Interfacial Reaction between Ti-Al Binary Alloys and High Carbon Steel

Yasuhiro Morizono¹, Takateru Yamamuro² and Minoru Nishida¹,*

¹Department of Materials Science and Engineering, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan
²Technical Division, Faculty of Engineering, Kumamoto University, Kumamoto 860-8555, Japan

Diffusion bonding of Ti-Al binary alloys (Ti-10 to 40 mol% Al) to high carbon steel was carried out between 1073 and 1273 K for 0.9 to 8.1 ks in a vacuum, and the effect of the alloy composition on the interfacial microstructures and the bonding strength was investigated. Three regions, which were composed of reaction products with Ti, Al and Fe, a TiC layer, and ferrite, were formed around the interface, regardless of the alloy composition. The thickness of each region changed with an increase in the Al content in the Ti-Al alloy. In general, the TiC layer formed in Ti/steel joints is known to act as a barrier for diffusion of constituent elements across the interface and to inhibit the formation of other reaction products. In this study, the barrier effect of the TiC layer was overcome by the existence of Al. Although the Ti-Al/steel joints showed a relatively high bonding strength of more than 150 MPa in many cases, the joint with Ti-20 mol% Al alloy separated near the interface promptly after bonding treatment at 1273 K for 3.6 and 8.1 ks. The details and the application of the separation phenomenon are discussed.

Keywords: titanium-aluminum alloy, high carbon steel, diffusion bonding, interface separation, TiC, surface modification

1. Introduction

Titanium aluminides (Ti-Al), which are typified by Ti₃Al and TiAl, are expected to be useable as high-temperature structural materials in the aerospace and automobile industries, because they have a low density and a high strength at elevated temperatures. However, their practical uses are limited due to poor ductility at room temperature, low fracture toughness, and poor workability. To overcome these disadvantages, alloy design and control of the microstructures have been studied extensively in relation to the processing techniques used in industrial applications. Joining, which is a fundamental and indispensable technique, has also been examined for the effective utilization of Ti-Al. Ti-Al has been joined to itself and other materials by various joining methods, such as diffusion bonding,°⁻⁵ brazing,°⁵ and electron beam welding.°⁸ In each case, it is important to avoid the formation of brittle phases and defects and to relieve thermal stress at the interface, since these are vital to achieving good bonding characteristics. In particular, Ti and Al have high reactivity, and interfacial reactions are difficult to control.

It is known that a TiC layer formed at the interface in Ti/steel joints acts as a barrier for diffusion of the constituent elements into each parent material and inhibits the formation of intermetallic compounds like FeTi and Fe₂Ti.°⁻¹¹ Because of this effect, the authors have previously investigated interfacial microstructures and bonding strength of diffusion-bonded joints of Ti-Al (Ti-50 mol% Al, i.e., Ti-36 mass% Al)/high carbon steel (Fe-0.82 mass% C).°⁵ The TiC layer formed at the interface does not suppress the formation of other reaction products.

In the present study, Ti-Al binary alloys having an Al content of less than 50 mol%, were diffusion-bonded to high carbon steel, and the influence of the alloy composition on the interfacial microstructures and the bonding strength was investigated from the viewpoint of the diffusion barrier effect of the TiC layer. It was found in the experiments that the specimen separated near the interface promptly after the bonding treatment, under certain conditions.°¹² The surface of the Ti-Al side undergoing this separation was hardened by the reaction product. This phenomenon has the potential to become the foundation for new surface modification techniques involving Ti materials, which show poor wear resistance; its details are discussed.

2. Experimental Procedure

Ti-Al binary alloys containing 10 to 40 mol% Al were produced by using an arc melting process. The alloys are hereafter referred to by their molar Al content, e.g., Ti-10Al means Ti-10 mol% Al. The obtained ingots were homogenized at 1273 K for 86.4 ks in a vacuum of less than 3 mPa and then cut into disks with a diameter of 5 mm and thicknesses of 0.2 and 0.5 mm by using an electric discharge machine. Commercially pure Ti and commercially produced carbon steel were used as base metals. The Ti was machined into a cylindrical column of 5 mm in diameter and 5 mm in height. The steel, which contained 0.82 mass% C, 0.18 mass% Si, 0.40 mass% Mn, 0.013 mass% P, 0.021 mass% S, 0.10 mass% Cr, and 0.08 mass% Cu, specified as SK5 tool steel by the Japanese Industrial Standards Committee, was machined into samples of two different shapes: one was a cylinder 5 mm in diameter and 5 mm in height, and the other was a rectangular block with dimensions of 10 mm × 10 mm × 5 mm. The bonding surfaces of all materials were finished with #1200 emery paper. Before bonding treatment, the specimens were degreased in acetone using an ultrasonic cleaner and dried with hot air.

The stacking sequence of bond couples is shown in Fig. 1. In most cases, the Ti-Al disk with a thickness of 0.5 mm was inserted between two steel columns. To investigate the surface modification of Ti, several couples composed of a Ti column, a Ti-Al disk with a thickness of 0.2 mm, and a steel
block were used. These couples were fixed in a jig consisting of two molybdenum rods and two austenitic stainless steel blocks. The assembly was heated in the range from 1073 to 1273 K for 0.9 to 8.1 ks in a vacuum of less than 3 mPa until the diffusion bonding was complete. The heating rate up to the bonding temperature was 0.17 K/s, and all specimens were allowed to cool in the furnace to room temperature after a holding step.

The specimens were cut perpendicular to the interface to reveal the microstructures. The cross sections were ground with emery papers and then finished with alumina powder. After etching, they were examined by using an optical microscope and scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscope (EDX). The bonding strength of the obtained specimens was evaluated at room temperature by a shear test, which was performed at a crosshead speed of 8.3 \( \text{m/s} \) using an Instron-type tensile machine equipped with a special gripping device. In addition, SEM-EDX analysis, X-ray diffraction (XRD), and a Vickers hardness test were carried out for the specimens showing interface separation. In the hardness test, a load of 2.94 N was applied at room temperature for 15 s.

3. Results and Discussion

3.1 Interfacial microstructures and bonding strength of Ti-Al alloy/high carbon steel joints

Figure 2 shows SEM micrographs of the interface in the Ti-Al alloy/high carbon steel joints bonded at 1273 K for 3.6 ks. The chemical compositions of the alloys in Figs. 2(a) to 2(d) were Ti-10, 20, 30, and 40Al, respectively; the upper and lower sides in the micrographs are the Ti-Al and the steel, respectively.

Three reaction regions indicated as I to III were observed around the interface in all cases. Region I was located in the Ti-Al and had needle- and/or band-shaped products. The morphology seems to depend on the alloy composition. Strictly speaking, the band-shaped product in Fig. 2(b) had an eutectoid-like structure. Region II was a continuous reaction layer. Its thickness also changed with the alloy composition. In addition, the morphology of region III, formed in the steel, varied from inhomogeneous to homogeneous with an increase in the Al content in the Ti-Al.

To identify these reaction regions, composition analysis of these specimens was carried out by using SEM-EDX. The results for the Ti-30Al/steel joint bonded at 1273 K for 3.6 ks are shown in Fig. 3. Ti, Al and Fe were detected in the needle- and band-shaped products in region I. It is thought that this region is formed by the diffusion of Fe into the Ti-Al. In region II, it is thought that TiC formed due to the larger Ti and C contents, leading to a relative loss of Ti in region I. Region III had a distribution of Fe and Al. Al and Ti are known to be ferrite stabilizers. The formation of the TiC layer in region II supported the enrichment of Ti and the decarburization of the steel. In addition, Al diffused into the decarburized layer, and thus, region III was identified as a ferrite phase.

Consequently, the interfacial microstructure of the Ti-Al/high carbon steel joints contained regions having reaction products that consist of Ti, Al and Fe, TiC, and ferrite, regardless of Al content in the alloy. The thickness of each region changed with an increase in the Al content in the Ti-Al, as shown in Fig. 2. The authors have previously reported the interfacial microstructures of Ti-50Al/high carbon steel joints fabricated by the same procedure.3 In that study, the joints had three kinds of the reaction regions, consisting of two products with Ti, Al and Fe, a TiC layer containing Fe-Al compounds, and a ferrite layer. Therefore, the configuration of the interfacial microstructure in Fig. 2 is essentially identical to that in those Ti-50Al/high carbon steel joints. In addition, although the TiC layer formed in the Ti/steel joints is known to serve as a barrier for diffusion of constituent elements across the interface and to inhibit the formation of
In the current study, the barrier effect was suppressed in the Ti-Al/high carbon steel joints due to the presence of Al. However, the C content in the steel is sufficient to produce the TiC layer.

As shown in Fig. 2(b), it is noteworthy that a space, indicated by the white arrow, was clearly seen between regions II and III. This means that the joint separated near the interface during or after the bonding treatment. In some instances, the joints using Ti-20Al were already broken when the specimens were removed from the electric furnace. In contrast, the Ti-10Al/high carbon steel and Ti-40Al/high carbon steel joints bonded at 1073 and 1273 K for 3.6 ks showed a bonding strength of more than 150 MPa. This value exceeded the lower limit of shear strength for Ti/steel joints (titanium clad steels) established by the Japanese Industrial Standards Committee (JIS G 3603, 140 MPa). It was thought that the Ti-30Al/high carbon steel joint had a strength equivalent to the joint using Ti-40Al, because of the similar interfacial microstructures, as shown in Figs. 2(c) and 2(d). Therefore, the separation between Ti-20Al and high carbon steel is of great interest, and its details will be discussed in the next section.

### 3.2 Interface separation in Ti-20Al/high carbon steel joint

Figures 4(a) to 4(c) show optical micrographs of the interface of the Ti-20Al/high carbon steel joints bonded at 1273 K for 0.9, 3.6, and 8.1 ks, respectively. Although the specimen shown in Fig. 4(a) had a sound interface, spaces, indicated by the arrows, formed at the interface with an increase in the holding time. It was confirmed that the space was located at the initial interface of the specimen. The three reaction regions shown in Fig. 2 were also observed in Figs. 4(a) and 4(b). In Fig. 4(c), the TiC layer became inhomogeneous and thin, and the ferrite region was not observed in the steel. Such a microstructural change is considered to be associated with the interface separation phenomenon. On the other hand, in Ti-20Al/high carbon steel joints bonded at 1073 and 1173 K for 0.9 and 8.1 ks (Fig. 5), the regions grew around the interface in relation to the bonding temperature and the holding time. The separation phenomenon did not occur under these bonding conditions. Furthermore, the Ti-20Al/high carbon steel joint bonded at 1073 K for 3.6 ks had a shear strength of 166 MPa. This value was almost equal to that of the joints using Ti and Ti-50Al, which were prepared under the same conditions.5)
From these results, the interface separation depends on the alloy composition of Ti-Al, bonding temperature, and holding time. This can be regarded as a unique and distinctive phenomenon. Thus, we tried to explain the reason why, in the Ti-20Al/high carbon steel joint, interface separation occurred after prolonged bonding treatment at 1273 K.

The influence of thermal stress occurring in the bonding process is considered to be one reason for the interface separation. However, the bonding treatment at temperatures between 1073 and 1273 K was conducted with the same heating and cooling rates. In addition, separation did not occur in the case of a short holding time, even when the bonding temperature was 1273 K. These facts suggest that thermal stress has little influence on the interface separation.

It is also assumed that the growth of a brittle reaction phase, such as one involving Fe-Ti compounds, leads to this phenomenon. To examine this possibility, the separated surfaces were investigated by SEM-EDX analysis. Figure 6 shows microstructural aspects of the separated surfaces after bonding treatment at 1273 K for 3.6 and 8.1 ks. The SEM images suggest that the joint is unlikely to be broken by brittle fracture. Figures 6(a) and 6(b) correspond to the separated surfaces of Ti-20Al and high carbon steel, respectively, in the joint bonded at 1273 K for 3.6 ks. The areas indicated as A and B in these micrographs were thought to be ferrite phases, since they consisted mainly of Fe and Al.
These phases disappeared with a holding time of 8.1 ks, and the separated surface became smooth, as shown in Figs. 6(c) and 6(d). In Fig. 6(d), the product indicated as C contained about 20 mol% Al, whereas a small amount of Al was detected in the gray matrix. It should be noted that the matrix in the Ti-20Al side was composed of fine grains with a diameter of about 300 nm. This was identified as TiC by using SEM-EDX analysis.

XRD analysis also suggests that a brittle compound does not cause interface separation. An XRD pattern of the separated surface shown in Fig. 6(a) is presented in Fig. 7. The matrix with fine grains was determined to be TiC. For the opposite surface shown in Fig. 6(b), the diffraction peaks corresponding to ferrite were also recognized. Therefore, it appears unlikely that a brittle compound induces interface separation.
According to the Ti-Al binary phase diagram in Fig. 8, Ti-20Al transforms from a Ti (α) + Ti3Al (α2) duplex structure to an α single structure at about 1273 K. It is known that Fe diffuses rapidly into α and α2, and the diffusion coefficient of Fe into α is larger than that into α2.14) Thus, the diffusion flux of Fe into Ti-20Al (J_{FeTi-20Al}) might further increase with bonding temperature. Actually, J_{FeTi-20Al} at 1273 K greatly increased in comparison to that at 1073 and 1173 K, based on the size of the region containing Ti, Al and Fe estimated from Figs. 4 and 5. In addition, J_{FeTi-20Al} at 1273 K should be greater than that for Ti-10Al showing an α single phase at 1273 K (J_{FeTi-10Al} < J_{FeTi-20Al}), as shown in Fig. 2. This may be attributed to the influence of the TiC layer, which hinders interdiffusion.

In contrast, the diffusion coefficients of Ti and Al into α-Fe are 13 × 10^{-14} m^2/s and 4.2 × 10^{-14} m^2/s at 1273 K, respectively (data for diffusion into γ-Fe at 1273 K are unavailable).15) Since Ti reacts with C and the TiC layer is formed at the interface, Al diffuses mainly into the steel, as mentioned above. Figure 9 shows the relationship between the thickness of the ferrite layer (region III in Fig. 2) and the alloy composition in the Ti-Al/high carbon steel joint bonded at 1273 K for 3.6 ks. Although, in the case of low Al content, the layer could not be measured due to inhomogeneous formation of ferrite, it was found to grow with an increase in the Al content in the alloy. This gives support to the diffusion of Al being dominant, although its diffusion coefficient is lower. Consequently, with the Ti-20Al/high carbon steel joint bonded at 1273 K, Fe atoms in the steel migrate unilaterally into the Ti-20Al side, considering J_{FeTi-10Al} < J_{FeTi-20Al}. In other words, the formation and accumulation of voids resulting from such a unilateral diffusion is part of the reason for the interface separation. The voids may be regarded as a kind of Kirkendall void, though the separation occurs at the initial interface in the specimen, as described above. A similar phenomenon related to interdiffusion has not been reported to the best of our knowledge, and the details are still under our investigations. If diffusion is responsible for the separation phenomenon, we can explain not only the holding time dependency but also the morphological change of the TiC layer and the smoothing of the separated surface, as shown in Figs. 4 and 6, respectively.

3.3 Application of interface separation phenomenon

The Ti-20Al/high carbon steel joint bonded at 1073 K had a high strength, whereas the joint bonded at 1273 K for 3.6 ks separated near the interface. The separation was dependent on the alloy composition of Ti-Al, the bonding temperature, and the holding time. This phenomenon can be used to prepare a reversible interconnection with bonding and separating abilities, and may be of use in recycling composite materials. Furthermore, interface separation is expected to become the foundation for new surface modification techniques. Figure 10 shows an optical micrograph of the cross-section of the Ti/Ti-20Al/high carbon steel joint bonded at 1273 K for 3.6 ks. After bonding, the steel came off very easily. As might be expected from Figs. 6 and 7, the TiC layer, indicated by the single arrow, formed uniformly on the surface. The Vickers hardness of the surface is shown in Fig. 11. The surface hardness of the specimen in Fig. 10 was about 1200, approximately 4 times higher than that of Ti and Ti-20Al before bonding. In Ti and its alloys, a plasma carburizing process has been used recently to modify surfaces due to difficulties in carburizing.16) However, the interface separation in the present study can be used successfully for surface modification. The present method was performed by using vacuum heating without any special equipment, and the obtained surface was harder than that from any other method. It has many advantages over conventional techniques.

4. Conclusions

Ti-Al binary alloys (Ti-10 to 40Al) were diffusion-bonded to high carbon steel to investigate the influence of the alloy
composition on interfacial microstructures and the bonding strength. During this study, an interface separation phenomenon was found to occur under certain bonding conditions. The main conclusions are summarized as follows. (1) The interfacial microstructure of the obtained joints was composed of three regions with reaction products consisting of Ti, Al and Fe, a TiC layer, and ferrite, regardless of the Al content in the alloy. The thickness of these regions changed with an increase in the Al content in the Ti-Al. (2) Although the Ti-Al/steel joints had a relatively high shear strength (>150 MPa), the joint using Ti-20Al separated near the interface after prolonged bonding treatment at 1273 K. It was confirmed that the phenomenon was governed by the chemical composition of the Ti-Al, the bonding temperature, and the holding time. (3) A TiC layer was produced uniformly on the surface of Ti-20Al, which underwent interface separation. Its hardness was about 1200, approximately 4 times higher than that of Ti and Ti-20Al before bonding. Therefore, the interface separation phenomenon has the potential to become the foundation for new surface modification techniques of Ti and its alloys.

Acknowledgements

The authors would like to express their appreciation to Mr. T. Terai, Mr. N. Nitta, and Mr. Y. Kodama for their kind assistance in the experiments. The present study was supported by the ISIJ Research Promotion Grant of The Iron and Steel Institute of Japan, and we greatly appreciate their support.

REFERENCES