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## Hot Corrosion Studies on As-received and HVOF Sprayed $\text{Al}_2\text{O}_3+\text{CoCrAlTaY}$ on Ti-31 Alloy in Salt Environment

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### Abstract

The present investigation is on the High Velocity Oxy-Fuel coating of Ti-31 alloy using fused, blended powder,  $\text{Al}_2\text{O}_3+\text{CoCrAlTaY}$ . Hot corrosion experiments were done on the coated and uncoated Ti-31 under a salt environment of 50%  $\text{Na}_2\text{SO}_4$  and 50%  $\text{V}_2\text{O}_5$  at 800°C. Thermogravimetric cycles of 1 hour heating and 20 minute cooling was followed for hot corrosion study. After each cycle weight measurement was carried out. After hot corrosion, the samples were characterized using XRD and SEM/EDS. It was observed that the coated sample is more resistant to hot corrosion than uncoated sample. XRD and SEM analysis indicated that the surface is rich in oxides. Gravimetric analysis indicated that the sample weight gain was following a parabolic relationship with time. A damage mechanism is discussed for the hot corrosion damage of the samples. Presence of high level of chromium in HVOF sprayed coating imparts improved hot corrosion resistance at 800°C, in a molten salt environment of  $\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5$ .

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*Keywords:* Hot corrosion; Ti-31; HVOF coating; Fused blend powder; Salt environment;

### 1. Introduction

Ti alloys are increasingly used in high temperature working environments because it offers the benefit of high strength to weight ratio, good fatigue resistance and elevated temperature resistance. Ti-31 alloy is a candidate

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material for gas turbine applications [1]. In many countries, especially, in developing ones, the fuel used for land based gas turbines are low grade fossil fuels, which invariably contain impurities like sodium, vanadium and sulphur. During coal burning, these impurities form compounds such as  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$ , which are low melting point compounds (Melting point of  $\text{Na}_2\text{SO}_4=884^\circ\text{C}$  and  $\text{V}_2\text{O}_5=670^\circ\text{C}$ ). During operation, these low melting point compounds or their mixtures, form a liquid film on the component surface and react with the components, causing accelerated corrosion [2-5]. Prakash et. al. [6] has reported that use of proper corrosion prevention strategy can reduce the maintenance cost and increase the life of the turbine component. One method of improving the life of turbine components, exposed to hostile environment is to provide a protective coating.

Of various coating procedures, thermal spray coatings using high velocity oxy-fuel (HVOF) process is highly promising due to the benefits of lower cost, better performance, ability to deposit coatings whose thickness ranges from several micrometers to tenths of a millimeter, ability to deposit on a wide variety of shapes and sizes, etc. [4, 7]. HVOF process produces a coating which is stronger and denser compared to other thermal spray processes like electric arc, plasma spray or flame spray processes [8-10] Sidhu et. al. [11] have evaluated the hot corrosion performance of HVOF sprayed Ni-20 Cr on Superni-75 and found that HVOF coating is effective in improving the hot corrosion resistance. Sidhu et. al. [12] have reported improvement in hot corrosion resistance, under cyclic conditions, of ASTM-SA210 GrA 1 steel by HVOF spraying of  $\text{Cr}_2\text{C}_3$ -NiCr, NiCr, EC-Co, Stellite-6 alloys. It is also reported [13] that thermal spray coatings through HVOF route has higher oxidation resistance compared to coatings through vacuum spray route.

Gurrappa et. al. [14] have investigated the hot corrosion kinetics of titanium based IMI-834 alloy, exposed to mixtures of  $\text{Na}_2\text{SO}_4$ , NaCl and  $\text{V}_2\text{O}_5$ , at  $600^\circ\text{C}$ . They reported that the weight gain of IMI-834 Ti alloy follows parabolic relationship with time. Anuwar et. al. [1] have reported that corrosion rate of Ti-31 in molten salt environment ( $\text{Na}_2\text{SO}_4+\text{V}_2\text{O}_5$  at  $750^\circ\text{C}$ ) is relatively high and a suitable protective coating is essential to enhance the life of the component used in turbines. For improved hot corrosion performance, the coating needs to have higher level of chromium or platinum group of metals [15]. Also, Toma et. al. [13] have suggested addition of alumina dispersions to HVOF coating to improve adherence of the HVOF coating to the substrate. To the best of our knowledge, there is no reported investigation of use of a blend of alumina and cobalt based (containing high level of chromium) coating through HVOF process on titanium based substrate. This investigation focuses on the performance of HVOF based  $10\%\text{Al}_2\text{O}_3+\text{CoCrAlTaY}$  coating on Ti-31 material. Resistance to hot corrosion is investigated and effectiveness is compared with the uncoated Ti-31.

## 2. Experimental

The substrate material used in the present investigation was Ti-31 (Ti-6Al-4V). The equivalent ASTM standard of the material is ASTM B338 grade 5. The substrate material was supplied by M/s Midhani, Hyderabad, India. The specimen of approximately 25mm x 25mm x 5mm were cut, ground and subsequently grit blasted with alumina powders. They were used as substrates for HVOF coating. Commercially available fused, blended oxide alloy powder was used for deposition. The details of the alloy powder and substrates used are given in Table 1.

Table 1. Composition of the substrate, powder and coating details.

Substrate composition (wt%)	6Al-4V-Ti (Bal.)
Powder composition (wt%)	10% $\text{Al}_2\text{O}_3$ +90%(23Cr-7Al-9Ta-0.68Y-Bal.Co)
Powdersize	-45 +15 $\mu\text{m}$
Powdershape	Spherical
Averagecoatingthickness ( $\mu\text{m}$ )	259
Coatingporosity	<1.5 %
Micro-hardness of coating (Hv)	580 (average)

The coatings were sprayed at Spraymet India Ltd., Bangalore, using a Metco DJ 2600 (India) gun. The spray parameters were; oxygen flow rate-270 liters per minute (LPM), fuel (LPG) flow rate-70 LPM, air flow rate-700 LPM, spray distance-about 20 cm, powder feed rate: 50 g/min, fuel pressure-7 kg/cm<sup>2</sup>, air pressure-5.5 kg/cm<sup>2</sup>, oxygen pressure-10 kg/cm<sup>2</sup>, nitrogen gas (powder carrying gas) pressure-5 kg/cm<sup>2</sup>. During spraying, the specimen was cooled with compressed air.

Uncoated and HVOF coated specimens were subjected to hot corrosion test at 800°C (±5°C). The samples were properly cleaned and dried before investigation. The physical dimensions of the samples were recorded carefully before hot corrosion experiments. The medium of corrosion was 50 wt% Na<sub>2</sub>SO<sub>4</sub>+50 wt% V<sub>2</sub>O<sub>5</sub>. Uniform coating was applied using 3 to 5 mg/cm<sup>2</sup> of Na<sub>2</sub>SO<sub>4</sub>-50%V<sub>2</sub>O<sub>5</sub>. Coating was applied using a Camel hairbrush on the uncoated and coated specimens. During hot corrosion study, the specimen was kept in an alumina boat and weight of the boat and the specimen was measured. The hot corrosion study was conducted under cyclic conditions. The tests were conducted for 50 cycles of which each cycle consisted of 1 hour heating at 800°C followed by 20 minutes cooling in air. The weight change values were measured at the end of each cycle with an aim to understand the kinetics of corrosion. Visual observations were made at the end of each cycle. Reproducibility in the experiment was established by repeating the experiments. The corrosion products of the uncoated and HVOF coated materials were analyzed by using x-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to reveal their microstructural and compositional features.

### 3. Results and Discussion

#### 3.1 Visual observations and Thermogravimetric analysis

From the visual observations, indication of oxide formation was noticed from the first cycle itself, both for uncoated Ti-31 and HVOF coated Ti-31. In the case of uncoated Ti-31, the surface became brownish in 23<sup>rd</sup> cycle and severe spalling was observed from 31<sup>st</sup> cycle onwards. In the case of coated Ti-31, cracks started to form during 9<sup>th</sup> cycle and in the 10<sup>th</sup> cycle the cracks got interconnected to have a web like appearance. Amount of crack was increasing with successive thermal cycles and from 39<sup>th</sup> cycle onwards the coating colour started to change to green. Samples after 50 cycles of hot corrosion are shown in Fig. 1.

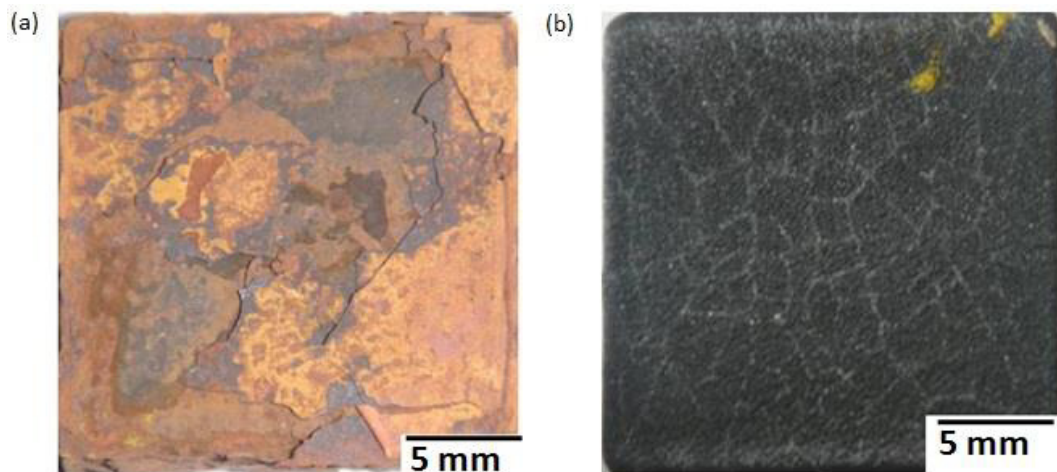


Fig. 1. Macro-views of samples subjected to hot corrosion in 50 wt% Na<sub>2</sub>SO<sub>4</sub>+50 wt% V<sub>2</sub>O<sub>5</sub>, (a) Uncoated Ti-31(b) Coated Ti-31.

The result of gravimetric analysis is displayed in the form of a plot of cumulative weight gain ( $\text{mg}/\text{cm}^2$ ) as a function of time expressed in number of cycles. It is shown in Fig. 2a. Weight gain data after 50 cycles of hot corrosion for uncoated and HVOF coated Ti-31 are  $72.3 \text{ mg}/\text{cm}^2$  and  $10.3 \text{ mg}/\text{cm}^2$  respectively. The weight gain data (Fig. 3.2a) clearly indicates that the HVOF coated Ti-31 is showing less weight gain and hence better corrosion resistance. Further, to investigate the possibility of parabolic relationship [15], weight gain square ( $\text{mg}^2/\text{cm}^4$ ) data is drawn as a function of number of cycles and is given in Fig. 2b. Parabolic rate constants obtained from the plots for uncoated and HVOF coated Ti-31 are 107.68 and  $2.48 \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$  respectively.

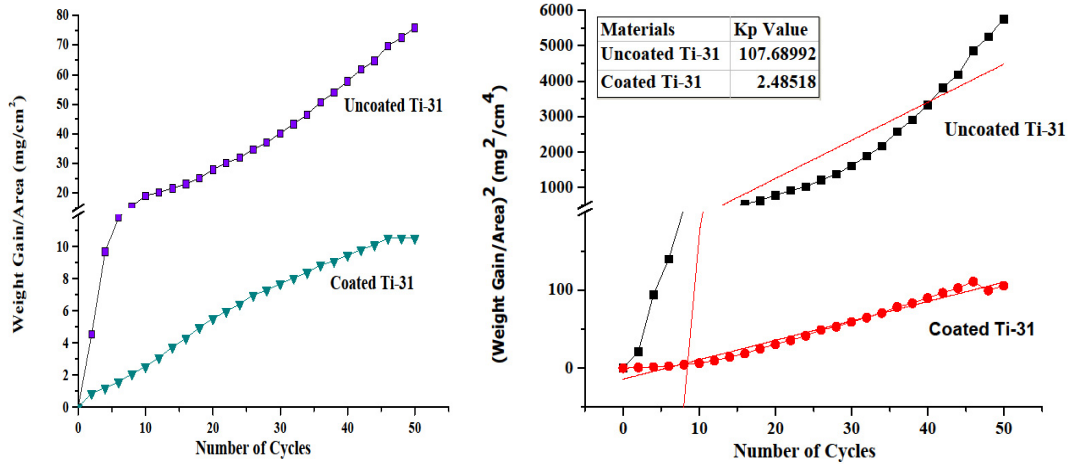


Fig. 2. Thermogravimetric data of samples subjected to hot corrosion, (a) Weight gain per unit area versus number of cycles (b) Square of weight gain/area versus number of cycles.

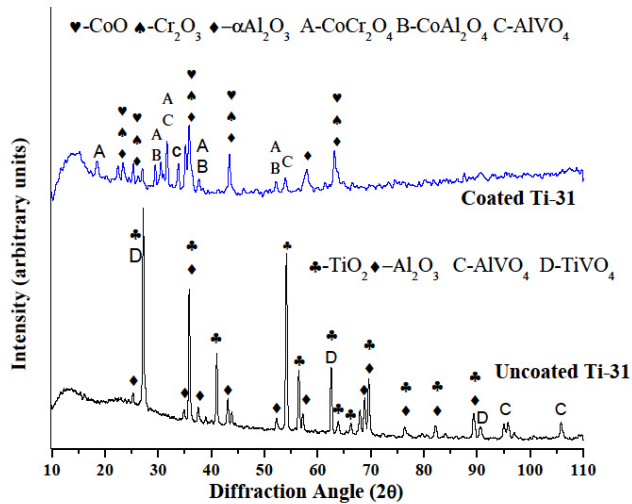


Fig. 3. XRD profiles of samples subjected to hot corrosion.

X-ray diffraction patterns of the top scale formed on the uncoated and HVOF coated Ti-31 are shown in Fig. 3. The scale on the uncoated Ti-31 contains  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiVO}_4$ , and  $\text{AlVO}_4$ , whereas the scale on the coated Ti-31 contains  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\alpha\text{-Al}_2\text{O}_3$ , as major phases. The scale also has some amount of  $\text{CoCr}_2\text{O}_4$ ,  $\text{CoAl}_2\text{O}_4$ ,  $\text{AlVO}_4$ , as minor phases.

Fig. 4 shows SEM micrograph of scales formed during hot corrosion of uncoated and HVOF coated Ti-31 substrates. Fig. 4a shows scales formed on the uncoated Ti-31. The morphology clearly indicates that the scale is flaky and non-compact type, which promotes continuous oxidation. This is also indicated in the weight gain data. EDS on the scales clearly indicates that, it is predominantly  $\text{TiO}_2$  with minor amount of  $\text{Al}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ . Similar observations are also reported by Anuwar et al. [1]. Fig. 4b shows morphology of HVOF coated Ti-31 subjected to 50 cycles of hot corrosion in  $\text{Na}_2\text{SO}_4+50\% \text{V}_2\text{O}_5$  at  $800^\circ\text{C}$ . The scale is continuous type. EDS analysis shows that it is rich in oxides of Co and Cr. It is reported that oxides of cobalt and chromium form continuous oxides and protect the substrate from further corrosion [16-17]. This is also indicated in the weight gain data, which is much lower for coated Ti-31 compared to uncoated Ti-31.

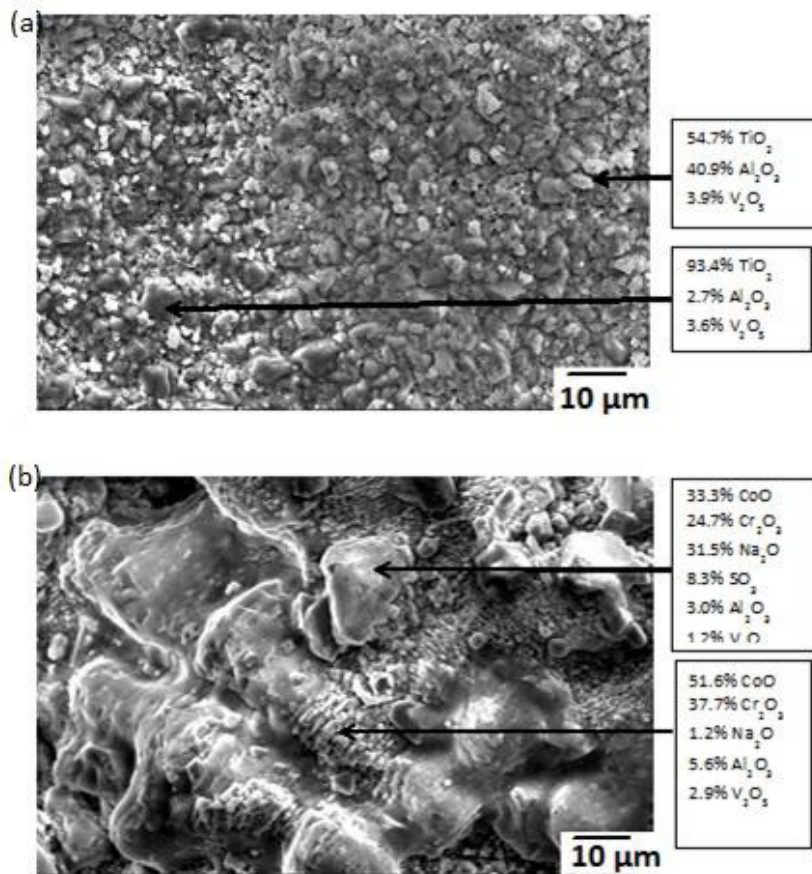


Fig. 4. Morphological investigation on hot corroded samples (a) Uncoated Ti-31 (b) Coated Ti-31. Typical EDS results are displayed at the right side.



### 3.2 Degradation mechanism

Titanium metal itself has a high affinity for oxidation to give a film of  $\text{TiO}_2$  [18]. The  $\text{TiO}_2$  film can re-heal itself almost instantly when exposed to air or water. But Ti alloys have limited oxidation resistance in air above  $650^\circ\text{C}$  [19]. As far as protection is concerned,  $\text{Al}_2\text{O}_3$  is better coating compared to  $\text{TiO}_2$ , especially at elevated temperatures [20]. But in Ti-31, the amount of aluminum is not sufficient for the formation of a continuous alumina scale. The titanium oxide rich scale starts to spall once coating reaches critical thickness. Gurappa's work [21] has shown that a coating rich in oxides of titanium spalls at high temperatures due to adherence problems. The environment in our investigation consist a mixture of  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$ . They have melting points  $884^\circ\text{C}$  and  $690^\circ\text{C}$ , respectively. They also form a number of compounds with melting points in the range of  $550\text{--}700^\circ\text{C}$  [22]. They will condense as liquid and spread over the component surface. They accelerate the attack on the component. This is clearly depicted in the increased weight gain data as shown in Fig. 2a. At temperatures exceeding  $700^\circ\text{C}$ , the  $\text{Na}_2\text{SO}_4$  decomposes to give  $\text{Na}_2\text{O}$  and  $\text{SO}_3$  [23-24]. The  $\text{Na}_2\text{O}$  reacts with  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  to form sodium titanate and aluminum titanate respectively. Also, the addition of  $\text{Na}_2\text{O}$  to liquid  $\text{V}_2\text{O}_5$ , causes an increase in the basicity of the melt, which in turn increases corrosivity of acidic oxides in the scale [25]. In Ti-O system, oxygen is an interstitial element and it can easily diffuse to form  $\text{TiO}_2$ . Since  $\text{TiO}_2$  is non-adherent, formation sodium titanate is much higher. On the other side, the coating consists of elements like Co, Cr, Al and Ta. Presence of large amount of  $\text{CoO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in the coating makes it relatively more adherent which in turn reduces oxidation of Ti in the substrate.  $\text{Al}_2\text{O}_3$  dispersions increases the adhesive strength of HVOF coating, Co in the coating introduces sufficient ductility and toughness to the coating and a part of Co is getting oxidized to  $\text{CoO}$  depending on the availability of oxygen at the interface. Chromium easily forms chromium oxide layer and it protects the component [26-28]. The chromium oxide forming as a result of oxidation of the alloy reduces oxide ion content of the fused salt to a low level so that the adverse reaction between scale and oxide ions does not take place [27]. This is responsible for improved corrosion protection and less weight gain in the HVOF coated Ti-31 compared to uncoated Ti-31. The improved protection continues as long as the protective oxide scale remains intact. It is also to be noted that the coating is having some amount of porosity which facilitates diffusion of oxide ions to interior causing continuous weight gain as shown in Fig. 2.

### 4. Conclusions

The Ti-31 material was coated using High Velocity Oxy-Fuel process using a fused blend powder of  $\text{Al}_2\text{O}_3\text{+CoCrAlTaY}$ . The coated and uncoated Ti-31 substrates were subjected to hot corrosion experiments under the environment of 50 wt%  $\text{Na}_2\text{SO}_4\text{+}50$  wt%  $\text{V}_2\text{O}_5$  at  $800^\circ\text{C}$  for 50 cycles of 1 hour heating followed by 20 minutes cooling. The weight gain during each cycle is estimated and observed that the weight gain follows a parabolic relationship with time. The rate constant for coated sample was much lesser compared to uncoated sample. XRD and SEM analysis indicates that the surface of the Ti-31, after hot corrosion is rich with oxides of Ti whereas the surface HVOF coated surface is rich in oxides of Cr, Co and Al. The oxides of chromium provides improved hot corrosion resistance property for the HVOF sprayed coatings and it reduces corrosion rate by more than 5 times compared to uncoated Ti-31.

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