PREPARATION AND PROPERTIES OF BORIDE LAYERS ON TIAL INTERMETALLICS

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Abstract

Ti-46.6Al, Ti-45.2Al-7.2Nb and Ti-44.8Al-6.6Ta alloys were borided by a simple pack-boriding method in this work. After boriding at 1150 °C for 12 hours the layer deposited on the binary alloy exhibited a homogeneous both structure and chemical composition. The layers on the ternary alloys were thicker than those on the binary alloy with significantly higher structural and chemical heterogeneity. The mixed borides TiB2.NbB2 or TiB2.TaB2 were formed on the surfaces of these alloys, and monoboride whiskers were found at the boride/substrate interface. The surface hardness and the wear resistances of the examined alloys were significantly improved through their boriding.

Keywords:
Titanium aluminides, boriding, pack cementation, hardness, wear resistance

1. INTRODUCTION

TiAl-based intermetallics are promising materials for high-temperature applications in the automotive, aerospace and power industries, where they can replace the Ni superalloys currently used. Because they are at least two times lighter than the nickel superalloys, the TiAl intermetallics bring significant weight reduction to devices. In addition to their low density, TiAl intermetallics are characterized by a high elastic modulus, and they exhibit greater strength and higher oxidation resistance at elevated temperatures in comparison to pure titanium [1]. However, these high-temperature properties are often insufficient; therefore, various alloying elements have been proposed for their improvement. In our previous studies, Nb and Ta were added to TiAl intermetallics and significantly increased their oxidation and creep resistance at 800 °C [2]. Niobium improves the creep resistance of the alloy by hindering dislocation slip and plastic deformation in the material. It also increases the high-temperature oxidation resistance through the so-called doping effect and supports the formation of an Al2O3 layer, which acts protectively against the high-temperature cyclic oxidation. However, the mechanism of the effect of Nb on the formation of Al2O3 is still unclear [3]. Because of its position in the periodic table, Ta is believed to exert an influence on the mechanical and chemical properties of TiAl-based intermetallics similar to that induced by niobium. This hypothesis was proven in our previous studies [2], and the mechanism of the influence of tantalum was similar to that of niobium. The TiAl-based intermetallics alloyed with tantalum are known as the last generation of TiAl intermetallics, which are often called the 4th generation [4]. These alloys are air-hardenable, and they are formed by alloying with elements that significantly reduce diffusion to achieve massive transformations at low cooling rates. The massive transformation enables the creation of a highly faulted γ massive phase, which is beneficial to the mechanical properties of the alloys [4, 5].

Despite their excellent properties, TiAl-based intermetallics are not suitable for wear-related applications because of their insufficient hardness [2]. To adapt TiAl-based intermetallics to these applications, various treatments have been applied to the surface of TiAl intermetallics to enhance their mechanical and chemical properties [6-9]. Apart from these techniques boriding is a promising way of improving the properties of alloy surfaces; moreover, when performed using the powder-pack boriding technique, it is also economical. However, few articles related to this topic have appeared [10]. In contrast, the boriding of pure titanium or the TiAl6V4 alloy has been widely discussed, and various methods have been described [11-13]. The most
commonly used technique is conventional powder-pack boriding, which is characterized by its simplicity and cost-effectiveness. It is often performed using a powder that contains the boron agent, an activator and a filler material at a high temperature, which causes the boron to be released from the agent by the activator. After the boron is released, it diffuses interstitially into the titanium lattice. The products of this process are dual TiB (inner) and TiB₂ (outer) layers deposited on the surface of the specimens, and these layers are characterized by high hardness and improved wear and oxidation resistance. As previously mentioned, data concerning the boriding of TiAl-based intermetallics are limited, and no data concerning the evaluation of deposited boride layers in relation to their mechanical and chemical properties and their protecting effect have been reported. To fill this significant gap, we considered the boriding of TiAl-based intermetallics (binary Ti-46.6Al, ternary Ti-45.2Al-7.2Nb and Ti-44.8Al-6.6Ta) in this work. We proposed a mechanism for the creation of borided layers and evaluated their structure, composition and mechanical properties.

2. MATERIAL AND METHODS

Boriding was applied to three alloys with the chemical compositions (in at. %) of Ti-46.6Al, Ti-45.2Al-7.2Nb and Ti-44.8Al-6.6Ta. During the boriding process, the samples were placed in a boriding powder and sealed in corundum crucibles, and an argon atmosphere was maintained to prevent oxidation. The boriding powder consisted of amorphous B (45 w. %), NH₄Cl (3 w. %) as an activator and Al₂O₃ (52 w. %) as a filler. The process was conducted at 1150 °C for 12 hours. These conditions were determined to be optimal after a series of experiments based on data retrieved from the literature [10, 11]. The borided samples were subjected to microstructural investigations which included both surface and cross-sectional analyses of the deposited layers and were performed using various analytical techniques, including SEM-EDS (Tescan VEGA 3 with attached ED spectrometer, acceleration voltage of 20 kV), WDS (Jeol JXA-733 Superprobe with attached WD spectrometers), X-ray diffraction (Phillips X’Pert, 30 mA, 40 kV, Cu Ka X-ray radiation) and glow discharge optical emission spectroscopy (GDOES, GD Profiler 2, Ar pressure of 650 Pa, source operated at 50 W, approximate sputtering rate of 2.5 μm/min). Concerning the mechanical properties the microhardness measurements were performed on a Struers Duramin-2 microhardness tester and the abrasive wear resistance was evaluated using a modified version of the pin-on-disc method [14], in which the pin was the tested material and the disc was P1200 grinding paper. The applied load was 5.8 N, and the sliding distance was defined as 2500 m. The wear rate was calculated from the measured weight losses according to Eq. (1) [15]: \( w = \frac{(\Delta m.1000)}{(S.l)} \), where \( w \), \( \Delta m \), I and S are the wear rate (mg.cm⁻².m⁻¹), weight loss (g), contiguous surface (S) and sliding distance on the grinding paper (m), respectively. The pin in this modified version did not follow the spiral path on the disc.

3. RESULTS AND DISCUSSION

3.1 Structure and composition of boride layers

As a result of the boriding process, atomic boron diffuses into the structure of the exposed alloy. Boron has very limited solubility in both the γ- and α₂-phases [16], so the boride layer forms rapidly on the surface of the exposed alloy. Further growth of this layer is then controlled by the diffusion rate of the boron in the boride towards the substrate. In the case of the TiAl-based alloys, the layer could be theoretically formed by both TiB₂ and AlB₂ borides. However, the thermodynamic stability of the borides is significantly higher for TiB₂ than for AlB₂ because their Gibbs free energies of formation at 298 K are -320 kJ/mol and -151 kJ/mol, respectively [17]. Therefore, the formation of TiB₂ is favored at the expense of AlB₂.

The back-scattered electron micrographs in Fig. 1 show cross-sections of obtained borided layers with thicknesses of 6.6 ± 0.7 μm, 8.9 ± 0.7 and 17 ± 3.4 μm on the Ti-46.6Al, Ti-45.2Al-7.2Nb and Ti-44.8Al-6.6Ta alloys, respectively. Theirs values correspond to the development of the elements concentration profiles measured using the GDOES method (Fig. 2). As evident in Fig. 1, the layer created on the binary alloy is
homogenous, and almost no whiskers of borides growing towards the substrate are observed (Fig. 1a). The layer on the Nb-containing alloy is primarily homogenous with some signs of heterogeneity, and it contains some boride whiskers growing towards the substrate (Fig. 1b). In contrast, the boride layer created on the Ta-containing alloy is significantly thicker and heterogeneous (Fig. 1c). The micrograph indicates that the layer consists of two sublayers, although their interface is not clearly distinguishable. The outer layer is highly heterogeneous and consists of easily observable dark and bright grains. The inner layer consists primarily of whiskers growing towards the substrate. This morphology suggests that the inner layer contains the boride TiB. Although the formation of TiB is only observed in the case of the Ta-containing alloy during our experiments, the literature contains reports of TiB whiskers being commonly found after boriding of the Ti-6Al-4V alloy [13]. The presence of TiB beneath the TiB$_2$ outer layer is generally explained by the fact that the concentration of boron in the matrix progressively decreases towards the alloy interior. The fact that the boride layers are created by TiB$_2$ and in the case of Ta-containing alloy by TiB as well is supported by results chemical composition analysis performed by WDS technique (Table 1) and also further confirmed by the results of XRD analysis (see Fig. 3). Moreover the XRD analysis revealed the existence of the mixed NbB$_2$.TiB$_2$ boride in the case of Nb-alloyed sample and the mixed TaB$_2$.TiB$_2$ boride in the case of Ta-alloyed sample. The boride layer formed on the surface of the latter sample exhibited more pronounced differences in the distribution of the ternary element which suggests that a larger amount of the TaB$_2$.TiB$_2$ was formed on this sample than the amount of the NbB$_2$.TiB$_2$ formed on the Nb-containing sample. The presence of the BN phase in the surface layers (Fig. 3) on all of the studied alloys is in agreement with the results of other authors [9], which show that this phase is a product of the reaction between boron and the NH$_4$Cl activator.

The gradual decrease in the relative intensity of boron in the direction of the matrix in the GDOES profiles (Fig. 2) suggests that the interface between the boride layer and the matrix exhibits a diffusive character. The relative intensity of nitrogen is observed to increase slightly at the beginning of all the GDOES profiles, which indicates the presence of a thin boron nitride (BN) layer on the surface of the borided layer (see Fig. 3). In the case of the ternary alloys, the distribution of Nb and Ta in the boride layers and in the base material shows no gradients.
3.2 Mechanical properties of borided coatings

Figure 4 shows the Vickers hardness measured on the surface of the boride layers compared with the Vickers hardness of the base alloys in the as-cast state. The boride layers are more than three times harder than the base alloys, and the Vickers hardness of the borided layers increases in the following order of the base alloys: Ti-46.6Al < Ti-45.2Al-7.2Nb < Ti-44.8Al-6.6Ta. The large standard deviations are produced by heterogeneities found on the surface (oxidic species, boriding powder residues, etc.). These heterogeneities are also responsible for the differences between the hardness values measured on the surface and those measured on the cross-section of the borided layers (see Fig. 5).

### Table 1 Element concentrations at the points indicated in Fig. 1

<table>
<thead>
<tr>
<th>Position</th>
<th>TiAl</th>
<th>TiAINb</th>
<th>TiAlTa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Al</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>37.8</td>
<td>0.0</td>
<td>62.2</td>
</tr>
<tr>
<td>2</td>
<td>35.7</td>
<td>0.0</td>
<td>64.3</td>
</tr>
<tr>
<td>3</td>
<td>34.4</td>
<td>0.0</td>
<td>65.6</td>
</tr>
<tr>
<td>4</td>
<td>32.2</td>
<td>0.0</td>
<td>67.8</td>
</tr>
<tr>
<td>5</td>
<td>31.1</td>
<td>0.0</td>
<td>68.9</td>
</tr>
<tr>
<td>6</td>
<td>31.5</td>
<td>0.0</td>
<td>68.5</td>
</tr>
<tr>
<td>7</td>
<td>39.0</td>
<td>37.5</td>
<td>23.5</td>
</tr>
<tr>
<td>8</td>
<td>47.5</td>
<td>50.6</td>
<td>1.9</td>
</tr>
<tr>
<td>9</td>
<td>49.4</td>
<td>50.1</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>51.1</td>
<td>48.9</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The observed increase in the hardness caused by boriding corresponds to the general purpose of the boride layers, which is to enhance the mechanical properties of the surface. The differences between the Vickers hardness values of the boride layers on particular alloys can be explained by the presence of mixed NbB<sub>2</sub>·TiB<sub>2</sub> or TaB<sub>2</sub>·TiB<sub>2</sub> borides. The mixed borides are formed when atoms of niobium or tantalum replace titanium positions in the lattice. Because the Nb and Ta atoms are larger than those of Ti, lattice stress is induced, which produces higher Vickers hardness values. As previously mentioned, this effect is more pronounced in the case of the layer formed on the surface of the Ta-containing alloy; therefore, its hardness is the highest. Another reason for the higher hardness values of the Ta-containing alloy is the greater thickness of the borided layer (Fig. 1). The effect of the soft base alloy is minimized in this case.
Wear tests were performed to determine the wear resistance of the boride layers. Both the borided and as-cast alloys were subjected to wear tests to assess and evaluate the effect of the boriding process. The results of the wear tests are summarized in Fig. 6 as relative wear rates (RWRs), which are wear rates related to the maximum wear rate of the Ta-containing alloy. It is evident from the figure that the boriding technique used in our experiments provides highly wear-resistant layers with RWR values of approximately 2%. Figure 6 also shows that the wear resistances of the as-cast alloys differ. The RWR values vary between 75 and 100%, and the Ta-containing alloy exhibits the worst wear resistance (RWR of 100%). The Nb-containing alloy and the binary alloy exhibit similar RWR values of 78% and 75%, respectively. These differences are somewhat surprising because the Vickers hardness results shown in Fig. 4 suggest that all of the alloys should have approximately equal wear resistance. This difference may be related to the presence of a network of the γ-phase in the structure of the Ta-containing alloy [2]. This network most likely reduces the intercohesion of the lamellar grains; therefore, parts of the grains may be easily torn out, thereby reducing the wear resistance.

4. CONCLUSIONS

Three TiAl-based alloys, one binary, one Nb-alloyed and one Ta-alloyed, were borided in this work. The presence of borides on the surfaces of the alloys caused an increase in the hardness of the surface, up to 3500 HV 0.01. The layer formed on the binary alloy was chemically and structurally homogeneous, whereas
those formed on the ternary alloys exhibited heterogeneity, and the presence of mixed borides was observed. Moreover, TiB monoboride whiskers occurred at the interface between the external boride layer and the base alloy in the case of the Ta-containing alloy. These whiskers in the case of the Ti-44.8Al-6.6Ta alloy and the stress in the lattice induced by the presence of Nb and Ta atoms in the mixed borides increased the surface hardness of the borided ternary alloys in comparison with that of the binary alloy. The presence of mixed borides was much more significant in the case of the Ta-containing alloy which, in addition to the presence of TiB monoboride whiskers, caused the Ta-containing alloy to have higher surface hardness than the Nb-containing alloy. The boriding process also significantly improved the wear resistance of all the examined alloys.

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**REFERENCES**


