Fabrication of TiB$_2$ reinforced Al$_3$Ti composite layer on Ti substrate by reactive-pulsed electric current sintering

Toshio Matsubara *, Tomohide Shibutani, Keisuke Uenishi, Kojiro F. Kobayashi

Department of Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1, Yamadaoka, Suita, Osaka 565-0871, Japan

Abstract

A TiB$_2$ reinforced intermetallic compound Al$_3$Ti composite coating layer was formed by reactive-pulsed electric current sintering of mechanically alloyed Al–Ti–B or Al–Ti–TiB$_2$ powders, and was simultaneously bonded to a Ti substrate to improve its wear and oxidation properties. The sintering behavior was investigated to obtain a fully dense and homogeneous Al$_3$Ti/TiB$_2$ coating. Bonding to substrate was achieved by the formation of reaction layers at the bonding interface and the reaction kinetics were investigated. Although the wear properties of monolithic Al$_3$Ti coating could be improved by the reinforcement of TiB$_2$, the oxidation properties at high temperature (1273 K) were degraded due to the decomposition of TiB$_2$ to elemental Ti and B. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Titanium trialuminide; Intermetallic matrix composite; TiB$_2$; Mechanical alloying; Surface modification; Pulsed electric current sintering; Wear and oxidation properties

1. Introduction

Titanium aluminides have several potential applications in the aerospace, automotive and turbine powder generation markets due to their light weight and considerable high-temperature strength [1]. In particular, Al$_3$Ti has superior strength, oxidation properties and the lowest density [2,3]. Although Al$_3$Ti has not yet been considered as a structural material because of its low ductility at ambient temperature, it is expected to exhibit excellent wear and oxidation properties as a surface modified coating. To protect the substrate from a severe environment, the coating must be thick and well bonded with the substrate. For the formation of such as Al$_3$Ti coatings, because of its negligibly small solubility in the phase diagram, it is not always advantageous to apply conventional liquid phase processing.

The authors have successfully applied powder metallurgical techniques such as combustion synthesis or mechanical alloying (MA) in surface modification and joining process [4–9]. Combustion synthesis is the process to obtain compounds starting from the mixture of the composing elements well below the melting temperature by using the negative heat of formation of the system [10]. When the mixture of Al and Ti powders with a composition of Al$_3$Ti pre-placed on the substrate is heated to the temperature higher than ignition temperature, Al and Ti in the mixed powders react with each other to form a Al$_3$Ti coating, and simultaneously bonding to the substrate was achieved by the heat of formation of Al$_3$Ti. However, in the combustion synthesized from only mixed powders, voids and residual unreacted elements are likely to be remained [4]. Applying finely mixed MA powders as starting materials has been shown to be advantageous in eliminating these inhomogeneities and forming a homogeneous coating, and also enables processing at a lower temperature [5–7,11]. Pulsed electric current sintering (PECS) in which a pulsed electric current is charged directly through the powders is found effective to achieve a shorter sintering time than conventional sintering processes [12]. By PECS of MA powders, dense Al$_3$Ti layer could be formed and exhibited almost the same properties as a cast bulk Al$_3$Ti for the hardness, wear and oxidation resistance [7].

In this research, we formed a TiB$_2$ particle reinforced Al$_3$Ti composite (intermetallic matrix composite (IMC)) coating on a Ti substrate by PECS to further enhance
The weight ratio of balls to powder was fixed to 80:1. To avoid the adhesion of powders to the balls and vial, 0.5ml of ethanol was added as a process control agent.

Furthermore, as is evident from the Al–Ti–B ternary phase diagram [13], TiB₂ has such a good compatibility with Al₃Ti that interfacial reactions leading to the degradation of the IMC will not occur. The combustion synthesis reaction and densification of MA powders started from the mixture of Al–Ti–TiB₂ or Al–Ti–B were investigated to form sound IMC layers. Effects of TiB₂ dispersion on the wear and oxidation properties of the obtained IMC coating were also examined as well as that on the bonding to a Ti substrate.

2. Experimental procedure

Al (99.9%, 27 μm), Ti (99%, 7 μm), B (95.7%, 1 μm) and TiB₂ (99%, 44 μm) powders were used. Al–Ti–B or Al–Ti–TiB₂ powder was mixed in the composition of Al₃Ti/10vol.%TiB₂. MA was performed with a rotational mill for 144 ks. Fifty grams of the mixed powder put into a cylindrical SUS304 vial (1.7 × 10⁻³ m³) with SUS304 balls (φ11 mm) in an Ar gas atmosphere. The weight ratio of balls to powder was fixed to 80:1. To avoid the adhesion of powders to the balls and vial, 0.5ml of ethanol was added as a process control agent.

A commercially pure Ti (99.9%, φ10 mm × 3 mm) was used as a substrate. Substrate surfaces were ground with 1.0 μm alumina powders to obtain a flat, clean surface prior to the formation of IMC coating. Fig. 1 shows a schematic illustration of the mold part of the PECS equipment (SPS510L, Sumitomo Coal Mining Co.) used in this research. MA powder and the Ti substrate, contained inside a carbon die with an inner diameter of 10.5 mm, were compressed in a vacuum of 5 Pa and at a uniaxial pressure of 40 MPa, then heated to various temperatures at a heating rate of 3.33 K s⁻¹.

A Vickers microhardness tester with an applied load of 1.96 N was used to measure the hardness distribution across the bonding interface. An Ogoshi abrasion test [14] was performed without lubricant at ambient temperature to evaluate the wear properties of the obtained surface IMC layer. The surface of the test sample was polished with 1.0 μm alumina powders. A heat-treated SUJ2 (HV650) ring was used as the opponent abraser. The abrasion distance (L), was fixed to 100 m, load (P) to 10 N, and speed to 4.36 m s⁻¹. The specific wear (Wₛ) was calculated according to Eq. (1) by measuring the volume of abraded indentation (W).

\[ Wₛ = \frac{1.5W}{PL} \]  

Oxidation resistance was evaluated by observing the oxidation layer formed by heating the sample for various times at 1273 K in an open air.

3. Results and discussion


Fig. 2 shows the microstructures of MA powders. For Al–Ti–TiB₂ or Al–Ti–B, the contrasting white TiB₂ particles and black elemental B particles are seen to be distributed homogeneously in the matrix, and these lamellar structures were further refined. Adding these particles seems to have enhanced the kneading effect.

Fig. 3 shows the DSC traces of these MA powders. Compared with the combustion synthesis of elemental Al–Ti powder mixture ignited at the Al melting point, the exothermal peak was broadened and shifted to a lower temperature. Fig. 4 shows the X-ray diffraction patterns of these powders continuously heated to 1003 K. Al₃Ti was found to form for all compositions, and a relative density (D) and the holding time (t) as shown in Eq. (2) [15].

Fig. 5 shows the changes in the shrinkage ratio of the MA powders to monitor the sintering behavior at 40 MPa during continuous heating by PECS. Densification was decelerated by adding TiB₂, but was not changed by adding B. TiB₂ with a high elastic constant seems to have prevented the densification.

Fig. 6 shows the changes in the relative density of the synthesized IMC coating from the MA powders of Al–Ti–TiB₂ and Al–Ti–B during isothermal sintering at various temperatures and 40 MPa. Increasing the sintering temperature and time promoted the densification. If the densification is controlled by plastic flow of materials at a sintering temperature (T), a Johnson–Mehl–Avrami type relation can be applied between the relative density (D) and the holding time (t) as shown in Eq. (2) [15].
\[
\ln(1 - D) = -K_s(T)t
\]

where \(K_s\) is the densification rate which is proportional to the pressure, and is also described as Eq. (3).

\[
K_s(T) = K_{so}\exp\left(-\frac{Q_s}{RT}\right)
\]

where \(K_{so}\) is a constant, and \(Q_s\) is the apparent activation energy required for densification. \(R\) is the gas constant.

Fig. 7 shows this relationship between \(\ln(1 - D)\) actually measured in this work and the holding time. These plots agree well with Eq. (2) except for the plots obtained from Al–Ti–TiB\(_2\) at 1173 K. The plastic flow model does not seem to apply in the last stage of densification. The \(K_s\) values can be estimated from the slope of regression lines. The \(Q_s\) value can also be estimated from an Arrhenius plot of the \(K_s\) value as shown in Eq. (3), and is shown in Table 1. To obtain a fully dense IMC coating was more difficult, i.e. required higher temperature and longer holding time than the monolithic Al\(_3\)Ti.

Although the IMC coating synthesized from Al–Ti–TiB\(_2\) was densified at 1173 K, that from Al–Ti–B required a higher temperature. As seen in Fig. 4, the

Fig. 7 relationship between ln(1 - D) actually measured in this work and the holding time. These plots agree well with Eq. (2) except for the plots obtained from Al–Ti–TiB\(_2\) at 1173 K. The plastic flow model does not seem to apply in the last stage of densification. The \(K_s\) values can be estimated from the slope of regression lines. The \(Q_s\) value can also be estimated from an Arrhenius plot of the \(K_s\) value as shown in Eq. (3), and is shown in Table 1. To obtain a fully dense IMC coating was more difficult, i.e. required higher temperature and longer holding time than the monolithic Al\(_3\)Ti.

Although the IMC coating synthesized from Al–Ti–TiB\(_2\) was densified at 1173 K, that from Al–Ti–B required a higher temperature. As seen in Fig. 4, the
layer formed from Al–Ti–B at 1003 K consisted of AlB₂ and Ti in the Al₃Ti matrix. As is evident from free energy (ΔG) for the boride formation, the affinity of B with Ti is much stronger than that with Al. When AlB₂ and Ti are heated, the following reaction is thus thermodynamically possible.

$$\text{AlB}_2 + \frac{4}{3}\text{Ti} \rightarrow \frac{1}{3}\text{Al}_3\text{Ti} + \text{TiB}_2$$

During this reaction, the molar volume change can be estimated from their crystal structures to be 4.2%. Because this reaction continues until a homogeneous microstructure is formed, a dense layer required a longer holding time at 1173 K. Fig. 8 shows the TEM micrographs of the IMC coating formed from Al–Ti–B at 1173 K for 180 s at 40 MPa. A plate-like 300 nm TiB₂ structure was observed to be homogeneously dispersed in the Al₃Ti matrix. The TiB₂ formed in-situ from Al–Ti–B was much smaller than that formed from Al–Ti–TiB₂.

### 3.3. Reaction with Ti substrate

Fig. 9 shows the microstructures of the bonding interface formed at 973 K and 40 MPa, for 180 s. Though there were some voids at the bonding interface

<table>
<thead>
<tr>
<th>Powder</th>
<th>Qₛ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–Ti</td>
<td>61.0</td>
</tr>
<tr>
<td>Al–Ti–TiB₂</td>
<td>107.6</td>
</tr>
<tr>
<td>Al–Ti–B</td>
<td>77.9</td>
</tr>
</tbody>
</table>
Fig. 8. TEM micrograph of the Al$_3$Ti/TiB$_2$ coating formed from Al–Ti–B at 1273 K for 180 s at 40 MPa.

Fig. 9. Microstructures of the bonding interface formed at 973 K for 180 s at 40 MPa. The coatings were formed from (a) Al–Ti, (b) Al–Ti–TiB$_2$ and (c) Al–Ti–B.

for single Al$_3$Ti compacts, few voids were observed for TiB$_2$ or B added compacts. Ashby et al. reported that local plastic flow was generated at the interface between the particle and the metal during the compaction of a metal containing particles with differing elastic constants [16]. In our experiment, there was little deformation at the bonding interface of the monolithic Al$_3$Ti coating, but a rugged interface was observed at that of IMC. This shows that the substrate deforms easily and fills up voids on the bonding interface with itself when particles with high elastic constants are added in the coating.

The reaction layers that formed at the bonding interface were investigated. To identify the initial interface, a mica sheet was inserted there as a marker before the bonding. Fig. 10 shows the general view and microstructure of the bonding interface formed from Al–
Ti–TiB₂ at 1173 K for 1800 s at 40 MPa. The reaction layers were found to form mainly in the direction of the Ti substrate. These layers were identified by EPMA analyses as α₅ (Ti₃Al), γ (TiAl) and Al₃Ti from the Ti substrate to the IMC coating. These results were consistent with those obtained by Loo et al. who investigated the interdiffusion phenomena of the Ti–Al₃Ti couple [17].

If the growth of the reaction layers is governed by diffusion, the thickness ($x$) is described as a function of the square root of time ($t$) [18].

$$x = K_g \sqrt{t}$$  \hspace{1cm} (4)

where $K_g$ is the growth coefficient, which is also described as Eq. (3) with apparent activation energy for layers growth.

Fig. 11 shows the relationship between the total thickness of reaction layers formed from Al–Ti–TiB₂ and the square root of the holding time. The growth of reaction layers exhibited a parabolic relation with holding time. The activation energy obtained from the Arrhenius plot of $K_g$ was 82.8 kJ mol⁻¹. Table 2 shows the activation energy for growth. The value obtained by the same calculation from the study of Loo et al. is also shown. The values obtained in this research were a little larger than those obtained by Loo et al. The reaction between the Al₃Ti coating and Ti substrate have been suppressed by the dispersion of TiB₂ particles.

### Table 2

<table>
<thead>
<tr>
<th>Powder</th>
<th>$Q_s$ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–Ti</td>
<td>70.3</td>
</tr>
<tr>
<td>Al–Ti–TiB₂</td>
<td>82.8</td>
</tr>
<tr>
<td>Al–Ti–B</td>
<td>79.8</td>
</tr>
<tr>
<td>Al₃Ti/Ti diffusion couple [17]</td>
<td>76.2</td>
</tr>
</tbody>
</table>

Fig. 10. (a) General view and (b) microstructure of the bonding interface formed from Al–Ti–TiB₂ at 1173K for 180 s at 40 MPa. The mica sheet indicates the original interface.

Fig. 11. Relationships between the total thickness of reaction layers (Ti₃Al + TiAl + Ti₃Al) formed from Al–Ti–TiB₂ on the bonding interface and the square root of holding time.

Fig. 12. Vickers hardness distributions of the IMC coating/Ti joints.
Table 3
Specific wears of Ti substrate, the obtained Al₃Ti and Al₃Ti/TiB₂ coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$W_s$ (10⁻¹⁴ m³ N⁻¹ m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti substrate</td>
<td>48.6</td>
</tr>
<tr>
<td>Monolithic Al₃Ti</td>
<td>2.72</td>
</tr>
<tr>
<td>IMC (Al–Ti–TiB₂)</td>
<td>1.29</td>
</tr>
<tr>
<td>IMC (Al–Ti–B)</td>
<td>1.07</td>
</tr>
</tbody>
</table>

3.4. Properties of IMC coating

Fig. 12 depicts the Vickers hardness distribution of these IMC/Ti joints as a function of distance from the bonding interface. The hardness of these IMC coatings were about HV800, a little higher than that of a monolithic Al₃Ti coating (HV600). Besides, the IMC coating obtained from Al–Ti–B powder exhibited a slightly greater hardness value, probably because the dispersed in-situ formed TiB₂ is much smaller than that Al–Ti–TiB₂.

Table 3 shows the specific wear of an IMC coating and Ti substrate. In the present abrasion condition, the wear can be considered to occur by adhesion wear due to the heat of friction between the sample and the abrading material and hence, wear properties are affected by the hardness and the melting point. Since Al₃Ti has a higher melting point and hardness, the obtained Al₃Ti coating shows sound wear properties. Furthermore, the IMC coating reinforced by TiB₂ particles that exhibit greater hardness exhibited better excellent wear properties than the single Al₃Ti layer.

Fig. 13 shows the microstructures of the IMC coating formed from Al–Ti–TiB₂ powder at 1173 K for 600 s after the samples were oxidized at 1273 K for 28.8 ks in open air. Though the monolithic Al₃Ti coating exhibited excellent oxidation properties and was hardly damaged, many cracks were observed in the IMC coating after oxidizing. Furthermore, TiO₂ scale was formed on the outer surface, though only a protective Al₂O₃ film was formed on the monolithic Al₃Ti coating. Pregger et al. investigated the isothermal oxidation of a NiAl/TiB₂ composite and showed that the oxide scale formed on it...
is not entirely protective [19]. They also indicated that TiB₂ dissociated within the void regions leading to the outward diffusion of titanium through the oxide scale and to the formation of TiO₂ at the outer surface. In this research, it seems that TiB₂ decomposes, Ti diffuses outward and TiO₂ is formed, similar to the results of their research. Since TiB₂ is not a proper reinforcement particle for obtaining excellent oxidation properties, other particles, such as Al₂O₃, should be applied.

4. Conclusions

A TiB₂ reinforced intermetallic compound Al₃Ti composite was formed by reactive-pulsed electric current sintering from MA powders of Al–Ti–TiB₂ or Al–Ti–B, and was simultaneously joined to a Ti substrate. The main results obtained in this research are presented below.

(1) A fully dense Al₃Ti/TiB₂ composite was formed by PECS of Al–Ti–TiB₂ MA powders at 1173 K for 600 s. Using the Al–Ti–B MA powders needed higher temperature 1273 K for full densification although the grain size of in-situ formed TiB₂ became smaller down to 300 nm.

(2) The existence of TiB₂ in coatings enhanced the elimination of voids on the IMC/Ti joint by deforming the surface of substrate, although it suppressed the growth of reaction layers formed at the bonding interface due to the decreased effective diffusion path between coating and substrate.

(3) While the microhardness and wear properties of Al₃Ti coating could be improved by the reinforcement of TiB₂, oxidation properties at 1273 K were degraded due to the decomposition of TiB₂ to elemental Ti and B.

Acknowledgements

The authors thank T. Wakita, Osaka University for his help in experimental work.

References