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Interfacial Reactions of Titanium and Aluminum during Diffusion Welding

A preliminary investigation evaluated the feasibility of joining laminated composites using cold-roll bonding followed by diffusion welding

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ABSTRACT. Multilaminated composites of titanium and aluminum, in the correct atomic ratios of Ti:Al for γ-TiAl, have been prepared by cold-roll bonding. The effects of reaction annealing temperature, time and atmosphere on the diffusion welding characteristics of titanium and aluminum have been studied. The resulting intermetallics, which formed at the Ti/Al interface, were characterized using light microscopy and scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer system. The hardness of the samples was evaluated by Vickers microhardness testing. Results of this study show the cold-roll-bonded multilaminated composites of titanium and aluminum can produce the intermetallic compound $TiAl_3$ in relatively short times at low reaction annealing temperatures. Good metallurgical bonds were also formed with diffusion welding. Preliminary investigation of the diffusion process between titanium and aluminum has been performed.

Introduction

As a class of materials, titanium aluminide intermetallic compounds are of technological interest because they are light in weight (low density) and maintain high strengths at elevated temperatures (>900°C). Limited breakthroughs in cost-effective processing techniques for these intermetallics (Refs.1–2) and the difficulty in fusion welding of Ti_3Al and TiAl (Refs. 3–5) are partially responsible for the lack of their widespread use in industry. Diffusion welding has emerged as an effective and potential joining process for several dissimilar or multiphase materials because it eliminates problems such as cracking, distortion and segregation usually associated with liquid-phase welding of these materials (Refs. 6–8).

To date, previous researchers have studied the mechanics of cold bonding in general for Ti and Al (Refs. 9–10). Others have studied the diffusion of titanium and its alloys containing various concentrations of aluminum (Refs. 11–18). However, the complete technology to develop titanium aluminides by the route of cold roll bonding of multilaminated Ti-Al composites followed by diffusion reaction at high temperature has not been investigated.

Multilaminated composites of titanium and aluminum have a larger diffusion surface than one- or two-part diffusion couples. This is more favorable for interfacial reactions during the diffusion welding process. Thus, cold-roll bonding of multilaminated Ti/Al composites followed by diffusion annealing is an ideal processing method for producing gamma titanium aluminide (γ-TiAl). This study investigates the interfacial reactions that occur when cold-roll-bonded multilaminated composites of titanium and aluminum are subjected to diffusion welding.

KEY WORDS

Interfacial Reactions
Diffusion Welding
Laminated Composites
Titanium Aluminide
Cold Roll Bonding
Annealing
Intermetallics

Experimental Procedure

Pure titanium (99.9%) and pure aluminum (99.0%) foils 0.074 and 0.070 mm thick, respectively, were employed. The foils were roughened with a wire brush, cleaned ultrasonically in methanol and then cut into 5 x 5-cm squares. Alternating layers of titanium and aluminum foils were stacked one on top of the other to form a "sandwich" of titanium and aluminum. As shown by Fig. 1, 17 layers of titanium and aluminum were stacked with aluminum on both ends. For every diffusion couple, the atomic ratio of Ti:Al to produce TiAl was obtained by the foil thickness.

The multilaminated Ti/Al sandwiches

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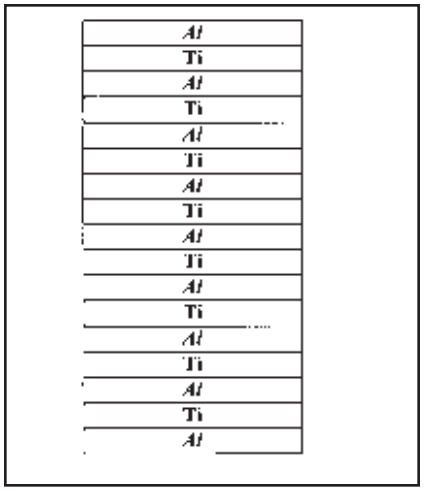

Fig. 1 — Schematic of sandwich structure of titanium and aluminum used for cold-roll bonding.

were fed through a rolling mill at room temperature to obtain samples with 56% reduction in thickness. The samples were sealed in quartz tubing and annealed in a furnace at two temperatures, 660 and 680°C, for times ranging from 0.5 to 4.0 h. The temperature of the furnace was controlled within ±1°C. After diffusion was allowed to take place, the samples were mounted, polished and etched using conventional metallographic procedures.

The concentrations of aluminum and titanium were determined as a function of position using a Philips XL30 scanning electron microscope (SEM) operated at 20 kV and equipped with an energy-dispersive X-ray spectrometer (EDS) system. The interaction volume was less than 0.5 µm (approximate range 0.25–0.4 µm) and no standards were used in the SEM/EDS analysis for determining the semiquantitative values. The concentration was determined for 20 points on each specimen with a distance of 1.02 µm between each point. The concentrations were entered as a function of distance into *BMD Pro Version 3.3* (Ref. 19) to analyze the diffusion of titanium in aluminum and the diffusion of aluminum in titanium. *BMD Pro* is a diffusion profiler software package that uses the Boltzmann-Matano method to determine the diffusivity (D) based on Fick's second law. Graphical integration must be used to determine D; thus, the solution to Fick's second law for the Boltzmann-Matano method is (Ref. 20)

$$D = -\frac{1}{2t}\left[\frac{\partial N_A}{\partial x}\right]^{-1}_{N_{A_1}} \int^{N_A} x dN_A \qquad (1)$$

where D = diffusivity or diffusion coefficient, t = time of diffusion, N_A = composition or atom fraction (molar fraction) at a distance x from the Matano interface, N_{A1} = concentration of one side of the diffusion couple at a point away from the interface where the composition is constant, X = distance, $\left[\frac{\partial N}{\partial x}\right]^{-1}$ is the inverse slope and $\int_{N_{A_1}}^{N_A} x dN_A$ is the integral.

Once the concentration (in molar fraction, N) as a function of distance (x) was entered into the software, *BMD Pro* plotted the data to make a composition profile (N vs. x). The user then found the position where the total fluxes of the two atomic species were equal. This is called the Matano interface, which is the position where the area above the curve of the concentration profile and the area below are equal. The software is interactive and informs the user when the correct position is located that denotes the Matano interface, as defined in chapter 12 of Reed-Hill and Abbaschian (Ref. 20), and uses this interface as the origin of the x coordinate. The software then prompts the user to specify a concentration of interest so the inverse slope at the concentration of interest can be calculated. In the next step, the program finds the value of the integral for the specified upper boundary. The diffusion coefficient was then computed from the values determined for the inverse slope and the integral.

The activation energy was determined using the Arrhenius equation (Ref. 20)

$$D = D_0 e^{-Q/RT} \qquad (2)$$

where D = diffusivity, D_0 = frequency factor, Q = activation energy, R = gas constant and T = temperature in K.

The values for D determined by *BMD Pro* for the two different temperatures were used to solve for Q. Since the Boltzmann-Matano method assumes D is a function of composition, Q was determined for several values of D that corresponded to various compositions.

Each specimen was also characterized before and after annealing using light microscopy. The hardness was determined using Vickers microhardness testing. The reported Vickers hardness numbers (VHN) correspond to the average values of six VHN measurements — three values from the aluminum-rich regions and three from the titanium-rich regions.

Results and Discussion

Microstructural Characterization

The light micrographs of the multilaminated Ti/Al samples both before and after annealing are shown in Fig. 2. The cold-roll-bonded samples exhibited good bonding with fairly straight lines at the interface between the titanium and aluminum foils — Fig. 2A. As a result of diffusion, the titanium-rich layers became thinner and the aluminum-rich

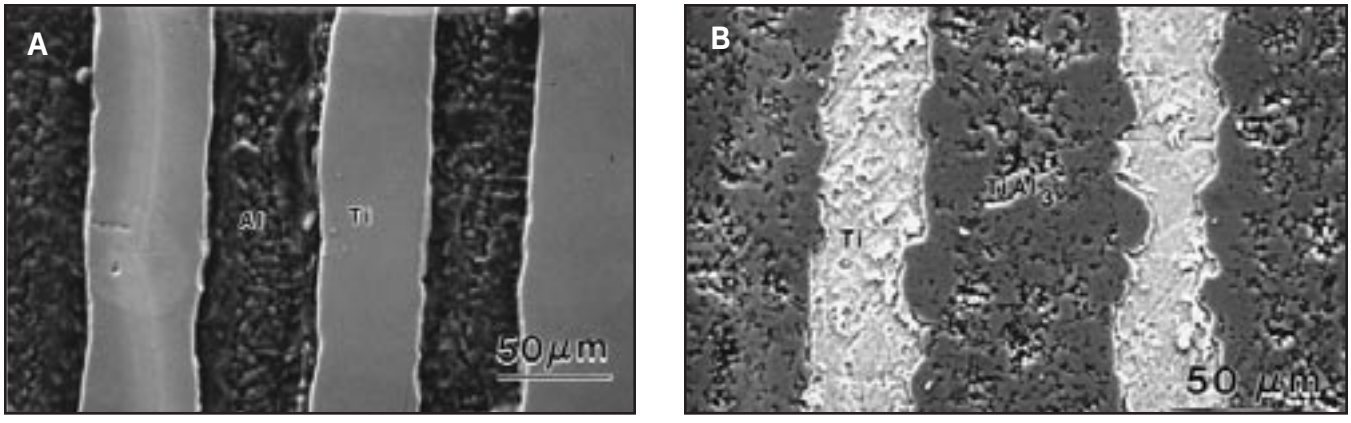

Fig. 2 — SEM secondary electron images of specimens. A — Before annealing; B — after annealing at 660°C for 4 h.

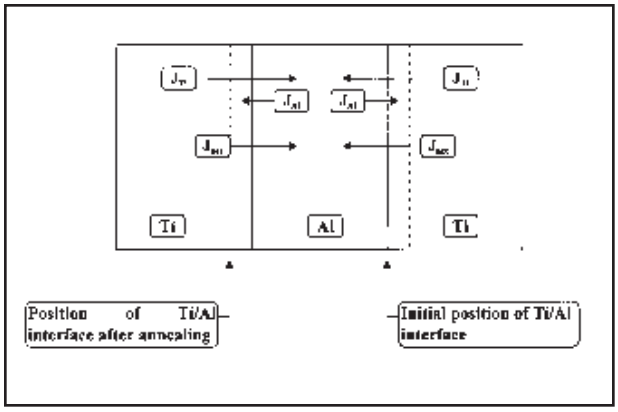

Fig. 3 — A schematic representation of the net flux of atoms and interface movement during diffusion of Ti and Al.

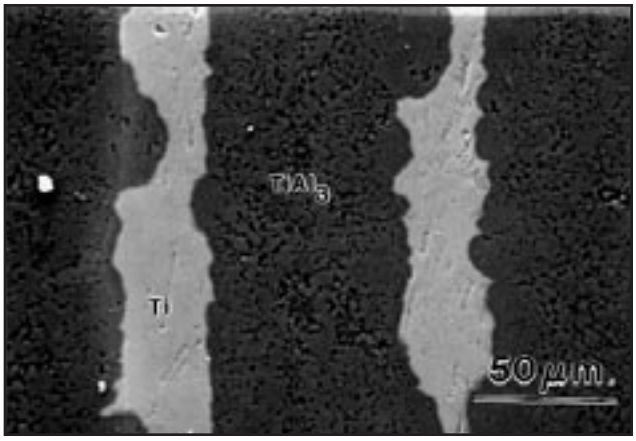

Fig. 4 — SEM secondary electron image showing the morphology of samples annealed at 680°C for 4 h.

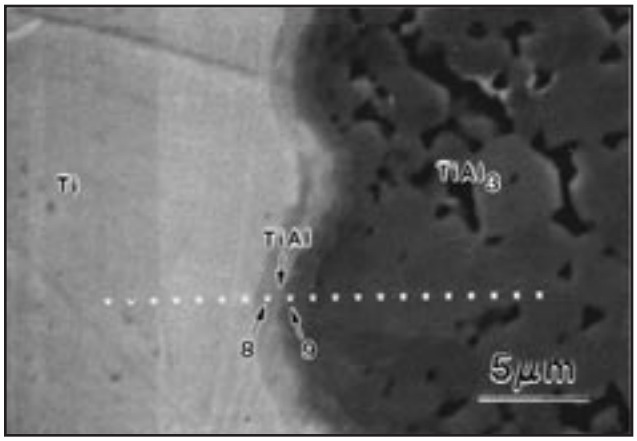

Fig. 5 — Data points used to determine the amounts of Ti and Al utilizing SEM/EDS. Representative sample of the 660°C, 4-h reaction anneal is shown.

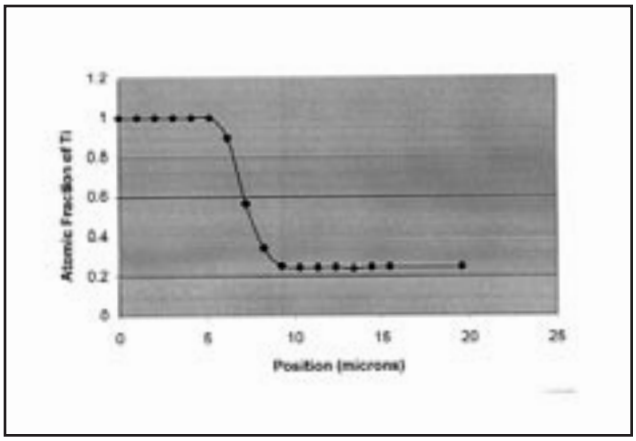

Fig. 6 — Composition profile for samples annealed at 660°C for 4 h.

layers expanded with increasing annealing temperature and time — Fig. 2B. This is believed to be due to the fact titanium atoms diffuse much faster than the aluminum atoms. In accordance with the Kirkendall effect, as evident from the void formation in the Al-rich layers, the net flux of atoms (J_{net}) was toward the Al-rich layers, which resulted in the interface moving toward the Ti-rich layers and away from the Al-rich layers. This resulted in widening of the Al-rich layers and thinning of the Ti-rich layers, as shown schematically in Fig. 3 and experimentally in Fig. 2B. The phenomenon was more pronounced when the annealing temperature and/or time was increased. The effect of increasing the annealing temperature from 660 to 680°C is illustrated in Figs. 2 and 4. These figures show the specimens for an annealing time of 4 h at the respective temperatures.

SEM/EDS Analysis

All phase identifications in this study were based on EDS data only. Although X-ray diffraction (XRD) and selected-area diffraction (SAD) patterns from transmission electron microscopy (TEM) are, in general, better methods for phase identification, tentative phase identification by EDS was best for this study. With XRD it would be extremely difficult to isolate the ~1.5-μm-thick, intermetallic layers that formed at the interface for identification and to ensure the data was generated from the region of interest. TEM/SAD analysis would also be quite difficult for these specimens since the techniques necessary to achieve thinning at or near the interface are quite tedious even by standard TEM sample preparation methods and would require numerous specimens. The authors are currently considering ways to effectively utilize XRD or TEM/SAD to complement the tentative phase identifications obtained by SEM/EDS analysis. Regardless, the SEM/EDS phase identification technique is sufficient for the scope of the present study since the resulting phases were in accordance with the Ti-Al phase diagram.

The 20 data points from which SEM/EDS data was collected to determine the composition profile across the interface is shown in Fig. 5 for the 660°C, 4-h sample. Similarly, 20 data points were collected for all samples. Only a very thin layer of the intermetallic compound TiAl formed. This occurred between positions 8 and 9 as denoted by arrows in Fig. 5. On the composition profile shown in Fig. 6, this corresponds to the data points occurring at positions of approximately 7 and 8 microns. In Fig. 5, SEM/EDS analysis of positions 1–6 (the first six asterisks) showed no aluminum was detected at these positions after an-

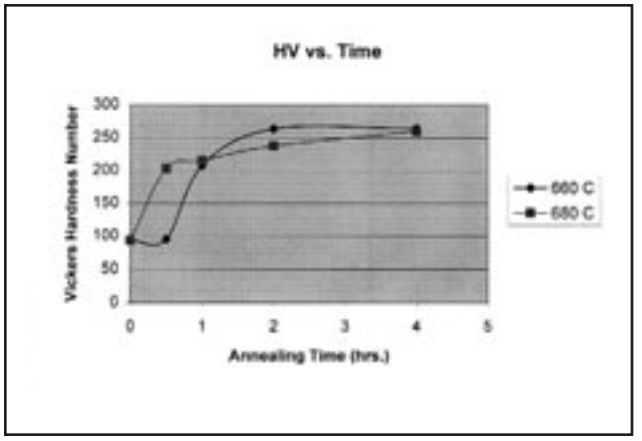

Fig. 7 — Vickers hardness numbers as a function of annealing time.

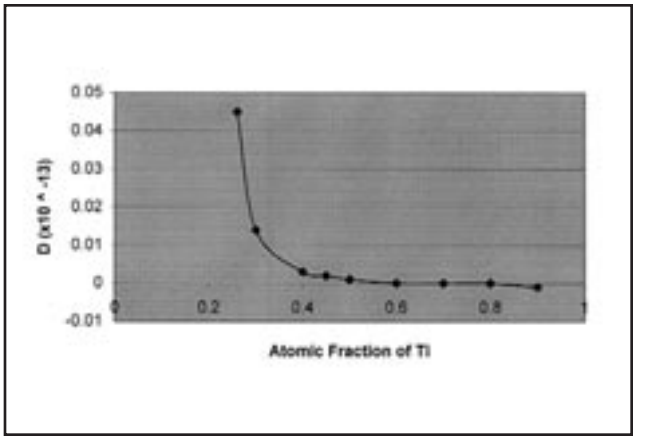

Fig. 8 — Plot of diffusion coefficient as a function of atomic fraction of Ti for samples annealed at 660°C for 4 h.

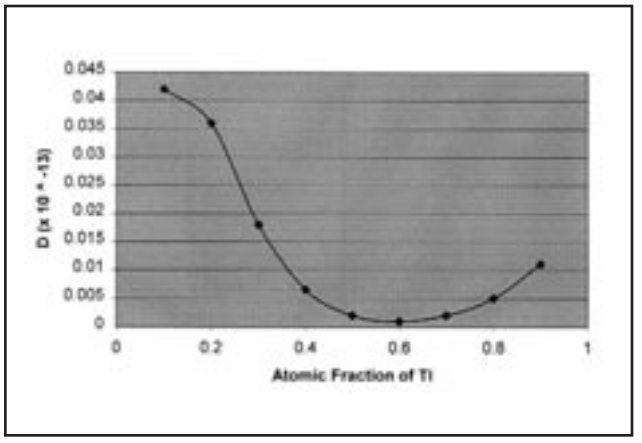

Fig. 9 — Diffusion coefficient as a function of atomic fraction of Ti for samples annealed at 680°C for 4 h.

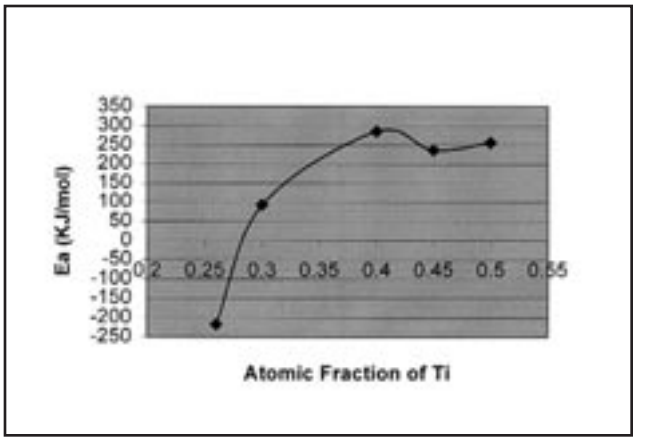

Fig. 10 — Activation energy as a function of atomic fraction of Ti.

nealing. However, the entire aluminum-rich region (starting at the asterisk after position 9 and ending at the last asterisk on the right, points 10–20) contained about 23–25 at.-% of titanium. This is close to the composition for the intermetallic compound $TiAl_3$. Thus, all of the layers that were pure Al prior to annealing were completely transformed into the intermetallic compound $TiAl_3$. These observations support the previously stated belief that titanium diffuses much faster than aluminum.

Hardness Measurements

The Vickers microhardness data of the specimens for different annealing conditions is shown in Fig. 7. The hardness increased as annealing time increased for both annealing temperatures. The hardness of the 660°C specimens was lower than the 680°C specimens up to an annealing time of one hour. After one hour, the hardness of the 660°C specimen increased slightly above the corresponding times for the 680°C specimens. The increased hardness after annealing can be attributed to the formation of the intermetallic compound $TiAl_3$ in the layers that consisted of pure aluminum prior to annealing. Also, the formation of Ti_xAl_y ($x<y$) occurred at the interface, which contributed to the observed increase in hardness as well. Reaction anneals for samples at 660°C or 680°C for 2 h resulted in an average VHN nearly three times greater than that prior to annealing. However, there was no significant difference in hardness between the samples annealed for 2 h and 4 h.

Determination of Diffusion Coefficient, D, and Activation Energy, Q

Figures 8 and 9 show the results of the diffusion coefficients calculated by *BMD Pro* as a function of atomic fraction of titanium. The plots shown are for the 660°C (Fig. 8) and 680°C (Fig. 9) samples annealed for 4 h. The plots show the highest diffusion coefficients occurred for atomic fractions less than 0.3. The activation energy, Q, was calculated for different atomic fractions of titanium using Equation 2. The values for Q were plotted as a function of atomic fraction of titanium, as shown in Fig. 10. The lowest values of activation energy occurred for atomic fractions less than 0.4.

Summary

The intermetallic compound $TiAl_3$ formed easily in the prior aluminum layers at temperatures of 660 and 680°C. The voids formed in the Al-rich layers are Kirkendall porosity formed due to the Kirkendall effect. Near the bond interface, TiAl and other Ti_xAl_y ($x<y$) intermetallic compound layers formed as thin layers and gradually grew with increas-

ing annealing time. From this observation, it can be said TiAl will develop fully upon annealing for longer times. In addition, the process can be accelerated by increasing the amount of cold working prior to and during annealing. Unpublished work by the authors supports this claim. Thus, it is believed the process leads to the complete reaction to produce TiAl from pure Ti and pure Al is as follows:

$$\begin{aligned} Ti/Al &\rightarrow Ti/TiAl/Ti_xAl_y(x<y)/TiAl_3 \\ &\rightarrow TiAl/Ti_xAl_y(x<y)/TiAl_3 \\ &\rightarrow TiAl \end{aligned}$$

Conclusions

A preliminary investigation of the interfacial reactions that occur between titanium and aluminum as a result of cold roll bonding followed by diffusion welding has been performed. The intermetallic compound $TiAl_3$ forms to a much greater extent than the intermetallic compound TiAl. The intermetallic compounds TiAl and Ti_xAl_y (x<y) formed only as very thin (~1.5 μm in thickness) layers at the interface. Based on the present study, it was concluded that longer annealing times and more cold work is required to promote the complete formation of the intermetallic compound TiAl throughout all layers.

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