TiAl Surface Coating on Titanium by Plasma Transferred Arc Surfacing and Its Oxidation Behavior

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In order to improve high-temperature oxidation resistance of titanium, fabrication of TiAl intermetallic compounds as a surface layer by plasma transferred arc surfacing (PTA surfacing) was investigated. Powder of unalloyed aluminum was fed into the plasma during the PTA surfacing and TiAl-based intermetallic layers were successfully synthesized. The surface layers had no cracks and porosities with optimized conditions of the PTA surfacing. The surface layers that largely consist of TiAl and Ti₃Al phase could be achieved, while the microstructures of them were significantly influenced by the conditions such as the arc current. The TiAl-based layers exhibited high resistance to oxidation under isothermal conditions at 1073 K or less and had practically the same resistance as SUS310S had.

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1. Introduction

The combination of high strength, low density and excellent corrosion resistance makes titanium and its alloys useful mainly in aerospace and chemical application. Such characteristics are suitable for automobile and jet-engine application, which enable us to achieve lightweight vehicles and high performance engines. On the other hand, titanium often results in seizure due to frictional heat caused by low heat conductivity of titanium. Moreover, oxidation of titanium proceeds rapidly over the temperature of 873 K because of its strong affinity for oxygen and hydrogen at elevated temperature.

TiAl-based intermetallic compounds (IMC) are promising for automobile and jet-engine application due to their low density and excellent high temperature strength. TiAl-based IMCs, however, requires highly-developed skills in hot plastic working, and their ductility at ambient temperature is not adequate for practical use. Therefore, some production processes of bulk and molding materials were investigated. The manufacturing process by isothermal forging and by isothermal rolling, the production of sintered compact by hot pressing of mechanically alloyed powder, and the production by reactive sintering are nearly in the stage of practical use.

We succeeded in producing NiTi and NiAl-base intermetallic surface layers by plasma transferred arc (PTA) surfacing, because use of IMCs in the form of a surface layer seems to be considerably efficient. Furthermore, producing a NiTi surfaced layer on a titanium substrate improves the wear resistance of the substrate without spalling of the layer occurring. As for the production of TiAl surface layers, however, deposition by Nd:YAG laser and by reactive thermal spraying and thin film by ion plating were reported.

Therefore, the purpose of the present paper is to produce TiAl intermetallic deposit by the PTA surfacing and to improve the oxidation resistance of the substrate. The surfacing powder used was unalloyed powder of aluminum. Microstructure and oxidation behavior of the surface deposits were investigated.

2. Experimental Procedure

The PTA surfacing is a surfacing process. The plasma arc is generated between the tungsten electrode and the substrate. Surfacing powder as a filler material is supplied into the plasma arc where it melts and fuses with the substrate. The conditions of the PTA surfacing are tabulated in Table 1. The electrode had a negative polarity and the torch oscillated at the amplitude of 6 mm. The PTA surfacing was carried out without preheat, although preheat has an effect on the prevention of cracking due to reducing the weld metal cooling rate.

The PTA surfacing was performed on substrates 50 × 120 × 8 mm of titanium (TP340H in accordance with JIS H4600). Powder of unalloyed aluminum was employed as surfacing powder. The composition of the powder is tabulated in Table 2. The particle diameter of the powder ranged from 75 to 147 μm.

The microstructure was assessed on the cross sections of single-pass surfacing deposits. Optical and scanning electron microscopic (SEM) observations, energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) analysis were performed.

The oxidation behavior of surfacing deposits has been

<table>
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<th>Table 1 Conditions of plasma transferred arc surfacing.</th>
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<td>Plasma arc current</td>
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<td>Travel speed</td>
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<td>Powder feeding rate</td>
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<tr>
<td>Plasma gas</td>
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<tr>
<td>Powder carrier gas</td>
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<td>Shielding gas</td>
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<td>Manipulation of electrode</td>
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<th>Table 2 Chemical composition of surfacing powder used (mass%).</th>
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<tr>
<td>Si</td>
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<tr>
<td>Aluminum</td>
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studied in air with isothermal conditions at 973, 1073 and 1173 K up to 432 ks (120 h). The oxidation resistance was evaluated by thickness of the oxide films formed on the surfacing deposits. The deposits were cut into test pieces 9 × 6 × 6 mm, as shown in Fig. 1. Prior to the oxidation tests, the measured surfaces of the test pieces were polished into a mirror finish. The transverse sections of oxidized surfaces were examined using SEM and EDX. For comparison, 25Cr–20Ni steel (SUS310S) and Co–Cr–W alloy (Stellite 6) deposits by PTA surfacing were examined as reference materials.

3. Results and Discussion

3.1 Formation of surface layer and microstructure

The optical micrographs of the surface layer with a current of 70 A and a travel speed of 1.6 mm/s (condition TA75) are shown in Figs. 2(a) and (b), while the structures and the morphologies are influenced by arc current and travel speed. The cross-sectional macrostructure was nearly uniform and had no defects such as cracking, spalling and porosities. The layer featured relatively smooth surface and had no obvious surface defects. The microstructure revealed typical lamellar structure and intergranular constituents, as shown in Fig. 2(b). The microstructure of the surface layer with a current of 75 A and a travel speed of 1.6 mm/s (condition TA95) revealed coarser lamellar structure than that of the TA75 layer, as shown in Fig. 2(c). Defects such as cracking and so on were not observed also for the condition TA95. The surface layer with a current of 65 A and a travel speed of 1.6 mm/s embrittled all over because the layer consisted of TiAl (γ) single phase including Al content of around 56 at% higher than TiAl stoichiometry. The hardness values of the TA75 and the TA95 layers uniformly ranged from 400 to 480 HV and hardened areas near the interface between the surface layer and the substrate were not observed.

Figure 3 shows SEM micrographs and EDX analysis results in the center of the surfacing layers. Both the TA75 and the TA95 deposits featured the lamellar structures and the intergranular constituents, although the lamellar grain size of the TA75 deposit was finer than that of the TA95 deposit. Furthermore, the both microstructures had no defects such as cracking and spalling. EDX analysis revealed the lamellar structure to be consisting of Ti₃Al (α₂) and TiAl (γ) phases, where Al contents with the TA75 and the TA95 deposits are 47.7 and 45.1 at%, respectively. Since the structure is very fine, EDX analysis is unable to distinguish the individual phases. EDX analysis further revealed the intergranular constituents to be γ phases owing to the Al contents of 54.2 and 51.4 at%.

![Fig. 1](image1.png) Location of oxidation test specimen and measured surface.

![Fig. 2](image2.png) Optical micrographs of TiAl surfacing deposit. (a) Macrostructure, (b) and (c) Center of the deposit.

![Fig. 3](image3.png) SEM images and EDX spot analyses of TiAl surfacing deposit. (a) TA75, (b) TA95.

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<th>Al</th>
<th>Ti</th>
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<tr>
<td>A</td>
<td>47.7</td>
<td>52.3</td>
</tr>
<tr>
<td>B</td>
<td>54.2</td>
<td>45.8</td>
</tr>
<tr>
<td>A'</td>
<td>45.1</td>
<td>54.9</td>
</tr>
<tr>
<td>B'</td>
<td>51.4</td>
<td>48.6</td>
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According to the phase diagram, the TA75 and the TA95 deposits should correspond to the $\alpha_2 + \gamma$ phase field. It appears that the lamella structure forms by nucleation and growth of $\gamma$ plates as a result of transformation from the $\alpha$ phase field during cooling to the $\alpha + \gamma$ phase field. On further cooling, the $\alpha$ phase is ordered to the $\alpha_2$ phase and then the $\alpha_2 + \gamma$ lamellar structure forms.\(^{15}\) The difference in grain size between the TA75 and the TA95 deposits is attributed to a change in arc current. Since the condition TA95 was an arc current of 75 A, which is larger than the TA75 by 5 A, the Al content decreased to 45 at% due to an increase in dilution by the Ti substrate. $\beta$-Ti can form in that Al composition.\(^{16}\) Moreover, an increase in arc current made the cooling rate lower. Thus, it appears that an increase in the amount of primary crystallization caused coarsening of $\beta$-Ti. Since $\beta$-Ti is only stable at high temperature, it readily transform to the $\alpha$ phase and then the $\alpha_2 + \gamma$ lamellar structure on cooling.

The X-ray diffraction patterns of the TiAl surfacing deposits under the conditions of three arc currents are shown in Fig. 4. XRD analysis confirmed the presence of TiAl and Ti$_3$Al intermetallic compounds for all the conditions, while the arc current varied from 70 to 80 A. As the arc current increases, $\alpha$-Ti was slightly detected in the XRD analysis. It seems that a part of $\alpha$-Ti was not transformed to $\alpha_2$ because of rapid cooling upon the leaving of the PTA torch.\(^{11}\)

The microstructure of the TiAl surfacing deposits is directly related to the composition of the molten metal and the cooling rate, but the surfacing deposits with the uniform microstructure and composition are produced by the PTA surfacing under the proper conditions like the TA75.

### 3.2 High-temperature oxidation behavior

Figure 5 shows SEM micrographs and EDX analysis result of the oxide film on the TA75 deposit after the oxidation test at 1073 K for 345.6 ks. Thin oxide film at a thickness of 1–2 $\mu$m formed uniformly on the surface and no spalling of the film occurred. The deposit had no voids right under the oxide film. EDX analysis revealed that O, Al and Ti were distributed equally in the oxide film, and aluminum oxide and titanium oxide mingled. The oxide film of at least two layers was found, as in Fig. 5(a). The oxide film of TiAl are reported to be composed of three layers, i.e., TiO$_2$, Al$_2$O$_3$ and TiO$_2$ + Al$_2$O$_3$ from the outer side.\(^{17,18}\) Although such three layers were not observed clearly at 1073 K, the oxide film layer enriched in aluminum which was interposed between two oxide film layers enriched in titanium was observed at 1173 K.

The relation between oxide film thickness and oxidation time is shown in Fig. 6. For a test temperature of 973 K, the film thickness on both the TA75 and the TA95 deposits was equal to that on SUS310S and Stellite 6 deposit [Fig. 6(a)]. For a test temperature of 1073 K, the film thickness on the TA75 deposit was nearly equal to that on SUS310S and Stellite 6 deposit, while the thickness on the TA95 deposit was slightly larger about 2 $\mu$m [Fig. 6(b)]. The oxide film thickness on the TiAl deposits besides SUS310S and Stellite 6 deposit seems to obey the parabolic law. For a test temperature of 1173 K, the oxide film thickness reached to 20–25 $\mu$m for 432 ks and spalling of the oxide film occurred.
Also at 1173 K, the TA75 deposit oxidized more slowly than the TA95 deposit.

The TA75 deposit oxidized slowly compared with the TA95 deposit. Shida and Anada have reported that the mass gains of TiAl during the oxidation decreased as the Al content of TiAl increased from 20.7 to 63.1 mass%. Since the standard free energy of formation of Al$_2$O$_3$ is lower than that of TiO$_2$, the oxidation can be retarded if a continuous Al$_2$O$_3$ layer forms. As to the effect of structure on oxidation, it is reported that the mass gains of single-phase $\gamma$-TiAl was small and those of the lamellar structure containing a large amount of $\alpha_2$ phases was large. However, it was not clear that the TA95 deposit had larger amount of $\alpha_2$ phases than the TA75 deposit. In this study, it appears that since both the TiAl deposits consisted of the lamellar structure and the intergranular $\gamma$ phase, the TA75 deposit with the higher Al content oxidized slowly.

4. Conclusion

The main results obtained in this study are summarized as follows:

(1) The PTA surfacing was capable of producing TiAl-based alloy surface layers on titanium substrate with unalloyed powder of aluminum.

(2) It was possible to produce the surface layers with no defects such as cracking and spalling.

(3) The surface layers mainly consisted of TiAl and Ti$_3$Al by XRD analyses.

(4) The TA75 surface layers showed the excellent oxidation resistance at 1073 K or less, which was nearly equal to that of SUS310S. The Al content of the surface layers affected on the progress of the oxidation.

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REFERENCES