Oxidation Studies on As-received and HVOF Sprayed Stellite-6 Coating on Turbine Alloys at 800ºC

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Abstract-Stellite-6 coating was deposited on Co-based superalloy, Titanium based alloy and Fe-based special alloy by high velocity oxy fuel (HVOF) process to enhance their high- temperature oxidation resistance. Oxidation studies were conducted on as-received as well as HVOF-coated alloys after exposure to static air environment at 800ºC under cyclic conditions. Each cycles consisted of 1 hr heating in the silicon carbide tube furnace followed by 20 min cooling in air. Thermogravimetric technique was used to approximate the kinetics of oxidation. Coating surface composition after oxidation studies was characterised by XRD and SEM. Cross section of coatings were analysed by SEM-EDX. The coating and the oxide scale formed on the exposed surface were protecting from the oxidation degradation of materials exposed to high temperature environment.

Keywords: Stellite-6 coating, Oxidation, Thermogravimetric, Superalloy

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1. INTRODUCTION

Cobalt based superalloy and Titanium and alloys are used in gas turbine engines and wide use of its alloys in aircraft and space industries [1-3]. Special alloys (Superalloys) have been developed for high temperature applications but they are not able to meet the requirements of both the high-temperature strength and the high-temperature oxidation and erosion-corrosion resistance, simultaneously [4-6]. However, poor oxidation resistance exposed to elevated temperatures. This poor oxidation resistance is due to formation of unprotected oxide scale consisting of a heterogeneous mixture of alumina and titania on high temperature environment [7-9].

One possible way to overcome this problem is use of coatings on the superalloy component [10-12]. Coatings take care of the problems related to oxidation, corrosion and erosion whereas the superalloys take care of the requirement of high temperature strength [16-20]. Use of coatings is often justified because of difficulties associated with mechanical properties, workability and high material price of highly alloyed superalloy material. Hence various types of coatings have become highly attractive. HVOF process can produce coatings satisfying some of the requirements of gas turbine applications.

The high velocity oxy fuel (HVOF) process belongs to the family of thermal spray techniques producing a coating having a unique microstructure [13-15]. The possibility of applying the HVOF process to cermets will be explored in the present study.

2 EXPERIMENTAL

2.1 Substrate Material and Coating

Selection of materials for the study: Titanium alloy (Ti 31), Cobalt based superalloy (Superco 605) and Special steel (MDN 121) which are candidate materials for turbine blades were procured form Mishra Dhatu Nigam Limited, Hyderabad, India. The stated composition of the substrate material is given in the Table 2.1. Materials were brought in sheet form and coupons of size 25 mm X 25 mm X 5 mm were cut and used for deposition.

Powder were chosen Stellite-6 based on their resistance against oxidation and the composition of coating is 58.6Co-28.8Cr-2.64Ni-4.51W-2.48Fe-1.15C-1.31Si-0.3Mn-0.02P-0.009S-0.04Mo, manufactured by Shanghai Zhong Zhou Special Alloy Materials Co Ltd, Spherical shape -45 to +15µm size. HVOF spraying was carried out using METCO DJ2600 equipment, which utilizes a supersonic jet generated by the combustion of liquid petroleum gas and oxygen mixture. The spraying parameters employed during HVOF deposition are listed in Table 2.2. Substrate steels were grit-blasted with Al_2O_3 before HVOF spraying to develop better adhesion between the substrate and the coating. The HVOF coating process was carried out in Spraymet Coating Industries, Bangalore, India.

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TABLE 2.1 SUBSTRATE MATERIAL COMPOSITIONS

Sl. No.	Name of the Material	ASTM Grade	Composition
1	Titanium alloys (Ti 31)	ASTM B338 Grade 5	Ti-6Al-4V
2	Cobalt base superalloy (Superco 605)	(ASTM F90-09)	Co-3Fe-10Ni-20Cr-1.5Mn-0.3Si-0.08C-15W
3	Special steel (MDN 121)	(ASTM A565 Gr616)	Fe-0.8Ni-12Cr-1Mo-0.6Mn-0.25Si-0.2C-0.3V

TABLE 2.2 HVOF PROCESS PARAMETERS

Oxygen flow rate	250 LPM
Fuel (LPG) flow rate	60-70 LPM
Air-flow rate	700 LPM
Spray distance	0.20-0.25 m
Powder feed rate	0.3-0.50 N/min
Fuel pressure	68 X10^4 N/m^2
Oxygen pressure	98 X 10^4 N/m^2
Air pressure	54 X 10^4 N/m^2
Nitrogen gas (powder carrying gas) pressure	49 X 10^4 N/m^2

The uncoated as well as coated specimens were subjected to oxidation in static air at 800°C for 50 cycles. Thermo gravimetric studies were conducted holding time in the furnace was one hour in which the boat with specimen was taken out and cooled to room temperature for 20 minutes. Following this, weight of the boat along with specimen was measured and this constituted one cycle of the oxidation study. Any spilled scale in the boat was also taken into consideration for the weight change measurements. The weight change values were measured at the end of each cycle with the aim to understand the kinetics of corrosion. Visual observation was made after the end of each cycle with respect to colour, luster or any other physical aspect of the oxide scales being formed. The oxidation products of the uncoated and HVOF coated materials are analyzed by using XRD, SEM and EDX to reveal their microstructural and compositional features for elucidating the oxidation mechanisms.

3 RESULTS AND DISCUSSION

3.1 Thermo gravimetric Oxidation Studies on Uncoated Samples

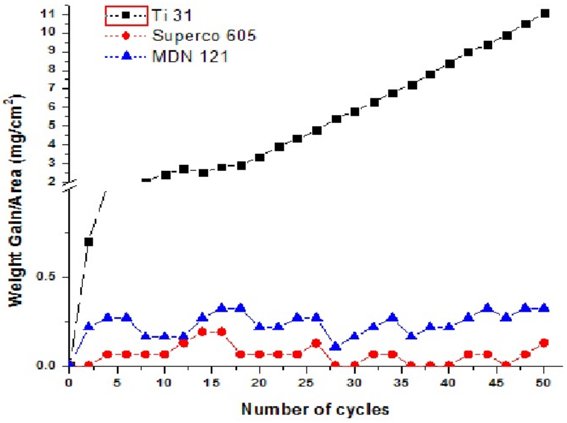
The uncoated of Ti 31, Superco 605 and MDN 121 have been subjected to oxidation in air environment for 50 cycles at 800°C. It can be observed that there is an intense spalling of oxide scale on the surface of Ti 31 and from the first cycle the scale starts separating from the substrate of Ti 31 forming a brown colour. On the surface of Superco 605 green colour was observed on the side surface initially which turned to ash colour at 14^{th} cycle and later green colour was observed at the edges after 37^{th} cycle. A light layer with red coloured dot points was observed on the surface of MDN 121 and after two cycles brown spots were formed and later a shining surface was found after 37^{th} cycle.

The plots of cumulative weight gain (mg/cm^2) as a function of time expressed in number of cycles are shown in Fig. 3.1a. The weight gain for Ti 31 at the end of 50 cycles is found to be 11.03 mg/cm^2. Evidently the Ti 31 showed a maximum weight gain [9] during the oxidation studies in air environment as compared to the Superco 605 and MDN 121. Superco 605 and MDN 121 exhibit weight loss during the complete cycles of oxidation studies as a result of intense spalling and sputtering of the oxide scale formed on the surface which made it difficult to measure the overall weight gain. Further the weight gain square (mg^2/cm^4) data is plotted as a function of time in Fig. 3.1b. The plot shows an observable deviation from the parabolic rate law for the Ti 31 which indicates that the oxide scale is not very protective in air environment. It is evident from the plot that the Superco 605 and MDN 121 follow parabolic behaviour. The parabolic rate constant, Kp for the Ti 31 is 210.7*10^{-8} g2$cm^{-4}s^{-1}$.

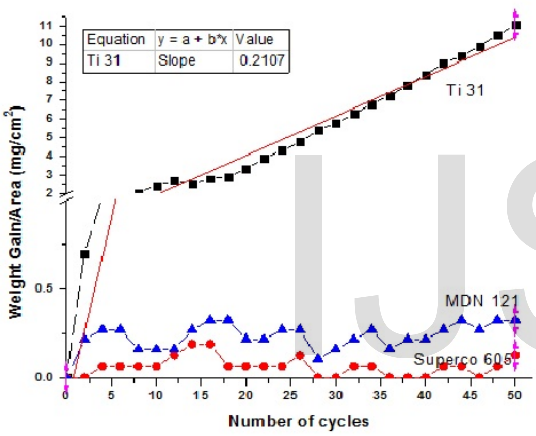
3.2 Thermo gravimetric Oxidation Studies on Stellite-6 Coated Samples

The HVOF sprayed Stellite-6 coatings on the Ti 31, Superco 605 and MDN 121 subjected to oxidation in air environment for 50 cycles at 800°C are illustrated in Fig. 3.2a. The colour of the as-sprayed coating was dark grey which remained same during the complete cycles of exposure to air environment. Superco 605 and MDN 121 did not show any specific observations during the oxidation studies whereas Ti

31 formed cracks on the top surface and at the sides after 15th cycle which propagated to unexposed surface after 32nd cycle.



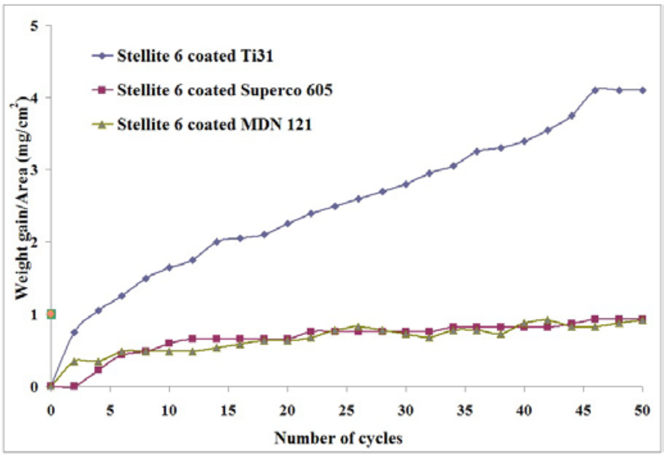
(a)

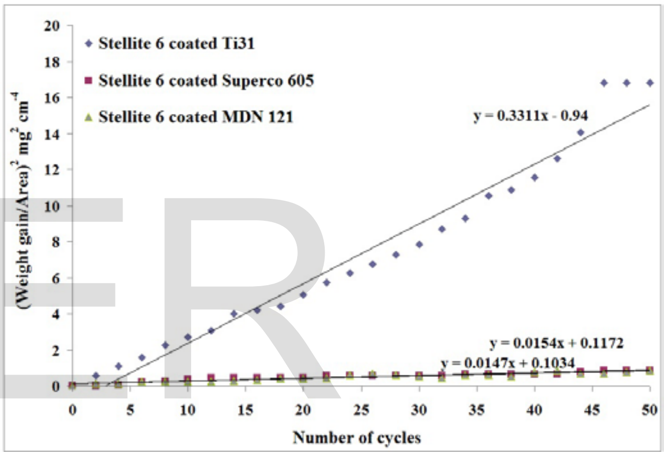


(b)

Fig 3.1 Uncoated samples subjected to oxidation in air at 800°C (a) Plot of weight gain/area versus number of cycles (b) (weight gain/area) ^{2} versus number of cycles

The plots of cumulative weight gain (mg/cm^2) as a function of time expressed in number of cycles are shown in Fig. 3.2b. The values of overall weight gain after 50 cycles of oxidation for Stellite 6 coated Ti 31, Superco 605 and MDN 121 are found to be 4.09, 0.92 and 0.92 mg/cm^2, respectively. Evidently the coated Ti 31 showed a maximum weight gain during the oxidation studies in air environment as compared to the MDN 121 and Superco 605 but MDN 121 has oxidized more than Superco 605 which has shown the least oxidation rate. Further the weight gain square (mg^2/cm^4) data is plotted as a function of time in Fig. 3.2b. The plot shows an observable deviation from the parabolic rate law for the Ti 31 which indicates that the oxide scale is not much protective in static air environment. It is evident from the plot that the MDN 121 and Superco 605 nearly follow parabolic behavior. The parabolic rate constants, Kp for the Ti31, Superco 605 and MDN 121 are 33.1*10^{-8}, 1.54*10^{-8} and 1.47*10^{-8} g^{2}cm-4s^{-1} respectively [12].





(a)

(b)

Fig. 3.2 Stellite 6 coated samples subjected to oxidation at 800°C (a) Plot of weight gain/area versus number of cycles (b) (Weight gain/area)^2 versus number of cycles.

3.3 X-ray Diffraction Analysis

The X-ray diffraction patterns of the top oxide scale, after its exposure to air environment at 800°C for 50 cycles are shown in Fig. 3.3. The oxide scale on the Stellite 6 coated on substrates Ti 31, Superco 605 and MDN 121 under study consisted of CoO, Cr_2O_3 and NiO as major phases on the surface. The samples also showed the presence of FeO, MnO, WO_3, SiO_2 as oxide scales, CrC, as intermetallic phase and $NiAl_2O_4$, $NiCr_2O_4$, $CoAl_2O_4$ and $CoCr_2O_4$ are spinel as minor phases found on the oxide surfaces [14].

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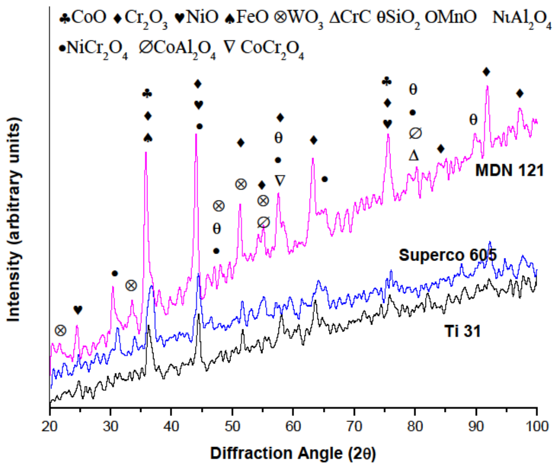
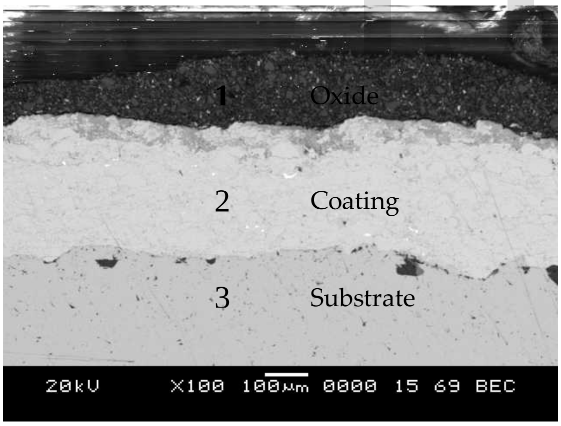
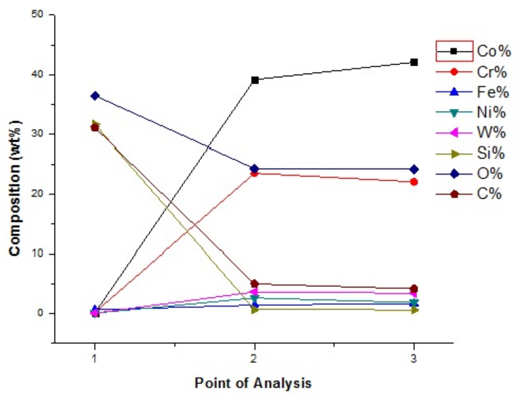


Fig. 3.3 X-ray diffraction patterns for Stellite-6 coated Ti 31, Superco 605 and MDN 121 subjected to cyclic oxidation for 50 cycles in air at 800°C

3.4 Cross-Sectional Analysis



(a)



(b)

Fig. 3.4 Back scattered image and EDX analysis (wt%) (a) The cross-section of the Stellite-6 coated Ti 31 material subjected to oxidation for 50 cycles at 800°C (b) Point of analysis

Results of the cross sectional analysis of the oxidized HVOF Stellite-6 coating on Ti 31, Superco 605 and MDN 121 are shown in Fig. 3.4. A continuous and adherent oxide scale is formed on the coating materials, which has retained the dense structure of the as sprayed coatings even after the oxidation run for 50 cycles. EDX analysis of oxidized Stellite 6 coated Ti 31 (Fig. 3.4) shows the top surface of the scale mainly as oxides of Cr and Co, with subsequent splat boundaries showing high amount of Cr_2O_3. Cross-sectional EDX analysis of Ti 31 shows that the Stellite-6 coating provided the necessary protection against the oxidation by forming a Cr_2O_3 scale on the uppermost part of coating there by CoO and NiO in the subscale region. Here also presence of oxygen in the coating may be due to in-flight oxygen during oxidation of coating, which leads to the formation of Cr_2O_3 [15].

3.5 X-ray Mapping Analysis

X-ray mapping of the cross-section of oxidized samples were done. X-ray mapping of the scale formed on Stellite-6 HVOF coated Ti-31 after oxidation in air environment at 800°C for 50 cycles are shown in Fig. 3.5.

4. CONCLUSIONS

From the (weight gain/area) vs. number of cycles graph of the Stellite-6 coated samples it was observed that the Stellite 6 coated substrate of Ti 31 showed a very high weight gain whereas the Superco 605 substrate has the least weight gain. The weight gain of the MDN 121 substrate is found to be comparatively higher than Superco 605. Thus it can be inferred that Superco 605 shows the highest resistance to oxidation whereas the Ti 31 coated substrate has the least resistance to oxidation. The weight gain after 50 cycles for the coated samples of Ti 31, Superco 605 and MDN 121 were found to be 4.09, 0.92 and 0.92 mg/cm^2, respectively. On comparing the parabolic rate constants Kp of the coated substrates it was found that the parabolic rate constant of the coated substrate of Ti 31 was very high when compared to the coated substrates of Superco 605 and MDN 121.

From these observations it could be inferred that since the Kp value is decreasing for the coated substrates of Superco 605 and MDN 121 the coating has provided good oxidation protection to the base materials whereas the higher Kp of the Ti 31 coated substrate shows that it has less oxidation resistance. It is observed that even though the oxidation resistance of the coated samples of Superco 605 and MDN 121 are high, Superco 605 is found to have a lower value of Kp of the two and thus it has the best oxidation resistance.

The Stellite-6 coating gave a noticeable improvement in oxidation resistance and the oxidation behaviour was parabolic in nature. The protection imparted by the Stellite-6 coating is due to the formation of oxides of Cr and Co. The Stellite-6 coating was dense and maintained its integrity, even after 50 cycles of heating and cooling in presence of salt mixture.

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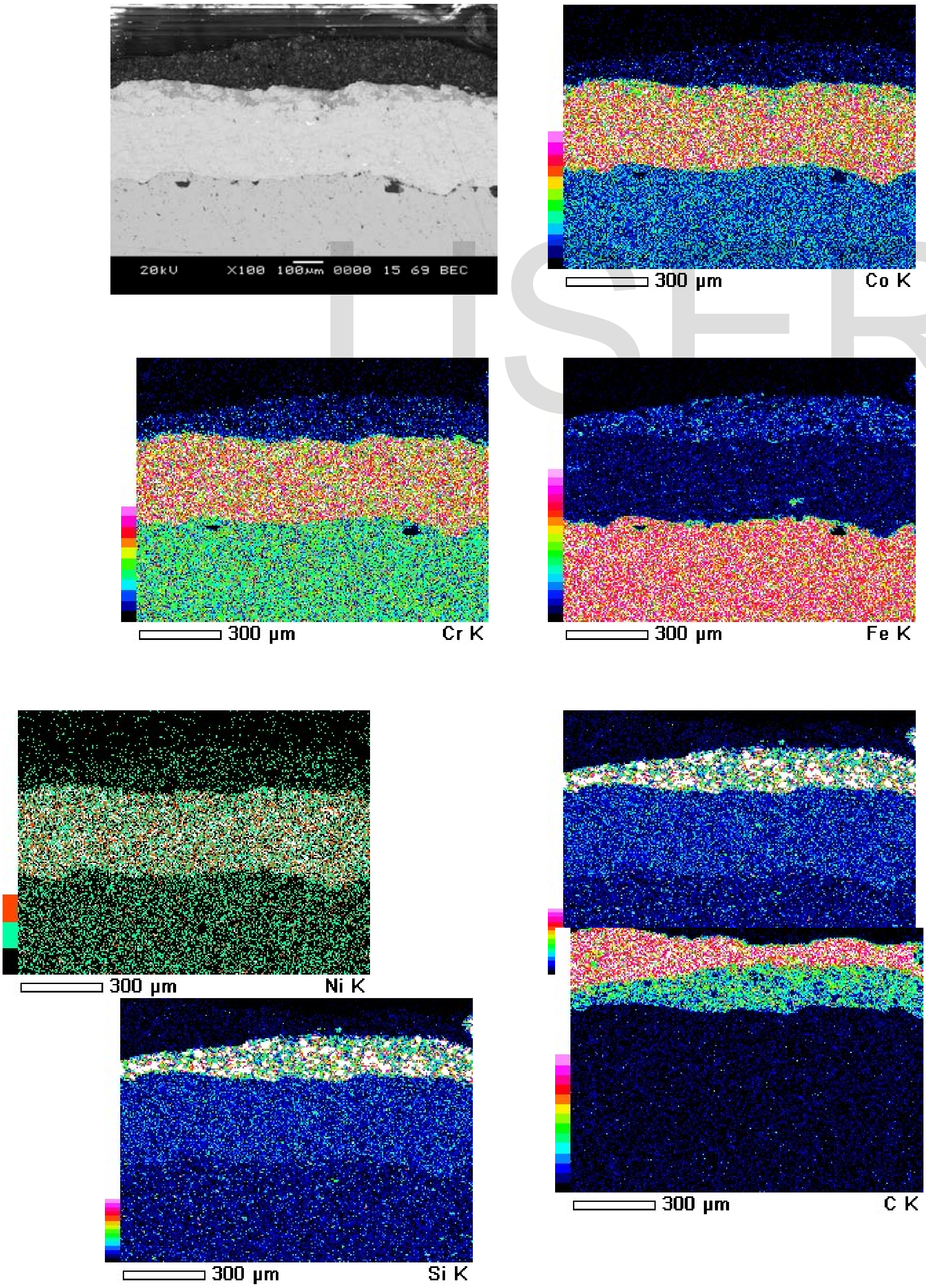

Fig. 3.5 X-ray mapping along the cross-section of the Stellite-6 coated Ti 31 material subjected to oxidation for 50 cycles at 800°C