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Microstructure of Reaction Zone Formed During Diffusion Bonding of TiAl with Ni/Al Multilayer

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In this article, the characterization of the interfacial structure of diffusion bonding a TiAl alloy is presented. The joining surfaces were modified by Ni/Al reactive multilayer deposition as an alternative approach to conventional diffusion bonding. TiAl substrates were coated with alternated Ni and Al nanolayers. The nanolayers were deposited by dc magnetron sputtering with 14 nm of period (bilayer thickness). Joining experiments were performed at 900 °C for 30 and 60 min with a pressure of 5 MPa. Cross sections of the joints were prepared for characterization of their interfaces by scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), high resolution TEM (HRTEM), energy dispersive x-ray spectroscopy (EDS), and electron backscatter diffraction (EBSD). Several intermetallic compounds form at the interface, assuring the bonding of the TiAl. The interface can be divided into three distinct zones: zone 1 exhibits elongated nanograins, very small equiaxed grains are observed in zone 2, while zone 3 has larger equiaxed grains. EBSD analysis reveals that zone 1 corresponds to the intermetallic Al_2NiTi and AlNiTi, and zones 2 and 3 to NiAl.

Keywords advanced characterization, intermetallics, joining

1. Introduction

Titanium aluminide alloys exhibit a set of properties that make them an alternative to the materials used in the manufacture of components for aerospace and automobile industries. The development of adequate joining technologies is essential for the application of these alloys (Ref 1-4).

Diffusion bonding is one of the most widely reported joining processes for the successful bonding of titanium aluminides (Ref 5-8). However, conventional diffusion bonding of TiAl alloys requires high temperature, pressure, and time. Çam and coworkers (Ref 5, 6) demonstrated that for diffusion bonding of titanium aluminides, temperatures above 1000 °C, times of 180 min, and a pressure of 20 MPa are required to obtain joints with a high shear strength value.

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The processing conditions of conventional diffusion bonding may be less stringent if we use alternative approaches. Reactive multilayer thin films are one of the possibilities to exploit in joining applications (Ref 9-13). These films consist of alternating nanolayers that can be used as local heat sources because of the heat released by the exothermic reaction of layers to form intermetallic compounds. In addition, these reactive multilayers improve diffusivity as a result of their nanocrystalline nature and high defect density. Multilayer systems containing aluminum, such as Ni/Al (Ref 14-17), Nb/Al (Ref 18, 19), Ti/Al (Ref 20), and Cu/Al (Ref 21), are the most commonly used, as they release larger amounts of heat. Duarte et al. (Ref 9) tested Ti/Al multilayer thin films in the diffusion bonding of TiAl alloys. Sound bonds were observed for samples processed at 900 and 1000 °C, under a pressure of 50 MPa for 60 min. These results indicate that a Ti/Al multilayer assists diffusion bonding, reducing the temperature and time relatively to conventional bonding conditions. Studies have been conducted by Simões et al. (Ref 11) in diffusion bonding of TiAl alloys with surfaces modified by Ni/Al reactive multilayer deposition. They used Ni/Al Multilayer systems because this system is more reactive and readily transforms into NiAl, releasing larger amounts of heat when compared with a Ti/Al multilayer. In fact, we observed that with a Ni/Al multilayer, we obtained sound joints at lower temperature and pressure than when we used the Ti/Al multilayer. Sound bonds were obtained using these multilayers for bonding at 900 °C for 60 min and at a pressure of 5 MPa; these samples exhibited a shear strength value of 313 MPa. This value is similar to that obtained in joints produced without multilayers and under demanding bonding conditions (Ref 5, 6). Based on these results, the diffusion bonding process was enhanced by the Ni/Al multilayer's modification of joining surfaces.

However, the microstructural characterization of these joints is a fundamental step to understanding the mechanisms that

occur during the diffusion bonding process. The present study is centered on the characterization of the interfacial microstructures of TiAl alloys bonded by Ni/Al reactive multilayers. The main objective was to understand the relationship between the microstructure and the phases formed at the interface. The processing conditions selected for this investigation were those that had produced the bonds with the highest shear strength in a previous study (Ref 11).

2. Experimental Procedure

The γ-TiAl alloy used in this investigation has a duplex microstructure with a chemical composition of Ti-45Al-5Nb at.%. Specimens of 10 × 10 × 10 mm were polished using diamond suspension down to 1 μm. Ni and Al alternated nanolayers were deposited onto γ-TiAl by dc magnetron sputtering using pure nickel and aluminum targets. The deposition parameters were selected to obtain an equiatomic average chemical composition. Films with a modulation period (Λ, bilayer thickness) of 14 nm and a total thickness ranging from 2.5 to 3.5 μm were deposited. Diffusion bonding joints were produced at temperatures of 900 °C, a pressure of 5 MPa, and with bonding times of 30 and 60 min, in a vertical furnace with a vacuum level better than 10^{-2} Pa. The diffusion bonding apparatus is described elsewhere (Ref 11).

Cross sections of the joints were prepared using standard metallographic techniques for the microstructural and chemical characterizations of the interface using scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), high-resolution TEM (HRTEM), and energy dispersive x-ray spectroscopy (EDS). The cross-sectional specimens for TEM and STEM observations were prepared using conventional double-jet electropolishing in a solution of 3% perchloric acid in 2-butoxy-ethanol at room temperature and a potential 2-6 V.

The crystallographic information from the joint interfaces was obtained by electron backscatter diffraction (EBSD). EBSD is a surface technique since only the topmost 50 nm of the sample contributes to the diffraction pattern. The indexation of the Kikuchi patterns obtained by EBSD allowed for phase identification in localized zones of the samples; for Ti and Al, the minimum lateral spread of the interaction volume ranges from 50 to 100 nm (Ref 22), with an accelerating voltage of 15 keV. The ICDD PDF2 (2006) database was used for indexation. Careful preparation of the surface of the samples for EBSD is the key factor critical in achieving good quality EBSD patterns. Therefore, the samples for EBSD were submitted to an additional polishing stage using colloidal silica. This final chemo-mechanical polishing reduced the surface damage. The Kikuchi patterns were obtained with the sample tilted at 70º from the horizontal.

3. Results and Discussion

Diffusion bonds obtained at 900 °C, for 60 min at 5 MPa appeared to be sound, as can be confirmed by the SEM images presented in Fig. 1. Even with the time reduced to 30 min at 900 °C, we observed an interface without pores or cracks. In both cases, the bond line can be identified. The interfaces are very thin; less than 10 μm.

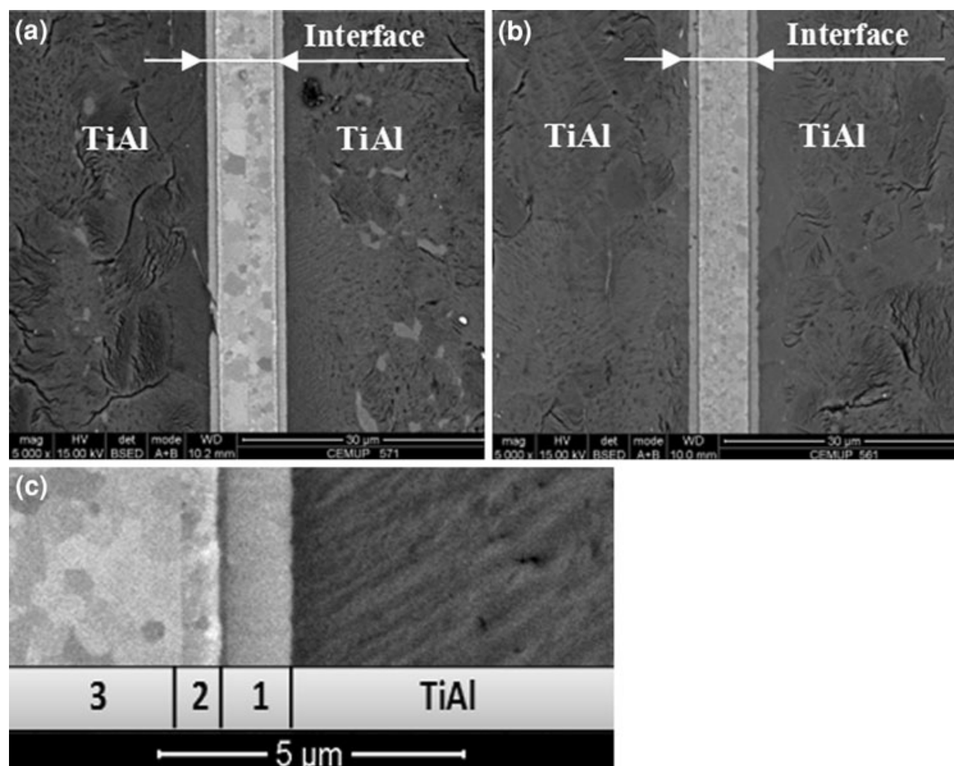

Fig. 1 SEM images of the bond interface obtained at 900 °C with 5 MPa: (a) 30 min and (b) 60 min. A detail of the interface with the identification of the three different zones is illustrated in (c)

The microstructure of the TiAl base alloy is unchanged by the diffusion bonding procedure. According to the observed microstructure, the diffusion bonding interface can be divided into three distinct zones identified in Fig. 1(c): zone 1 (close to base material) exhibits small grains; very small equiaxed grains are observed at zone 2; while at the center of the interface, zone 3 has larger equiaxed grains.

In order to investigate the interfacial microstructure formed by the diffusion bonding process in more detail, the interface was studied using TEM. TEM images of zones 1 and 3 are shown in Fig. 2; zone 2 was not observed because of its preferential dissolution by the electropolishing process used to prepare the thin foils. These images evince the columnar morphology of grains in zone 1 and confirm the presence of the equiaxed grains in zone 3 already observed by SEM.

The phases present in each reaction layer were characterized using a combination of EDS and EBSD pattern analysis. An EDS line scan of Al, Ni, and Ti across the bonding interface is presented in Fig. 3. For the base material, TiAl alloy, only Al and Ti are detected. Zones 1 and 2 show the presence of Al, Ni, and Ti; Ti decreases from the base material to the center of the interface. Only Al and Ni were detected at zone 3.

EBSD patterns are particularly important for the phase identification of the thinner compounds, where the layer's thickness is smaller than the interaction volume of EDS measurements, as is the case for zones 1 and 2. With the EBSD technique, we obtain the Kikuchi pattern of a very small area. The indexing of the patterns allows for phase identification in the localized zones of the sample. Figure 4 shows the EBSD pattern indexation for a joint processed at 900 °C for 60 min. These results indicate that the interdiffusion between the TiAl (base material) and the Ni/Al multilayers leads to the formation of two intermetallic phases in zone 1: AlNiTi and Al_2NiTi. In zone 2, only a NiAl phase can be identified, in spite of the presence of Ti detected by the EDS analysis. At the center of the interface, in zone 3, only Al and Ni are detected by EDS; the EBSD analysis identified intermetallic NiAl.

The diffusion of elements from the base material is restricted to zones 1 and 2; zone 3 is the result of the Ni/Al multilayer's transformation into equiaxed grains of NiAl during the bonding cycle. The structure of the central region of the interface is similar to the structure of the multilayer when heated to 700 °C (Ref 16). The intermetallic phase is the same as in zones 2 and 3, the only difference being the slightly higher Ti content of zone 2, which is associated with a smaller grain size. The association of a higher Ti content with smaller grain size suggests that Ti retards the formation and/or growth of NiAl.

These results suggest that bonding between the TiAl alloy and the multilayer is promoted by the interdiffusion of Al, Ni, and Ti to the boundary between the multilayer and the base alloy, with the formation of the intermetallic compounds AlNiTi and Al_2NiTi. Bonding throughout the central region is associated with the transformation of the Ni/Al multilayer into NiAl.

Observations of the bonding interface in STEM mode and the Ti map obtained by EDS analysis, presented in Fig. 5, shows one line with a higher Ti content in the center of zone 3, along the bonding line. The presence of this line rich in Ti in this central area was examined by HRTEM and analyzed by EELS; small Ti rich grains were observed along that region. These observations suggests that Ti diffusion reached the center of the interface, although very low concentrations were attained; with the decrease in solubility of Ti in NiAl with

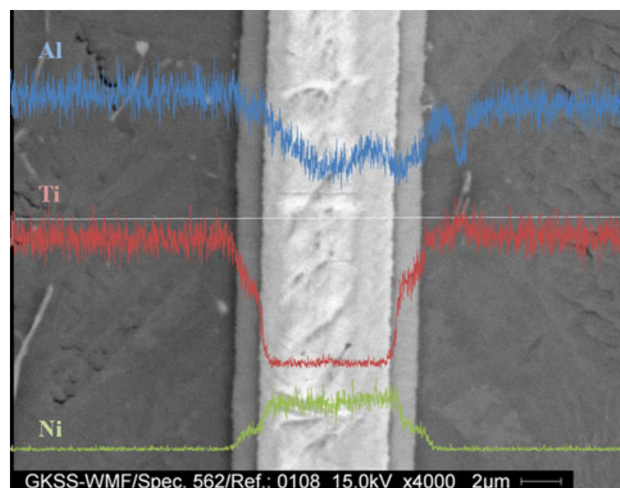

Fig. 3 EDS line scans of Al, Ni, and Ti across the bonding interface

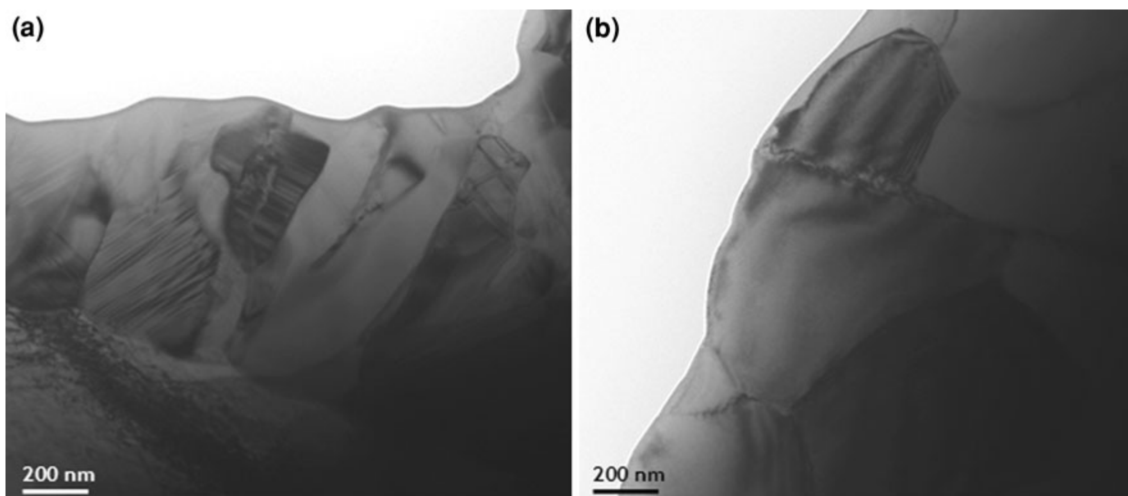

Fig. 2 TEM images of the bond interface obtained at 900 °C with 5 MPa for 60 min: (a) zone 1 and (b) zone 3

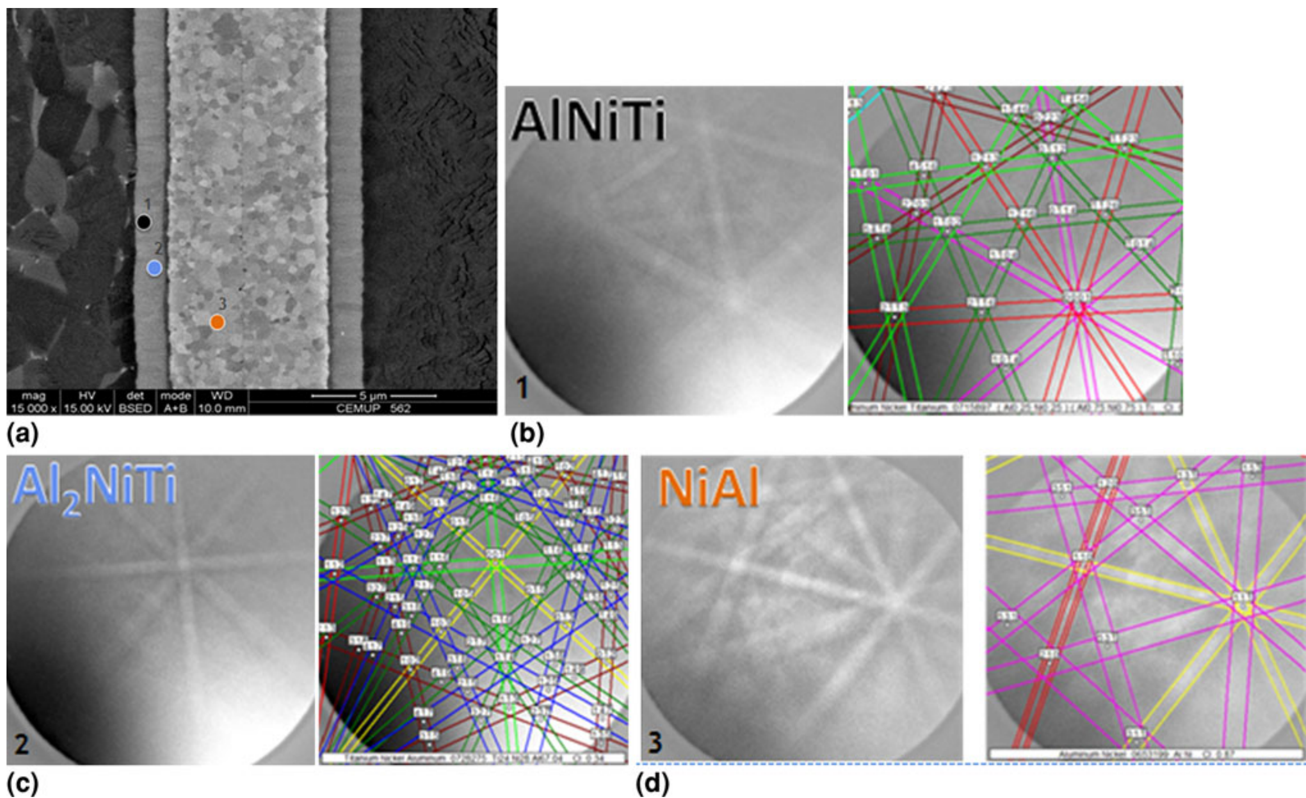

Fig. 4 (a) SEM image of bond interface obtained at 900 °C with 5 MPa for 60 min. EBSD Kikuchi pattern indexation: (b) AlNiTi phase (zone 1), (c) Al_2NiTi phase (zone 1), and (d) NiAl phase (zone 3)

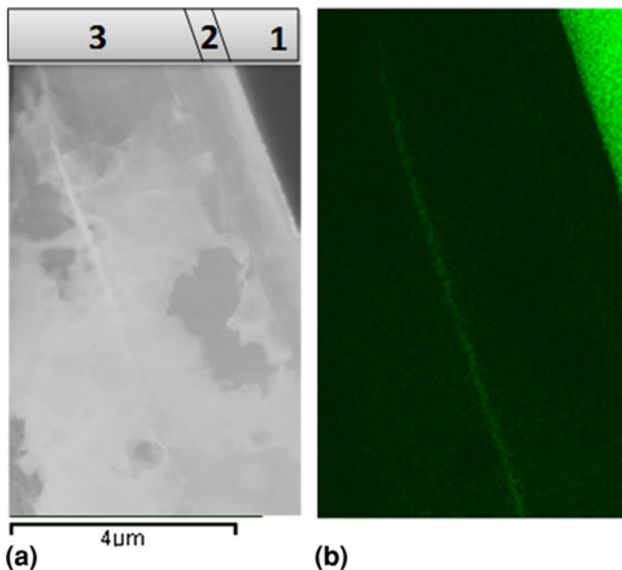

Fig. 5 (a) STEM DF images of the diffusion bonds processed at 900 °C for 60 min (zones indicated at the top of image) and (b) elemental maps of Ti determined by EDS

decreasing temperature, Ti is segregated to a less compact region (the bonding line) forming these grains.

Diffusion bonding of TiAl alloys with Ni/Al multilayers have being reported by other authors with apparent success. Cao et al. (Ref 12) produced defect-free samples by diffusion bonding at 900 °C with NiAl multilayer. The interfaces reveal several complex compounds of Ni-Al-Ti, such as $Ni_3(AlTi)$, $AlNi_2Ti$, and Al_2NiTi. The difference in the structures of interface can be attributed to variation in multilayer period and in the Al/Ni ratio: 1 μm and 1/3 in Cao et al.'s study; 14 nm and 1/1 in the present one. The 14-nm period multilayer used in this study was chosen based on previous results (Ref 16); a multilayer with this period and an equiatomic composition transforms in a single-step reaction into NiAl, releasing all the heat at the same time, thus functioning as a better heat source to the diffusion bonding process. The larger Ni content and multilayer period leads to several steps reaction and the formation of Ni richer intermetallic phases: $Ni_3(AlTi)$ and $AlNi_2Ti$ (Ref 12).

4. Conclusion

In this study, a modified diffusion bonding technique was used to join TiAl alloys. Using Ni/Al multilayer thin films, it is possible to obtain sound and reliable joints using reduced temperature, pressure, and time when compared to the processing conditions in conventional diffusion bonding. The interfaces formed are very thin and can be divided into three distinct zones: zone 1 (close to base material) exhibits columnar grains, very small equiaxed grains are observed in zone 2, while zone 3 (close to the bond line) has larger equiaxed grains.

The interdiffusion between TiAl (base material) and Ni/Al (multilayer) leads to the formation of a layer constituted by two intermetallic phases: AlNiTi and Al_2NiTi. At the center of the interface, the Ni/Al multilayer thin film transforms to NiAl

grains. The joining mechanism appears to depend on the diffusion of Al, Ni, and Ti across the interface.

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