayer conducive to strong bonding. Therefore, the adhesion is poor. For longer times (40-75 s), the Cu is not completely consumed when the IR furnace is turned off, and the specimens still have Cu remaining on the surface. The solidified liquid provides the bond between the remaining Cu and Ti-6Al-4V. If the time is increased further (90 or 120 s), Cu is exhausted.
6. When the IR furnace power is terminated, the liquid solidifies into TiCu$_2$ and βTiCu$_4$, which can be observed in the

optical photomicrographs. Limited solid-state diffusion of Cu from the interlayer into Ti-6Al-4V or Ti/Al/V from the interlayer into the Cu.

It is to be noted that the actual temperature for the reaction shown in 3 can be lower than 875 °C (for Ti-Cu), due to the presence of Al and V in the base material.

4. Conclusions

The conclusions from this study are summarized as follows:

- A process of providing a strongly adhering Cu layer on Ti-6Al-4V was developed without dichromate dipping.
- For the sample heat treated at 875 °C for 20 s, adhesion is poor. For a longer holding time, sufficient liquid formed during IR treatment, and strong bonding developed between the remaining Cu layer and Ti-6Al-4V.
- Adhesion is poor for the specimens heat treated at 860 °C for 600 s, due to slow solid-state diffusion with respect to the rapid heating rate of IR furnace.
- Adhesion of Cu onto Ti-6Al-4V is mainly improved by an interlayer that solidified from the liquid phase at 875 °C.
- The resistivity of remaining Cu is on the order of that for pure Cu.

References

1. R.R. Boyer: "An Overview on the Use of Titanium in the Aerospace Industry," *Mater. Sci. Eng.,* 1996, *A213,* pp. 103-14.
2. C.G. John: "Electroplated Coating of Titanium for Engineering Applications," in *Proceedings International Conference, Designing with Titanium,* Institute of Metals, London, UK, 1986, pp. 160-65.
3. M. Thomas, "Plating on Titanium," *Plat. Surf. Finish.,* May 1983, pp. 96-98.
4. T.D. Uzunov, S.P. Stojanov, and S.I. Lambov: "Thin Films of Intermetallic Cu/Ti Compounds and Their Possible Uses," *Vacuum,* 1999, *52,* pp. 321-25.
5. A. Bloyce, P.H. Morton, and T. Bell: "Surface Engineering of Titanium and Titanium Alloys," *ASM Handbook* Vol. 5, *Surface Engineering,* ASM International, Materials Park, OH, 1994, pp. 845-66.
6. D.H. Wilson: Surface Cleaning, Finishing, and Coating, Vol. 5, *Metals Handbook,* 9th ed., American Society for Metals, Metals Park, OH, 1982, pp. 650-68.
7. J.L. Murray: *Phase Diagrams of Binary Titanium Alloys,* ASM International, Materials Park, OH, 1987.
8. J.H. Li and R.Y. Lin: *Infrared Heat Treatment of Copper Coated Ti-6Al-4V,* ASM International, Surface Modification, Materials Park, OH, 2002.
9. C.J. Smithells: *Metals Reference Book,* ASM International, Materials Park, OH, 1992.