Oxidation and Hot Corrosion Behaviour of Novel Ti(Al,O)/Al₂O₃ Composite Coatings Produced by Plasma Spraying

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(Received February 15, 2005; final form February 25, 2005)

ABSTRACT

Ti(Al,O)/Al₂O₃ composite powder was produced using high energy mechanical milling followed by heat treatment and grinding. Thermal plasma spraying was used to coat this powder onto Ti6Al4V alloy substrates. The high temperature oxidation and hot corrosion properties of the coatings were studied in dry air and Na₂SO₄ + NaCl vapour containing atmosphere. The results showed that Ti(Al,O)/Al₂O₃ coatings have a much improved oxidation and hot corrosion resistance compared to the substrate Ti6Al4V alloy. The oxide scales have excellent adhesion to the surface, showing superior scale spallation resistance. The mechanisms with which the coatings improved the oxidation resistance were studied based on microstructure analysis. It is believed this development can provide a new generation of coatings to the Ti based alloys, and will be able to raise the application temperature of Ti alloys from 900K to 1073-1173K.

1. INTRODUCTION

TiAl based intermetallic compounds have drawn great attention for their high strength and low density, and have been regarded as potential materials to replace Ni-based superalloys for turbine blades and engine parts. They have good high temperature mechanical properties but only a half of the density of Ni-based super alloys /1/. The drawbacks of TiAl intermetallics

as structural materials are the low ductility at temperature below 873K and insufficient oxidation resistance at temperatures above 973K. Many attempts has been made in order to overcome these shortcomings by modification of the microstructure using ternary alloying elements such as Nb, Cr and Si /2/. However, the achievements have been limited to a few special intermetallics. An alternative method, which introduces a second phase into intermetallic phases to form intermetallic matrix composites (IMCs), has been recognized as a promising way for structural applications /3/.

TiAl based intermetallics/Al₂O₃ composites consisting of interpenetrating phases have drawn great interest due to their unique structure, i.e. a continuous matrix penetrated by a three-dimensional alumina reinforcement network /4,5/. An *in situ* fabrication process of Ti(Al,O)/Al₂O₃ composite powders has been developed recently /6/. The process involves high-energy mechanical milling of powder blends consisting of cheap raw materials (i.e. anatase Ti oxide and Al powder) to produce Al/TiO₂ composite powder and heat treating to produce Ti(Al,O)/Al₂O₃ composite powder. The bulk Ti(Al,O)/Al₂O₃ composites obtained by sintering the as-milled Al/TiO₂ or as-reacted Ti(Al,O)/Al₂O₃ composite powders have shown superior oxidation resistance and excellent scale spallation resistance up to 1173K /7,8/. However, the high brittleness of these composites limits the scope of application of these materials in making structural components. An attempt has been made in previous

work aiming to overcome this limitation by using the composite powder as a feedstock material to produce thermal spraying coatings [9]. The present work is a systematic study on the oxidation and hot corrosion properties of thermal sprayed coatings of Ti(Al,O)/Al₂O₃ composites on Ti6Al4V substrates. To compare these novel coatings with high temperature alloys, NiCrAlY and NiCrAl coatings were also applied on Ti6Al4V sheets and tested.

2. EXPERIMENTAL

2.1 Composite powder production

The raw materials used to produce the composite powder were TiO₂ powder (99.5%) with particle size ranging from 100~200 nm and Al powder (99.5%) with size of 50~300 μ m. TiO₂ and Al powders were blended at a molar ratio of 3:4 with 5 mass % surplus Al. The milling was performed in a discus mill. During the milling operation, the bowl vibrated at a high frequency, causing the discuses shift, rotate and vibrate at a high speed. In this way the powder in the milling bowl experienced high-energy impacts and repeated deformation.

Each charge to 500 g of the powder mixture together with 10 ml of isopropyl alcohol as the process control agent was used. The milling was conducted under an Ar atmosphere for 2 hours. The as-milled powder was thereafter heat treated at 1073K for 2 hours in Ar. Then the powder was characterised by using X-ray diffraction (Bruker D8 Diffractometer) and scanning electronic microscopy (Phillips XL-30S FEG-SEM). After heat treatment, the composite powder was further ground with a centrifugal mill (Retsch S100) and sieved with a mechanical shaker. The particles with size of 38~60 μ m was selected for thermal spraying.

2.2 Plasma spraying

The substrates were rectangular coupons of Ti6Al4V plate with a size of 15×10×2 mm. The coupons were blasted with Al₂O₃ particles at a pressure of 20 Psi before spraying. A specially designed sample holder was used to ensure the deposition covers the full surface of the coupons.

Plasma spraying was carried out using a 2MC Metco Plasma Spray Gun. The plasma spray conditions were listed in Table 1.

Table 1
Condition for the plasma spraying

Parameter	Condition1	Condition 2
Voltage (V)	50	65
Current (A)	400	500
Argon gas (l/min)	80	80
Hydrogen gas (l/min)	20	20
Feed rate (g/min)	40	40
Spray distance (mm)	200	200

NiCrAl and NiCrAlY coatings (Ni122 and Ni164/211, Praxair Surface Technologies) were also sprayed onto the Ti6Al4V substrates with the same spraying conditions.

2.3 Oxidation and hot corrosion tests

Isothermal and cyclic oxidation tests were carried out at 1073K in ambient air. The hot corrosion was conducted at 1073K with the presence of 80 mass % Na₂SO₄ + 20 mass % NaCl salts vapour. The specimens were suspended with hooks in a covered crucible containing molten mixture salts, where they were surrounded by the salt vapour. After a certain time of exposure, the specimens were withdrawn from the crucible, cooled in air, washed in boiling water to remove salt deposition on the surface and dried in hot air. Then the mass changes caused by the exposures were measured using an electronic balance (accuracy 0.01 mg). The reaction kinetics obtained by this method was quite reproducible as the corrosion conditions were easy to control.

The specimen surface and the cross-sections were examined with HRSEM/EDS. The corrosion products were characterized using an XRD with Cu-K α radiation source.

3. RESULTS AND DISCUSSION

3.1 Powder characterisation

The microstructure of the as-milled powder particles is as shown in Fig. 1. The particles exhibited a sandwich structure with one or several deformed Al cores incorporated with surrounding TiO_2 particles. After heat treatment, the XRD phase analysis showed that the

composite consists of $\text{Ti}(\text{Al},\text{O})$, $\text{Ti}_3\text{Al}(\text{O})$ and Al_2O_3 (Fig. 2). SEM examination revealed that the microstructure of the heat treated particles consists of discrete Al_2O_3 particles (dark phase in Fig. 3) embedded in $\alpha\text{-Ti}(\text{Al},\text{O})/\alpha_2\text{-Ti}_3\text{Al}(\text{O})$ matrix (white phase in Fig. 3). The majority of the particles were sized in the range of 20–40 μm after grinding, which was favourable for the plasma spraying.

Fig. 1: Optical micrograph of the cross sections of the powder particles in the as-milled Al/TiO_2 composite powder

Fig. 2: XRD pattern of the heat treated $\text{Ti}(\text{Al},\text{O})/\text{Al}_2\text{O}_3$ composite powder.

Fig. 3: Cross sectional morphology of typical Ti(Al,O)/Al₂O₃ composite powder particle obtained after heat treatment and crushing.

The TiO₂-to-Al molar ratio was chosen as 3:4 in the starting powder blend to yield the Ti(Al,O)-Al₂O₃ composite throughout milling and heat treatment. The nominal reaction was suggested as follows:

However, due to the slightly inhomogeneous mixing during milling, the local composition of Al/TiO₂ composite particle can be different from the average composition of the blend. Therefore the reaction could also happen as follows:

It is generally accepted that coatings with fine microstructure are desirable in order to achieve good performance [10]. The microstructure of the composite powder obtained by the present process can be controlled by milling duration. It has been found that the size of the Al₂O₃ particles decreases with increasing milling time up to ~6 hours in a similar discus milling process [11].

3.2 Plasma sprayed coatings

Fig. 4 shows the surface and cross-sectional morphologies of the plasma sprayed coatings. The surface morphology of the coating indicates that the particles were partially melted during the transfer; and the size of the splats varied due to the wide range of particle size.

The XRD analysis and SEM cross section examination (Fig.4b) showed that the phases and microstructure of the coatings are similar to those of the typical composite powder particles, except for that some of the Al₂O₃ particles (dark areas) were longitudinally deformed, and became significantly coarsened. This was probably caused by the high speed impacts that occurred when the partially molten particles hit the substrate surface. Pores with a size of 10~20 μm can be seen inside the coating; and they are expected to degrade the high temperature performance of the coatings. The thickness of the coating is in the range of 80~100 μm. No morphological difference can be seen from the composite coatings produced with two sets of spraying parameters listed in Table 1.

(a)

(b)

Fig. 4: The surface (a) and cross-section (b) morphologies of the plasma sprayed coating.

3.3 Oxidation and hot corrosion properties

Figures 5 and 6 show the results of isothermal and cyclic oxidation tests. Ti(AlO) -1 and Ti(AlO) -2 are the coatings produced by plasma spraying using condition 1 or 2, respectively. Kinetics of the commercial MCrAl

coatings was also plotted on the same graph for comparison. All oxidation kinetics followed a parabolic law, while the NiCrAl and NiCrAlY showed less mass gain than $\text{Ti(Al,O)}/\text{Al}_2\text{O}_3$ composite coatings. However, no spallation was found from all coatings during the oxidation tests.

Fig. 5: The kinetics of the iso-thermal oxidation test at 1073K.

Fig. 6: Kinetics of the cyclic-oxidation test at 1073K.

Figure 7 shows the results of hot corrosion tests. It can be seen that the corrosion reaction during the tests still obeys a parabolic law. NiCrAlY coating showed the best performance in all three tests. However, Ti(Al,O)/Al₂O₃ composite coatings also showed protective behaviour under this severe hot corrosion condition.

Compared with our previous work on the similar Ti(Al,O)/Al₂O₃ based composites, which showed excellent oxidation resistance at 973K – 1173K [7,8], the present coatings did not reach that level. The main reason of this is probably that the porosity of the coatings is higher than that of the bulk composites. The oxidation rate is therefore high, especially at the early stage of the test (first 20 h as shown in Figs. 5 and 6). The oxidation rates of Ti-Al based composite coatings were faster than MCrAl coatings only at the first stage of exposure, because there was a very large reaction area when the coatings are porous. It can be seen that the oxidation rates of Ti(Al,O)/Al₂O₃ composite coatings are very similar to the MCrAl coatings after the first 20 hours' exposure, when the effects of porosity no longer play an important role.

Figures 8 and 9 show typical cross-section SEM

micrographs of Ti(Al,O)/Al₂O₃ and NiCrAlY coatings after 160 hours oxidation at 1073K. It can be seen that Ti-Al based coating contains a large amount of pores, while NiCrAlY coating showed a dense structure. This again supports the explanation for the results of oxidation and hot corrosion tests: the main reason for the relatively high oxidation rate of Ti(Al,O)/Al₂O₃ composite coatings is the high porosity of the coatings. This result also implies that the spray process is of great importance to the oxidation properties of the coatings since it strongly affects the microstructure and porosity of coatings. Optimisation of the coating process in order to produce less porous coatings is being conducted at the present time.

The most encouraging result from this work is that the Ti(Al,O)/Al₂O₃ composite coatings possess superior scale protective ability. No scale spallation could be observed during whole 200 hours high temperature exposure, including cyclic oxidation. The cross-section micrographs shown in Fig. 9 also indicated that the oxide formed was tightly bonded to the coating, and there was no gap or crack between the coating and alloy substrate.

Fig. 7: The kinetics of the hot corrosion test at 1073K with presence of 80 mass % Na₂SO₄ + 20 mass % NaCl salts vapour.

Fig. 8: Cross-section micrograph of CrNiAlY coating after iso-thermal oxidation at 1073K for 160 h.

Fig. 9: Cross-sectional morphology of Ti(Al,O)/Al₂O₃ coating after cyclic oxidation at 1073K for 200 h.

4. CONCLUSIONS

Ti(Al,O)/Al₂O₃ composite powder has been successfully produced by high energy discus milling and heat treatment. The microstructure of the composite powder particles consists of Al₂O₃ particles embedded in a Ti(Al,O)/Ti₃Al(O) matrix.

Plasma thermal spraying has been applied to produce Ti(Al,O)/Al₂O₃ composite coatings. The coatings have very good adhesion to the Ti6Al4V alloy substrates. However, the spraying parameters are yet to be optimised to reduce the porosity of the coatings.

Isothermal oxidation, cyclic oxidation and hot corrosion tests at 1073K indicated that the commercial NiCrAlY coating exhibits the best high temperature performances on Ti alloy substrate. The Ti(Al,O)/Al₂O₃ composite coatings showed a relatively high oxidation rates at the initial exposure stage due to the porosity inside the coatings. However, the oxide formed on the Ti(Al,O)/Al₂O₃ coatings showed excellent protective ability as no scale spallation can be seen during 200 hrs isothermal or cyclic oxidation.

ACKNOWLEDGEMENT

The project is partially supported by the Foundation for Research, Science and Technology, New Zealand through a Postdoctoral Fellowship and a NERF Grant. The authors would like to thank the Department of Chemical & Materials Engineering, and Research Centre for Surface and Materials Science, The University of Auckland, for various support. Dr. Byung-

Young Choi would like to acknowledge the financial support from the research funds of Chonbuk National University.

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