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## Cyclic Oxidation of Aluminide Coated Two Phase $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl Alloys at 1000°C

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### Abstract

Titanium aluminide alloys have been considered as the candidates to substitute nickel-base superalloys for high temperature applications in aircraft turbine engines, as the alloys has lower density. For such applications, the alloys should exhibits both strength and high temperature oxidation or corrosion. Therefore, external protective scale of Al<sub>2</sub>O<sub>3</sub> has to be easily developed in the alloys, and the scale should resist for cyclic thermal operations. Recently, pack aluminide coatings have been developed on two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys of Ti-47Al-2Nb-2Cr-0.5Y-0.5Zr, to provide TiAl<sub>3</sub> based coatings capable in providing external scale of Al<sub>2</sub>O<sub>3</sub>. Nevertheless, no cyclic oxidation test has been conducted in this system. This paper reports the cyclic oxidation behavior of un-coated and pack aluminide coated  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys at 1000°C.

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*Keywords:* TiAl alloys; pack aluminide coating; cyclic oxidation.

### 1. Introduction

Nickel based superalloys have been long considered as materials suitable for aircraft turbine blade materials<sup>1</sup>. However, these materials are relatively heavy. Lower density materials of TiAl based intermetallic alloys have been recently attracting intensive attention to replace nickel-based superalloys<sup>2</sup>. Besides their low density (3.9–4.1 gr/cm<sup>3</sup>), TiAl based alloys have high creep and oxidation resistance<sup>3</sup>. Nevertheless, these materials are relatively brittle. Two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys have been considered to have higher toughness. However, these alloy systems are lack in oxidation resistance and the solution is to apply TiAl<sub>3</sub> based aluminide coating to the  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys. Pack aluminide coatings have been developed on two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys having chemical composition of Ti-47Al-2Nb-2Cr-0.5Y-0.5Zr<sup>4</sup>. The

isothermal oxidation and hot corrosion of these coated alloy systems have been recently studied. No cyclic oxidation, however, has been conducted for these system.

Increasing the strength of the alloys by addition of Nb and Cr to the simple  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys have been carried out by a number of researchers<sup>5,6</sup>. Coating on these alloys with higher aluminium content phase, such as TiAl<sub>3</sub>, provides external protective layer of Al<sub>2</sub>O<sub>3</sub> at high temperatures<sup>7,8</sup>. Addition of small amount of Y and Zr increases the spalling resistance of the protective oxides in nickel base superalloys and similar behaviour is predicted to occur in the pack aluminide coated two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys. For this mechanism to apply, both Y and Zr are expected to diffuse from the substrate of  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl to the external zone of TiAl<sub>3</sub> layer in the coating. TiAl based alloys are normally operated at 900°C. Nevertheless, abnormal combustion or mulfunction of the engines can lead to overheating and alter the performance of the material. The aim of this study was to investigate the effect of overheating to 1000°C on the cyclic oxidation behavior of the aluminide coated  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys.

## 2. Experimental Procedures

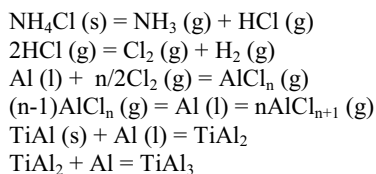
To obtain two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloy with chemical composition of Ti-47Al-2Nb-2Cr-0.5Y-0.5Zr, pure metals were mixed after weighing. The metals mixture was then melted in electric arc furnace purged with argon. Melting were carried out four times in order to have homogenous alloy substrate. Extra homogenization was done by heating the alloy sample at 1100°C for 10 hrs. in a tube furnace with argon gas atmosphere. The homogeneous substrate alloy was then cut using wire cutting to had several coupons with approximately 1.6 cm<sup>2</sup> in surface area for each coupon. Prior to coating process, the coupons were polished and ultrasonically cleaned in acetone.

An aluminide coating of TiAl<sub>3</sub> was applied to substrate coupon using pack aluminizing process. The pack consisted of a powder mixture of 20 wt.% Al as master alloy, 2 wt.% NH<sub>4</sub>Cl as activator and 78 wt.% Al<sub>2</sub>O<sub>3</sub> as inert filler. The pack powder was filled into a cylindrical alumina container into which four coupons were inserted. The spacing between coupons in the pack was about 1.7 cm. The container was then covered with alumina cement and leaved air dried prior to pack cementation process. Coating deposition was carried out by heating the pack in a horizontal tube furnace at 900°C for 10 hrs. in argon atmosphere. The pack was then furnace cooled to room temperature. The coated samples were then removed from the container and cleaned in acetone using ultrasonic cleaner.

Cyclic oxidation test was carried out by heating the coated and un-coated samples in a vertical furnace at 1000°C up to 20 cycles. Every cycle represented heating the samples at 1000°C for 1 hour and cooling to room temperature for 15 minutes. The weight change for each sample at each cycle was then measured and plotted the  $dW/A_0$  for each cycle where  $dW$  and  $A_0$  represent weight change and original total surface area of each sample, respectively. The microstructures of the alloys as well as coatings were observed using optical and scanning electron microscopes. Using energy dispersive spectroscopy (EDX) facility attached on a scanning electron microscope (SEM), the chemical compositions as well as the phases thereof, can be obtained. Nevertheless, to identify the oxide formed on the surface of the coating after oxidation test, an X-ray diffraction method was performed.

## 3. Results and Discussion

Using NH<sub>4</sub>Cl as activator, the pack cementation process essentially occurs through four main stages *i.e.*, (i) reaction between the activator and the master alloy (Al), (ii) transport of the gaseous metal chlorides to the substrate surface, and (iii) condensation and decomposition of the aluminium halides to deposit Al metal on the substrate surface, and (iv) formation of the coating. The reactions involved during pack cementation process can be described as follows.



In the pack, the chlorine gas resulted from the decomposition of the activator reacts with aluminum as master alloy. Due to the activity difference of the aluminum in the pack and the in the substrate, the aluminium halide diffuse to the substrate surface and decomposes to deposit aluminum atoms. The decomposed aluminum halide returns back to the pack to react with Al powder. Based on the phase diagrams of binary Ti-Al and thermodynamics consideration, the deposited aluminum reacts with Ti in the substrate of  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl to form coating containing TiAl<sub>3</sub> and TiAl<sub>2</sub> layers.

A representative microstructure of the two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloy and the as-coated sample are shown in Fig.1 (a) and (b) respectively. It is seen that the substrate has essentially lamellar structure of  $\alpha_2$ -Ti<sub>3</sub>Al and  $\gamma$ -TiAl, and this is similar with that obtained by other researchers<sup>9,10</sup>. The as-deposited coating has about 60 $\mu$ m thick. The EDX analysis revealed that the coating was TiAl<sub>3</sub> with average chemical composition of 73.83 at.%Al, 23.32 at. %Ti, 0.40 at.% Cr, 0.35 at.% Zr and 2.10 at.% Nb. This chemical content also indicates that the coating formed by high activity pack aluminizing process as alloying elements were found in relatively high content in the coating. The TiAl<sub>2</sub> layer could not be revealed in the microstructure of the as coated sample due to the low diffusivity of both Ti and Al in this phase<sup>11</sup>.

Microstructure of coated sample after cyclic oxidation at 1000°C for 20 cycles is shown in Figure 2. Due to limited space available, only microstructure of one sample is presented in this paper. Based on the XRD analysis (Fig. 3), the outer oxide is essentially Al<sub>2</sub>O<sub>3</sub>, but mixed with TiO<sub>2</sub> and Ti<sub>2</sub>AlN. In addition, it is clearly seen from Fig. 2 that pitting type corrosion can also formed.

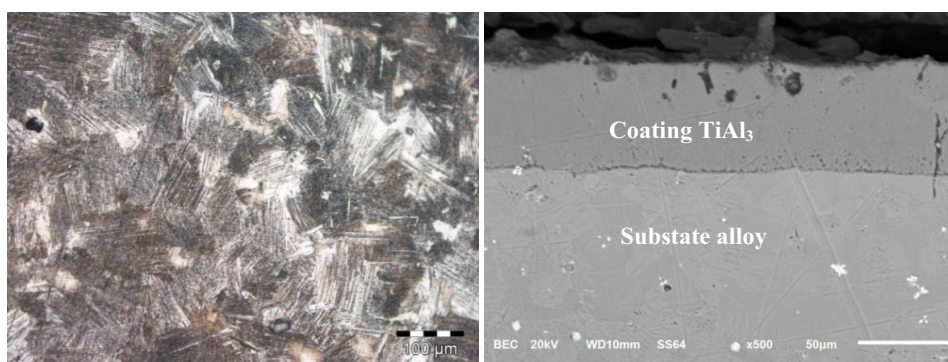


Figure 1. (a) Microstructure of the substrate alloy, (b) as coated sample.

The occurrence of Ti<sub>2</sub>AlN on the scale has been previously predicted in earlier study done by Schuster and Bauer<sup>[11]</sup> based on thermodynamics study of Ti-Al-N system at 1273 K. They reported that Ti<sub>2</sub>AlN is in equilibrium with TiN and  $\alpha_2$ -Ti<sub>3</sub>Al or  $\gamma$ -TiAl. Therefore, it seems that the Ti<sub>2</sub>AlN should be formed on substrate-oxide interface. The occurrence of Ti<sub>2</sub>AlN on the surface of the oxide scale is predicted due to the reaction between TiN and Al<sub>2</sub>O<sub>3</sub>, or alternatively as the results of reaction between TiN and TiAl<sub>3</sub> as the matrix of the coating. Even though the mechanism of nitride formation on the surface has not been clearly revealed, it is confirmed that this nitride alter the formation of Al<sub>2</sub>O<sub>3</sub> in the outer scale.

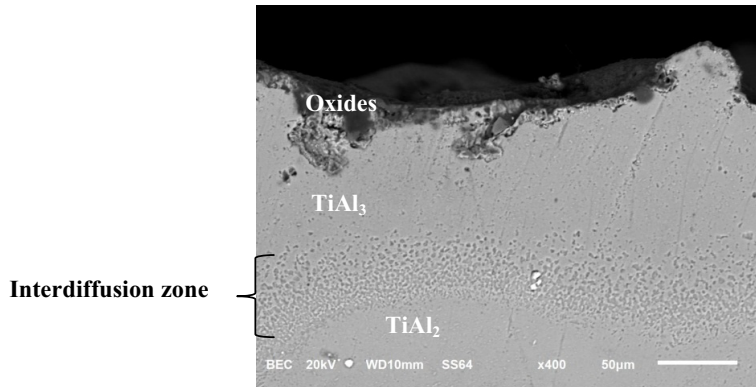


Figure 2. Microstructure of coated sample after cyclic oxidation at 1000°C for 20 cycles.

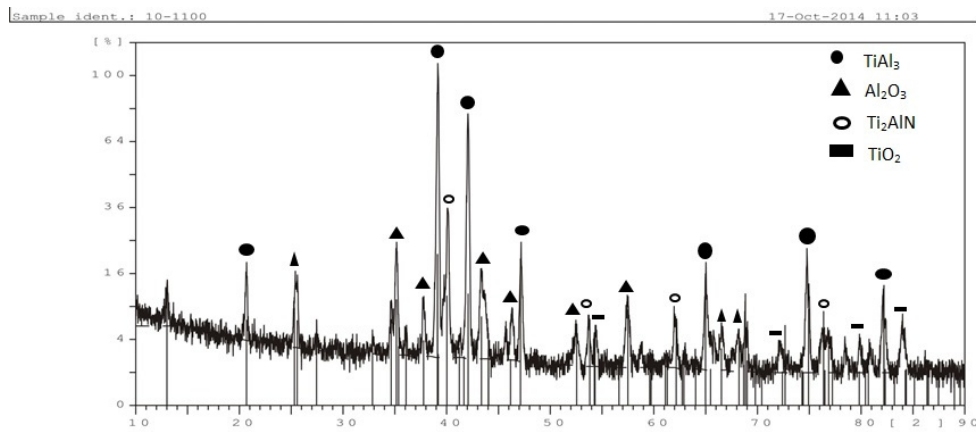


Figure 3. XRD pattern of the coated sample after cyclic oxidation at 1000°C for 20 cycles.

The weight change of three coated and three un-coated samples exposed at 1000°C in cyclic manner is shown in Fig. 4. It is seen that un-coated samples have larger weight changes compared with that of coated samples for all the three different samples oxidized for 10, 15 and 20 cycles. The flatness of the weight change curves for coated samples indicated that the oxide scale of the coated samples have better adherence compared with that of un-coated samples. Spallation of oxide occurred significantly in un-coated sample for both 10 and 15 cycles. Earlier spallation had found in sample of 10 cycles. Nevertheless, it was then followed by relatively high weight gain due to formation of  $\text{TiO}_2$ . The XRD analysis on the surface of un-coated samples after cyclic oxidation for 20 cycles revealed that the oxide scales were dominated by  $\text{TiO}_2$  rutile, which is known as unprotected scale. Other oxides occurred in the scale are oxides of alloying elements such as  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and low intensity of  $\text{Y}_2\text{O}_3$ . Surprisingly, no oxide of Nb was found in the scales.

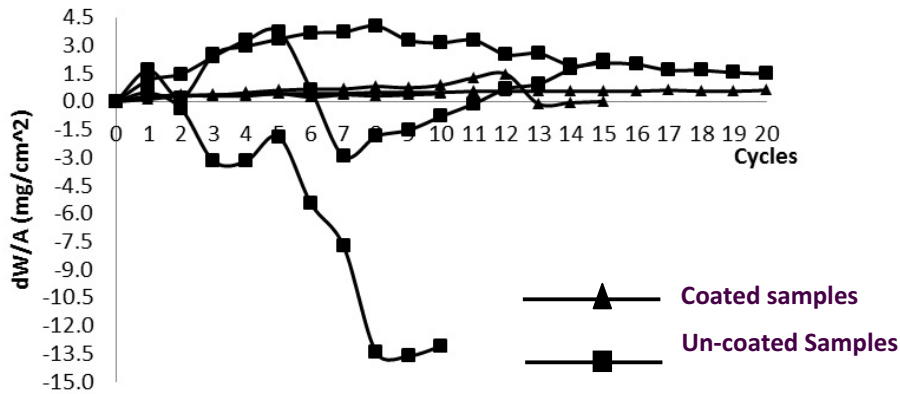


Figure 4. Weight change of coated and un-coated samples after cyclic oxidation at 1000°C for 10, 15 and 20 cycles.

The role of yttrium in the cyclic oxidation behaviour of  $\gamma$ -TiAl base intermetallic alloys has been studied by Ying Wu *et.al.*<sup>12</sup>. They found that intensive oxide spallation still occurred when only 0.1 at.% of yttrium was added. However, no oxide spallation was found when the concentrations of yttrium in the alloy were increased up to 0.3, 0.6 and 1 at.%. In this study, the addition of 0.5at.% Y in the substrate alloy can reach the outer zone of the coating and give better protection to the coatings. The mechanism of  $Y_2O_3$  formation on the coating-oxide scale interface is shown schematically in Fig. 5. The  $Y_2O_3$  formed on the coating-oxide interface strengthened the adherence of the oxide scale and therefore increase the spallation resistance of the oxide. This fact confirmed diffusion of Y as well as Zr from the substrate into the pack aluminide coating and modified the coating in providing Y and Zr for improvement of oxide scale spallation resistance of the coating.

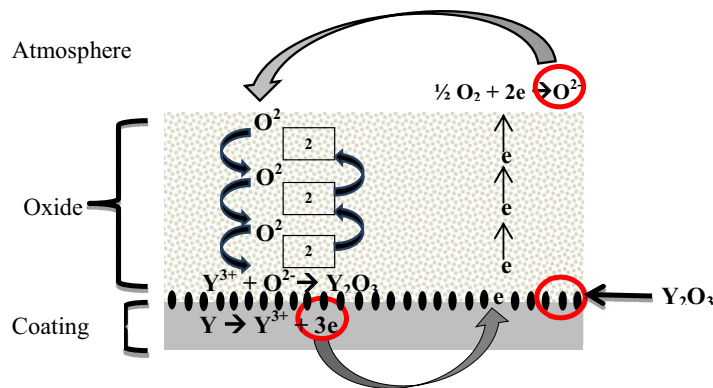


Figure 5. Schematic diagram for the formation of  $Y_2O_3$  on the coating-oxide interface.

#### 4. Conclusions

Pack aluminide coated two phase  $\alpha_2$ -Ti<sub>3</sub>Al/ $\gamma$ -TiAl alloys has better cyclic oxidation resistance at 1000°C compared with that of un-coated samples. The coating has high aluminium content of TiAl<sub>3</sub> phase layer containing alloying elements of the substrate. This phase provides external protective scale of predominantly Al<sub>2</sub>O<sub>3</sub>. In contrast, un-protective oxide of TiO<sub>2</sub> is the major constituent in the scale of un-coated substrate. Nitride of Ti<sub>2</sub>AlN was formed on the surface of the oxide

scale as the results of reaction between TiN and Al<sub>2</sub>O<sub>3</sub> or TiN and TiAl<sub>3</sub>. Addition of Y and Zr in the substrate provide adequate spallation resistance to the protective scale of Al<sub>2</sub>O<sub>3</sub> on the surface of the Pack aluminide coatings.

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