

# Oxidation And Corrosion Resistance Of TiAl<sub>3</sub> Coatings

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## ABSTRACT

Titanium aluminides based on TiAl, TiAl<sub>3</sub> and Ti<sub>3</sub>Al are potential materials for high temperature aerospace applications. Their low density, high temperature creep resistance, high temperature strength and high oxidation resistance make them excellent coating materials. However these coatings are likely to be subjected to high temperature and corrosive environments during service. Hence it is aimed to study the oxidation and corrosion resistance of TiAl<sub>3</sub> coatings on various types of substrates. In the present work, TiAl<sub>3</sub> is coated on high speed steel, stainless steel 304, stainless steel 316, copper and aluminum substrates by physical vapor deposition technique. X-ray diffraction analysis confirms the presence of TiAl<sub>3</sub> phase. The hardness studies reveal that better hardness can be achieved with thick coatings. The oxidation behavior of the coatings is studied by carrying out step stress experiments at elevated temperatures. Coated samples are heated up from 400°C in the steps of 100°C for 1h in each step to 1000°C. The mass gain caused by oxidation was determined. The oxidation curve drawn as a function of mass gain versus temperature reveals that TiAl<sub>3</sub> film started to oxidize above 800°C, where as oxidation of the uncoated substrates began at a much lower temperature of 550°C. The excellent oxidation resistance of the coatings can be attributed to the formation of an amorphous Al<sub>2</sub>O<sub>3</sub> film. Scanning electron microscope (SEM) and EDAX analysis confirm the presence of an amorphous Al<sub>2</sub>O<sub>3</sub> film. The corrosion behavior of TiAl<sub>3</sub> coatings are investigated by the polarization resistance experiments in NaCl aqueous solution at ambient temperature. According to the Tafel plot analysis, the coatings show lower corrosion rate than the untreated substrates. The major corrosion in the coatings arose from electrolyte penetration into the pores of the coatings. In fact, a dense coating showed a high corrosion resistance in an aqueous medium.

## 1. INTRODUCTION

TiAl-based alloys have low density and excellent strength and modulus retention properties at operating temperatures up to 850°C<sup>1</sup>. It offers enormous potential in critical strength application areas for aerospace and power industries where high specific strength and stiffness are required in order to enhance performance. These parameters are essential for fulfilling ever increasing technical, economical as well as environmental requirements. However, in order to fully utilize their potential, efficient and effective technologies must be developed that can ensure its long term mechanical and

structural integrity in oxidative and corrosive environments at high temperatures. Microstructure modification and control through additions of ternary alloying elements such as Nb, W, Cr and Si can improve the room temperature ductility and also moderately increase the high temperature oxidation and corrosion resistance<sup>2</sup>. However, further alloying usually lead to deterioration of their mechanical properties. It is now generally recognized that deposition of coatings that can form dense, adherent and slow growing oxide scales on its surface offers the most promising approach to provide solutions for the long term environmental stability at high temperatures<sup>3</sup>. More recently, the topic area of designing coating systems for TiAl based alloys has been reviewed by Datta et al.<sup>4</sup>. In this work, it is planned to study the oxidation and corrosion resistance of TiAl<sub>3</sub> coatings prepared by thermal reactive evaporation technique on various metal substrates.

## 2. EXPERIMENTAL

The TiAl<sub>3</sub> alloy used in this study was prepared as ingots from the raw materials of titanium (99.7%) and aluminum (99.98%) by high temperature melt growth technique. The ingots were remelted at least six times to promote the homogeneity of the ascast structure. After homogenization of the ingots at 1000°C for 100 h, pellets for thermal evaporation were prepared by sectioning the ingots into coupons of smaller dimensions. High speed steel (HSS), stainless steel 304, stainless steel 316L, copper and aluminum samples were used as substrate materials in this work. Surfaces of the samples were ground and polished to a 1200 grit finish. Samples were then degreased and ultrasonically cleaned before placing them into the vacuum chamber. TiAl<sub>3</sub> films were deposited on mirror polished steel substrates (25mm x 75mm x 1mm) by thermal evaporation method through resistive heating. TiAl<sub>3</sub> source material in the form of pellet was heated to its vaporizing temperature in a tungsten filament boat by passing a current of 40 A at a vacuum of 4 x 10<sup>-6</sup> torr. The deposition rate was controlled by varying the current in the heating element. The deposition was carried out for 15 min.

### 2.1 Characterization

X-Ray analysis of the coated samples was done using X-Ray Diffractometer (Rigaku Miniflex) having copper target (30kV, 15mA) with a K<sub>α</sub> filter. The diffracting angles were set to 20° to 80° with a scanning speed of 4°/min in continuous mode. The films deposited on various substrates were

analyzed using JEOL JSM-6380LA scanning electron microscope. Thickness of the coatings was measured using profilometer. Here the step height of the film from the substrate was measured. This, however, necessitates leaving or producing an uncoated region (by masking during deposition) over which the step can be measured. The oxidation behavior of the coatings was studied by carrying out step stress experiments at elevated temperatures<sup>5,6</sup>. Coated samples were heated up in the steps of 100°C for 1 h in each step. The mass gain caused by oxidation was determined using a plot between mass gain and temperature. Polarization tests were performed with a CH chemical analyzer Corrosion Measurement System<sup>7,8</sup>. 3.5N NaCl electrolyte was prepared by using reagent grade chemicals in deionised water. Tests were carried out in a standard three-electrode cell at room temperature (~ 26°C), with the specimen as the working electrode, a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The area that was exposed to the electrolyte is 1.0 cm<sup>2</sup>. The corrosion current (I<sub>corr</sub>) of the newly polished samples was measured and compared with the I<sub>corr</sub> of the coated samples, with the use of Tafel plots. Experiments were performed by sweeping potential from -0.2 to -1.5 V at a scan rate of 0.01 V/s. The samples were then examined by an optical microscope.

### 3. RESULTS AND DISCUSSION

XRD spectrum of the high speed steel sample coated with TiAl<sub>3</sub> show the peak corresponding to TiAl<sub>3</sub><sup>9</sup> (Fig.1). The hardness increases linearly with the coating thickness. TiAl<sub>3</sub> coating has higher oxidation resistance as compared with untreated samples. The untreated samples oxidize at temperatures higher than 600°C, whereas TiAl<sub>3</sub> film shows resistance to oxidation up to a temperature of 800°C. The formation of a fine Al<sub>2</sub>O<sub>3</sub> top layer increases the oxidation resistance of TiAl<sub>3</sub> film<sup>10</sup>. The thin layer of Al<sub>2</sub>O<sub>3</sub> is able to reduce further oxidation of the film substantially. Figures 2 show that TiAl<sub>3</sub> film started to oxidize above 800°C, where as oxidation of untreated samples began at a much lower temperature of 600°C. The initiation of oxidation of TiAl<sub>3</sub> film depends on its Al content. Isothermal oxidation of TiAl<sub>3</sub> coated samples exhibited a mass gain as low as 0.5 mg/cm<sup>2</sup> even after 1h at 1000°C. The excellent oxidation resistance can be attributed to the formation of an amorphous Al<sub>2</sub>O<sub>3</sub> film.

The oxidation curves of TiAl<sub>3</sub> coatings follow the similar pattern irrespective of the different types of substrates. The

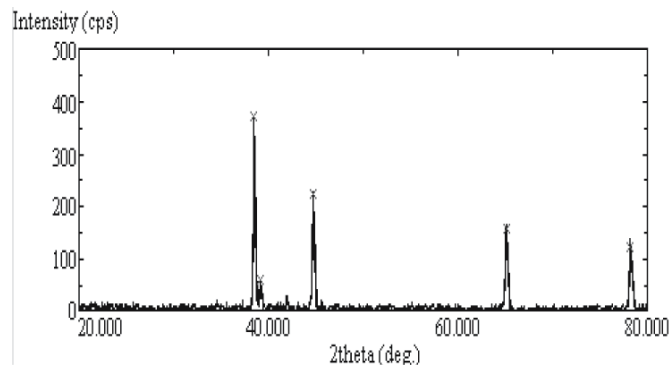


Fig. 1 : X-RD Pattern of the TiAl<sub>3</sub> Film on HSS substrate.

SEM micrographs and EDAX results show the presence of amorphous oxide layers (Fig.3). It is predictable that the coating on heat treated HSS sample at 1000°C has a thick oxide layer compared to the other samples heat treated at lower temperatures. Polarization curves for the uncoated samples and TiAl<sub>3</sub> films on stainless steel 316 samples measured in an aqueous solution of 3.5N NaCl are shown in Figs. 4 and 5.

The TiAl<sub>3</sub> films had better corrosion resistance than that of the uncoated steel substrates. The differences between the

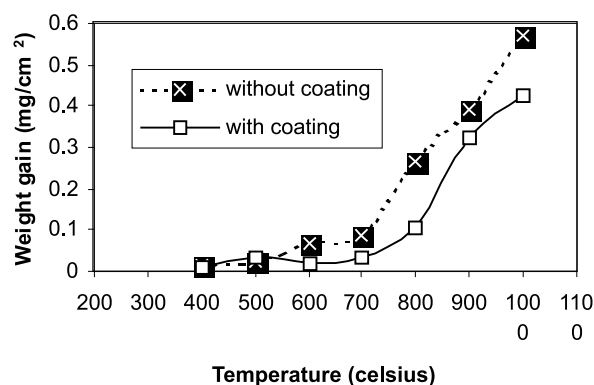


Fig. 2 : Oxidation curves of high speed steel with and with out coating

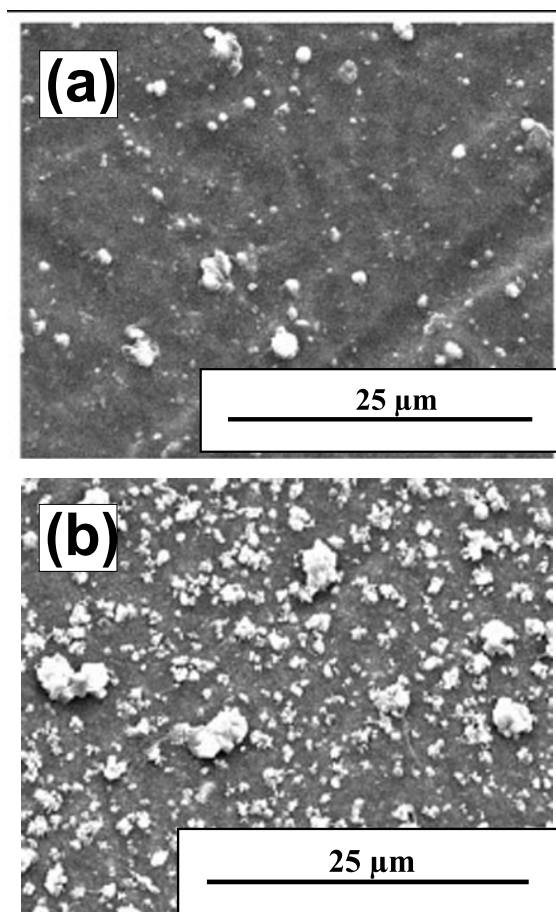


Fig. 3 : SEM micrographs of surface morphology showing oxide layers (a) TiAl<sub>3</sub> film coated on HSS sample heat treated at 600°C (b) TiAl<sub>3</sub> film coated on HSS sample heat treated at 1000°C.

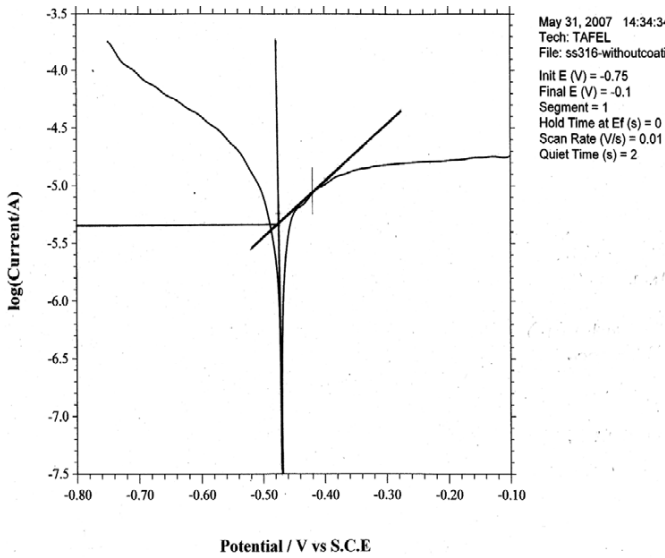


Fig. 4 : Tafel plot of stainless steel 316 sample without TiAl<sub>3</sub> coating

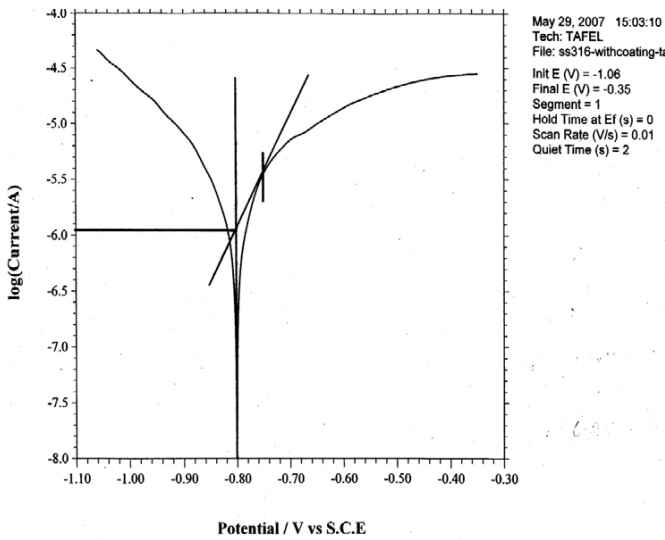


Fig. 5 : Tafel plot of stainless steel 316 sample with TiAl<sub>3</sub> coating.

**Table 1**

Corrosion rate of uncoated and TiAl<sub>3</sub> coated samples in aqueous solution of 3.5 N NaCl.

Substrate material	Corrosion rate (mpy)	
	With out coating	With coating
High Speed Steel (HSS)	21.91	10.06
Stainless steel 304	16.18	11.29
Stainless steel 316L	14.59	06.27
Aluminum	09.06	10.85
Copper	17.89	12.76

individual curves are small and the test did not reveal marked differences between the individual coatings, since all the films have more or less same thickness. The shape of the curves of TiAl<sub>3</sub> coatings resembled the curve of the uncoated samples, reflecting the fact that despite some improvement in corrosion resistance, none of these coatings could isolate the substrate material completely from the electrolyte, since the thickness of the coating is of the order of few mm<sup>11</sup>. The corrosion rate for the uncoated samples and the TiAl<sub>3</sub> coatings on different samples are listed in Table 1. Irrespective of the substrates, TiAl<sub>3</sub> coatings had lower corrosion rate because of the higher aluminum content and uniformity in thickness.

**4. CONCLUSIONS**

The oxidation behavior of TiAl<sub>3</sub> coating on different metal substrates was studied using step stress measurements. The coating exhibited better oxidation resistance compared to the uncoated substrates. A fine layer of complex alumina formation took place during oxidation and it reduced the further oxidation of the coatings. SEM micrographs and EDAX analysis confirmed the presence of an amorphous Al<sub>2</sub>O<sub>3</sub> layer. Coating thickness influenced the hardness. The corrosion behavior of TiAl<sub>3</sub> coating on different metal substrates was investigated by the polarization resistance experiments in NaCl aqueous solution at ambient temperature. According to the Tafel plot analysis, the coatings showed lower corrosion rate than the untreated substrates. However, it was not possible to compare the corrosion rates of TiAl<sub>3</sub> coatings on different metal substrates. The major corrosion in the coating arose from electrolyte penetration into the pores of the coatings. Therefore, a dense coating provided high corrosion resistance in an aqueous medium.

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**REFERENCES**

1. Brady P, Brindley W J, Smialek J L and Locci I E, *J.O.M.*, **8**(11) (1996) 46.
2. Kaysser W, *Surf. Eng.* **17**(4) (2001) 305.
3. Brady M P, Gleeson B and Wright I G, *J.O.M.*, (1) (2000) 16.
4. Datta P K, Burnell-Gray J S and Natesan K, *Intermetallic Compounds: Principles and Practice*, Wiley, **3** (2002) p 561.
5. Knotek O, Munz W D and Leyendecker T, *J. Vac. Sci. Technol.* **A5** (4) (1987) 2173.
6. Knotek O, Bohmer M, Leyendecker T and Jungblut F, *Mater. Sci. Eng.* **A105-106** (1988) 481.
7. Souto R M and Alanyali H, *Corrosion Sci.* **42** (2000) 2201.
8. Choi I S and Park J C, *Surf. Coat. Technol.* **131** (2000) 383.
9. Van Loo F J J and Rieck G D. *Acta Metall.*, (1973) 21.
10. Munro T C and Gleeson B, *Metallur. Mater. Trans.*, **27A** (1996) 3761.
11. NASA, Evaluation of Candidate Alloys for the Construction of Metal Flex Hoses in the STS Launch Environment (1988).