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EFFECT OF ALUMINIDE-YTTRIUM COMPOSITE COATING ON THE OXIDATION RESISTANCE OF TiAl ALLOY

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ABSTRACT

Yttrium(Y) coating was incorporated by ion-plating method either directly on the TiAl substrate or after pack aluminizing on TiAl to improve the oxidation resistance of TiAl alloy. After Y-coating, heat treatment at low oxygen partial pressure was carried out. Performance of various coating was evaluated by isothermal and cyclic oxidation tests. A simple Y-coating without pack aluminizing can give a detrimental effect on the oxidation resistance of TiAl alloy, because it enhances formation of TiO_2 . On the other hand, a composite coating of aluminide- yttrium has shown excellent oxidation resistance. A continuous protective Al_2O_3 scale is formed on the aluminized TiAl, and Y-coating improves Al_2O_3 scale adherence and substantially prevents depletion of Al in the aluminide-coating layer.

INTRODUCTION

Intermetallic compound TiAl alloy is expected to be one of the promising candidates for high temperature systems such as aircraft engines, because it has a high specific strength at elevated temperatures.^[1, 2] However, the major drawbacks of intermetallic compound TiAl as an engineering material are its poor room-temperature ductility and poor oxidation resistance above $800^\circ C$ ^[2]. The former has been successfully overcome by modification of the microstructure using ternary element addition or advance processing techniques. The latter can be improved to some extent by addition of alloying element such as Nb, Si or W. However, improvement of oxidation resistance by addition of alloying ele-

ment may not be desirable for practical application since alloying element may have deleterious effect on the mechanical properties of the material. Therefore, surface treatments are thought to be more attractive.

Although there are many coating processes for improvement of the high temperature corrosion resistance of TiAl alloy,^[3-10] diffusion coating seems to be the best. Al diffusion coating is widely used as a coating method for high temperature materials because of its practical advantages over other coating method. The high temperature oxidation resistance is dependent on the formation of a protective surface oxide scale that is stable and has a slow growth rate. The Al_2O_3 which forms on aluminide-coating layer generally meets these requirements. However, the main wea-

kness of Al_2O_3 scale is its susceptibility to cracking and spalling, especially under thermal cyclic condition. Therefore, one of the important requirements for a protective oxide scale to provide high temperature oxidation resistance is the scale adherence to the substrate. According to our previous study, oxygen active element (OAE) such as yttrium (Y) coating are found to improve the adherence of Al_2O_3 scales.^[11-13]

In this study, a composite coating by pack aluminizing and Y-coating has been performed to improve the oxidation resistance of TiAl alloy. Performance of composite coating is evaluated by isothermal and cyclic oxidation tests. To elucidate the role of composite coating, isothermal and thermal cyclic oxidation tests were carried out at 950°C. The purpose of this study is to establish a composite-coating process of pack aluminizing and Y-ion plating and examine the effect of Y-coating on the oxidation resistance of TiAl alloy.

EXPERIMENTAL PROCEDURE

The substrate material used in this study was a Ti-47.7Al-2.8Nb alloy. The TiAl alloy ingot was sectioned into $12 \times 10 \times 2$ mm specimens by electrical discharge machining. Prior to coating, all the specimens were polished by 1200-grit paper and ultrasonically cleaned in acetone.

The TiAl alloy coupons were coated by pack aluminizing using a high-activity process. Fifteen w/o of pure Al powder was used as a source metal, 3w/o of NH_4Cl powder as an activator, 82w/o of Al_2O_3 powder as a filler material, and Ar gas as a carrier gas. The high-activity pack aluminizing was carried out at 950°C for 6 hours.

Y was deposited by an ion-plating process. The initial vacuum level of the chamber and the substrate temperature were set to 10^{-5} torr at 400°C. The accelerator voltage of the electron beam was 10kV, and the biases voltage applied to the substrate was -200V. The ion-plating time was controlled for 10 minutes. The post heat treatment after Y-ion plating was performed at 950°C for 16 hours in a vacuum.

Isothermal oxidation tests were performed using Cahn 1000 thermogravimetric electrobalance apparatus. The weight change was observed as a function of test time. Oxidation tests were performed at 950°C in flowing air condition. After loading the specimens, the furnace was heated at a rate of 25°C/minute under helium environment until it reached the test temperature. Then, dry air was introduced and the weight change was measured with precision in a range of 10^{-6} g. The cyclic oxidation test was performed in a tube furnace equipped with a program controller providing a stable thermal cycle. For each cycle, the specimens were exposed at 950°C for 45 minutes and cooled at 100°C for 15 minutes. In general, the specimens were cooled to room temperature after every 20 cycles for weight measurement. Analysis of the oxide layer included phase identification using X-ray diffractometry, scale morphology and composition distribution using scanning electron microscopy with energy dispersive X-ray analysis.

RESULT AND DISCUSSION

Y-Ion Plating

Recent work in our laboratory has shown that the Y-coating on Ni_3Al can improve

high temperature oxidation resistance.^[11] Especially, the post heat treatment at low oxygen partial pressure after the Y-coating is essential to improve high temperature oxidation resistance of Ni₃Al. A simple deposition of the Y on Ni₃Al did not change the oxidation kinetics, but the Y-coating with post heat treatment decreased the oxidation rate of Ni₃Al. And the best cyclic oxidation resistance was obtained for the Y-coated Ni₃Al with post heat treatment.

In order to examine the effect of Y-coating on the oxidation resistance of TiAl alloy, the specimens were coated with Y by ion plating and post heat treatment was performed at low oxygen level. All the oxidation tests were performed at 950°C. Contrary to the case of Ni₃Al, Y-coating may give a det-

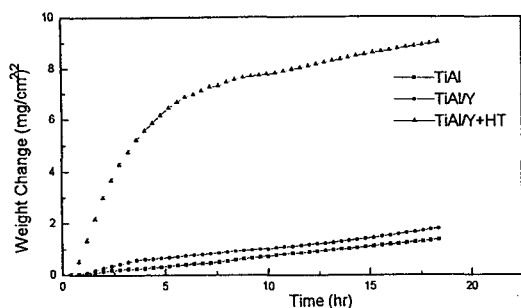


Fig. 1 Plot of square of weight gain per unit area vs. oxidation time at 950°C

perimental effect on the oxidation resistance of TiAl alloy. The isothermal-oxidation curves for the each specimen are shown in Figure 1 in parabolic plots. The Y-coated TiAl without post heat treatment (TiAl/Y) did not change the oxidation rate of TiAl alloy significantly. However, the oxidation rate of Y-coated TiAl alloy with post heat treatment (TiAl/Y+HT) was much larger than that of TiAl alloy.

After isothermal oxidation tests, the oxidized specimens were fractured in liquid nitrogen, and the fracture surface of the oxide scale were observed by SEM and energy dispersive X-ray analysis. Figure 2 shows the fractographs of the oxide scale formed on each specimen. The oxide scale formed on the TiAl alloy is multi-layered one consisting of TiO₂/Al₂O₃/TiO₂+Al₂O₃ from the gas side interface. This morphology was in good agreement with the one reported by other group.^[14] For the TiAl/Y and TiAl/Y+HT specimen, the oxide scales formed beneath the Y-coating layer are similar to that formed on the base TiAl alloy, although thickness of each layer was different. Especially, the thickness of oxide layer containing Ti-oxide in the TiAl/Y+HT specimen is very larger than that in the other specimen.

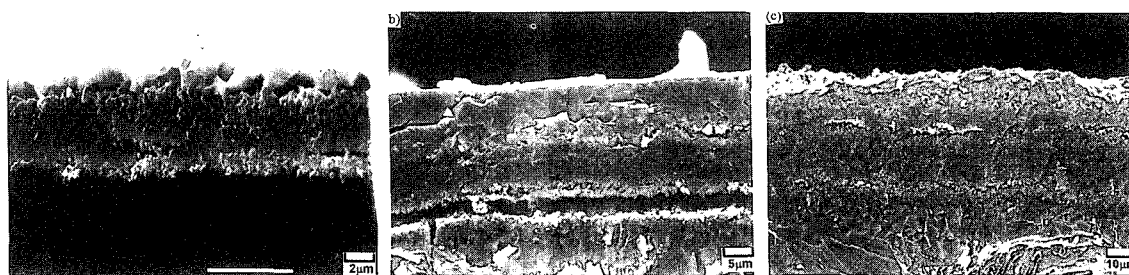


Fig. 2 Fractography of oxide scale formed on the various specimens after oxidation at 950°C for 20 hours. (a) TiAl (b) TiAl/Y (c) TiAl/Y+HT

Cyclic oxidation test was performed to evaluate the oxidation resistance of each specimen. Figure 3 shows the weight change per unit area of the three different specimens of TiAl, TiAl/Y and TiAl/Y+HT. In TiAl and TiAl/Y+HT specimens, significant spallation started after few cycles. The TiAl/Y specimen showed no weight loss up to about 40 cycles, after which time a significant decrease in weight was observed. This result indicates that Y-coating did not improve the oxidation resistance of the TiAl alloy at all.

In case of Ni₃Al, Y-coating layer could reduce oxygen partial pressure at the alloy surface and suppress the formation of NiO. However, Y-coating on the TiAl alloy can not suppress the formation of Ti-oxide. This difference can be explained from thermodynamic point of view. The oxygen equilibrium pressure of Al/Al₂O₃ is many orders of magnitude lower than that of Ni/NiO. On the other hand, the oxygen equilibrium pressures of Al/Al₂O₃ and Ti/TiO are very similar. Moreover, the activities of metals in the Ti-Al system can depart significantly from the ideal behavior.^[15] The oxygen equilibrium pressure of metal/oxide in the Ti-Al system can be calculated using the given thermodynamic data.^[16] Figure 4 shows the variation of the oxygen equilibrium pressure of Ti/TiO

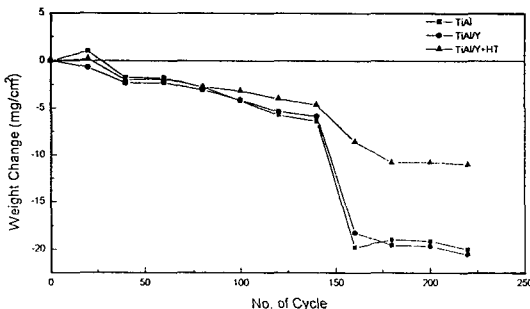
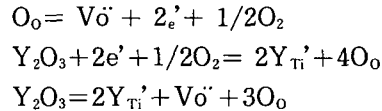


Fig. 3 Plot of weight change vs. number of cycle during cyclic oxidation test at 950°C

and Al/Al₂O₃ in the Ti-Al-O system. In the composition of specimen used in this study, the oxide TiO is more stable than Al₂O₃. Therefore, Ti-containing oxide was formed beneath the Y-coating layer.

The Y-coating enhanced the oxidation rate. This is probably due to the doping of TiO₂ with the Y that has a lower valence than Ti⁴⁺. Generally, the TiO₂ can take oxygen vacancies in the inwardly growing scale. According to Wagner-Hauffe theory, doping by the lower-valence cations in the N-type oxide causes an increase in the defect concentrations.^[17] The process can be represented by the following equations



The oxidation resistance of TiAl alloy can be obtained by formation of a continuous protective Al₂O₃ scale without Ti-containing

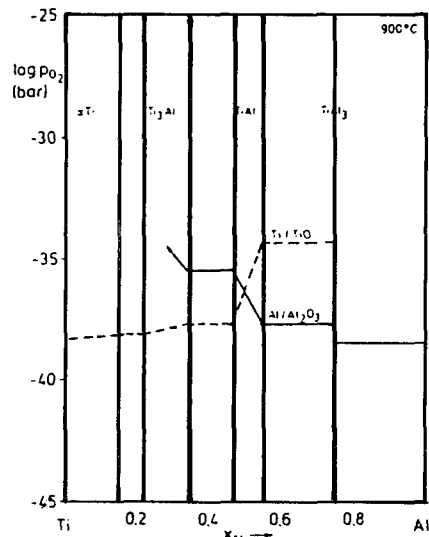


Fig. 4 Various of the metal/oxide equil. pressures in the Ti-Al-O system at 900°C^[16]

oxide. From these results, we suggest that the improvement of oxidation resistance of TiAl should be favored by increase in Al content up to the TiAl/TiAl₃ composition in the surface region.

Composite Coating of Pack-Aluminizing and Y-Ion Plating

When the surface is coated with TiAl₃, a protective Al₂O₃ film can be expected to form and improve the oxidation resistance. The oxidation resistance of the pack-aluminized coatings depends on the stability of Al₂O₃ scale forming on the coating layer. However, under thermal cyclic condition, Al₂O₃ layer easily spalls. Recently, Kim et al. have shown that Y-coating after pack aluminizing on the Ni-base superalloy improves the Al₂O₃ scale adherence and substantially prohibits the depletion of Al in the aluminide-coating layer.^[12, 13] Therefore, in order to examine the effect of composite coating on the oxidation behavior of TiAl alloy, a composite coating is prepared by high activity pack aluminizing followed by Y-ion plating (TiAl+PC/Y). And heat treatment at low oxygen pressure after Y-coating was performed (TiAl+PC/Y+HT).

Figure 5 shows the results of X-ray diffraction and EPMA analysis of aluminized TiAl alloy. These results show that the aluminized layer consisted of mainly of TiAl₃ layer. The thickness of TiAl₃ layer was approximately 70 μ m. Some cracks was found on the surface of the aluminized layer, particularly on a edge portion.

Isothermal oxidation tests were performed to understand the oxide growth mechanism of the composite coating. Figure 6 shows the weight gains of specimens with a single

aluminide coating (TiAl+PC) and the composite coating. The oxidation rate of TiAl+PC specimen is much smaller than that of TiAl alloy. This result indicates that a protective Al₂O₃ oxide scale has grown on the TiAl+PC specimen during oxidation test. For TiAl+PC/Y specimen, the isothermal oxida-

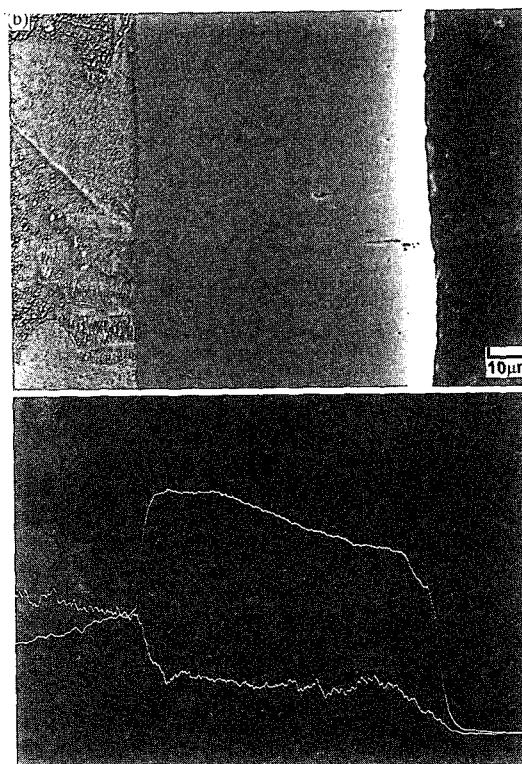
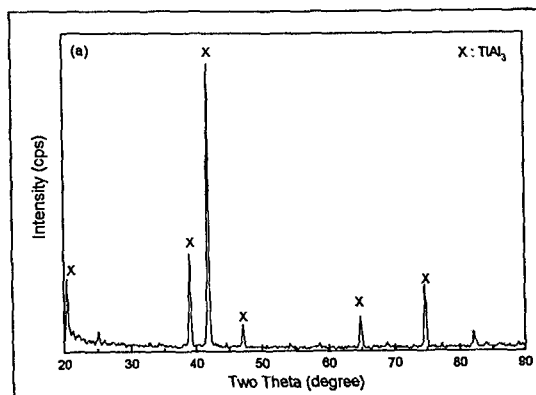


Fig. 5 (a) X-ray diffraction pattern and (b) EPMA analysis of aluminized TiAl alloy .

tion curve is classified into two parts. In the early stages of oxidation, the oxidation of this specimen is much faster than that of TiAl alloy. This is simply due to the additional amount of coated Y and the corresponding weight gain by oxidation of the coated Y. Similar behavior was also observed on TiAl+PC/Y+HT specimen. However, the fast increase in weight can not be explained by oxidation of coated Y, because coated Y has already been oxidized to Y_2O_3 during post heat treatment. It is expected that outward diffusion of small amount of Ti as well as Al occurred during post heat treatment. During oxidation test, this diffused Ti reacts with oxygen to form TiO_2 . Therefore, the fast increase of weight can be explained by oxidation of Ti. In the prolonged stage, however, the oxidation rates of TiAl+PC/Y and TiAl+PC/Y+HT specimens are similar to that of TiAl alloy.

Oxide scale formed on each specimen was also observed in cross section. Figure 7 shows fractographs of each specimen after oxidation for 100 hours. The alumina scale formed on TiAl+PC specimen shows a typical columnar structure. The oxide scale formed on TiAl+PC/Y specimen shows a composite scale morphology of an inner Al_2O_3 and outer Y_2O_3 layer. The scale on TiAl+PC/Y+HT

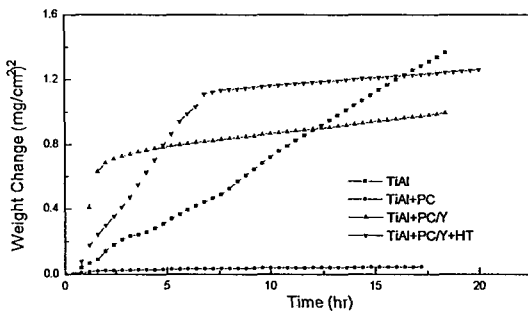


Fig. 6 Plot of square of weight gain per unit area vs. oxidation time at 950°C

consists of an outer layer of Y_2O_3 , an intermediate Al-Ti-Y mixed oxide, and an inner layer of Al_2O_3 . The intermediate Al-Ti-Y mixed oxide is considered as $Al_2O_3+TiO_2$ layer containing a small amount of Y_2O_3 . This

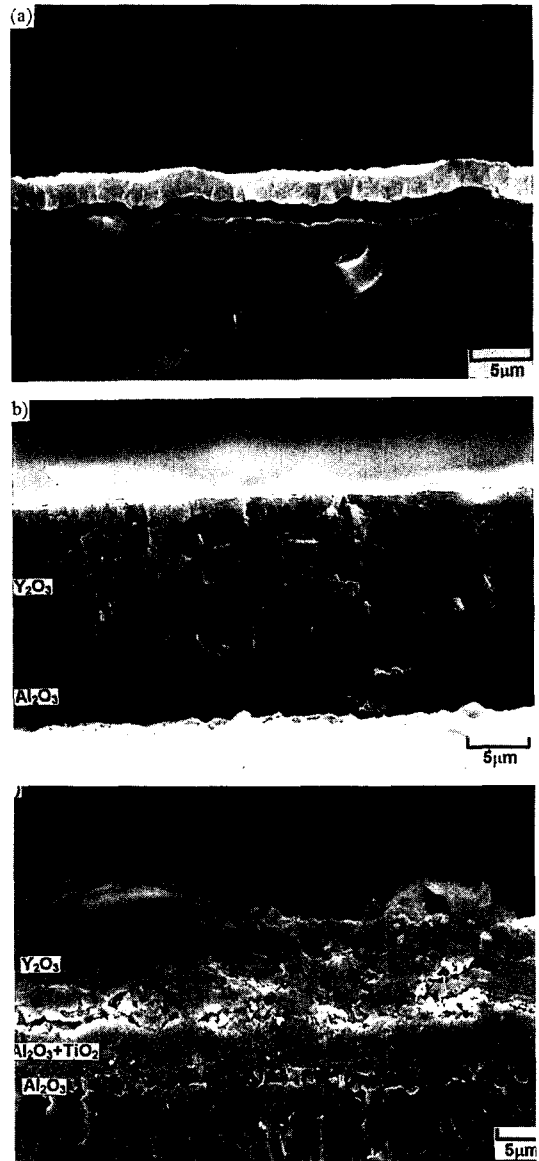


Fig. 7 Fractography of oxide scale formed on the various specimens after oxidation at 950°C for 100 hours.
(a) TiAl+PC (b) TiAl+PC/Y (c) TiAl+PC/Y+HT

morphology is consistent with the result of isothermal oxidation test. Thickness of Al_2O_3 layer formed on the all specimen is the same (about $2\mu\text{m}$). This means that Y-coating after pack aluminizing did not significantly affect the oxidation mechanism of aluminized TiAl alloy in the prolonged stage of oxidation.

Figure 8 shows the weight changes observed during the cyclic oxidation test. All the aluminized specimens showed a very good oxidation resistance. The TiAl+PC specimen showed no weight loss up to above 1000 cycles. TiAl₃ is reported to be more brittle than TiAl, the surface layer should be spalled off easily with the cracks under prolonged oxidation or certain stresses.^[18] In this specimen, however, spallation of aluminide-coating layer was not observed. In TiAl+PC/Y specimen, weight loss started after 100 cycles, but weight loss stopped after 140 cycles. This weight loss is simply due to the spallation of Y-coating layer. Contrary to TiAl+PC/Y specimen, TiAl+PC/Y+HT specimen showed no weight loss up to above 1000 cycles. This clearly indicates that the post heat treatment can improve the adherence of Y-coating layer. In the data of weight change, the difference between TiAl+PC and TiAl+PC/Y+HT specimen was not observed. The speci-

mens of TiAl+PC and TiAl+PC/Y+HT show no weight loss over 1000 cycles. (This test is presently under going) From observation on the surface, however, some difference between two specimens was observed. The TiAl+PC specimen showed imprint of partial spallation of oxide scale. On the other hand, the TiAl+PC/Y+HT specimen did not show imprint of partial spallation. This current result suggests that Y-coating with post heat treatment can improve the adherence of scale formed on the aluminized TiAl alloy. Therefore, it is expected that the cyclic oxidation resistance of TiAl+PC/Y+HT specimen is much better than that of TiAl+PC specimen. To understand the effect of Y-coating on the oxidation resistance of aluminized TiAl alloy, various analyses are currently under evaluation.

SUMMARY

A single coating of Y can not improve the high temperature oxidation resistance of TiAl alloy. A single coating of Y can not suppress the formation of TiO_2 scale. In particular, the post heat treatment at low oxygen level after Y-coating gives a detrimental effect on the oxidation resistance of TiAl alloy because it enhances formation of TiO_2 . In order to improve the oxidation resistance of TiAl alloy, the Al content in the surface region must be increased up to or even above the TiAl/TiAl₃ equilibrium composition. TiAl₃ layer having thickness of 70mm formed on the surface of TiAl alloy by pack aluminizing. Sufficient Al transport from TiAl₃ assists the formation of the Al_2O_3 scale which acts as a protective film against oxidation. The Y-coating after pack aluminizing can improve the adherence of Al_2O_3 scale formed on the aluminized TiAl

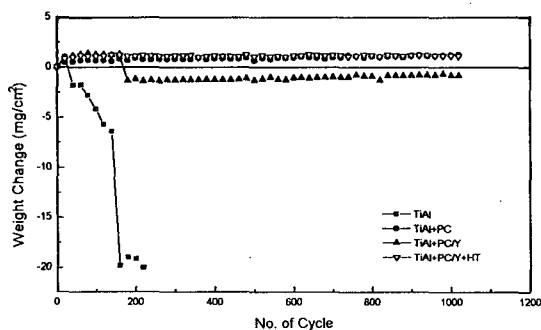


Fig. 8 Plot of weight change vs. number of cycle during cyclic oxidation test at 950°C

alloy, although it does not affect the oxidation mechanism of aluminized TiAl alloy.

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