

Corrosion behaviour of WC-Co coating on Ti6Al4V using Detonation Spray

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Abstract

In this work, thermal barrier surface coatings were applied on Ti6Al4V substrate using high velocity oxy fuel (HVOF) to improve corrosion resistance. The ceramic coating (WC-Co) were deposited on Ti6Al4V substrate with different thicknesses such as 250 μ m, 350 μ m and 450 μ m. In the present investigation, hardness of both coated specimens and substrate were found by conducting Vickers hardness test. The cross sectional and surface morphology of substrate and coated system with varying thickness were made using SEM. In the present investigation, hardness of both coated specimens and substrate were found by conducting Vickers hardness test. The porosity of coated system was carried out by using SEM. The bonding strength of the coatings was examined by pull-off test using Instron tester (Model 1121) with a stretching rate of 2mm/min. XRD characterisation was performed for substrates and coated samples. The cross sectional and surface morphology of substrate and coated system with varying thickness were made using SEM.

Potentiodynamic polarization tests were conducted in Ringer's solution (at 37°C and pH value was set to 5.7) to investigate the corrosion performance of coated samples and substrate. Finally the results reveal that 250 and 350 μ m thickness coated samples showed substantial improvement in corrosion resistance compared to bare substrate. However, the 450 μ m thickness coated samples showed poor corrosion resistance compared to substrate. The scale formed on the samples upon corrosion was characterized by using SEM analysis to understand the degradation mechanisms

Keywords - Ti6Al4V, HVOF, WC-Co, Corrosion, Potentiodynamic polarization

1. Introduction

With the rapid development of modern industry, quality of surfaces of structures, products and components are important from many aspects such as, reliability, surface life, maintenance and economics. A local failure on the surface usually causes the entire component to be rejected or it may lead to a failure of a machine or structure. Thus, many countries have taken great efforts in

improving the surface performance of parts in order to enhance the reliability of mechanical equipment parts and prolonging their service life.

2.Literature Review

Effect of grinding on the erosion behaviour of a WC–Co–Cr coating deposited on medium carbon steel by HVOF and detonation gun spray process was investigated by J. K. N. Murthy et al.[1]. They presented detailed characterization of the WC–Co–Cr coating in both ‘as-coated’ and ‘as-ground’ form. A detailed analysis indicated that the increase in residual stress in the ground specimen is a possible cause for the improvement in erosion resistance.

Microstructure and mechanical properties of detonation gun sprayed NiCrAlY+CeO₂ alloy coatings deposited on superalloys was investigated by K. Subash et al.[2] The morphologies of the coatings were characterized by using the techniques such as optical microscopy, X-ray diffraction and field emission scanning electron microscopy/energy-dispersive analysis.

A. K. Basak et al. [3] studied on the corrosion and corrosion–wear behaviour of a thermal sprayed nano-structured FeCu/WC–Co coating were investigated in a Hank’s solution and compared to stainless steel AISI 304 and nano-structured WC–Co coatings.

The corrosion behaviour of Ti6Al4V alloy with nitride coatings was investigated by I. M. Pohrelyuk et al. [4] in Ringer’s solution at 36 and 40°C. They demonstrated that the nitride coatings improve anticorrosion properties of alloy at both solution temperatures. Corrosion resistance of alloy increases with the content increase of TiN phase in nitride coating. With increase of temperature from 36 to 40°C the corrosion resistance of alloy is determined significantly by quality of nitride coating.

TiN and Ti–O/TiN films have been deposited on Ti6Al4V substrate using plasma immersion ion implantation and deposition (PIII&D) technique by G.J. Wan et al. [5]. It has been proved that TiN and Ti–O/TiN films both enhance the corrosion resistance of substrate materials. Potentiodynamic polarization curves showed that both Ti6Al4V substrates deposited with these two kinds of films have lower dissolution currents than that of the uncoated one.

The oxidation and H₂O/NaCl-induced corrosion behaviours of Ti6Al4V with and without Ni–Si coatings were investigated by C. Yu et al. [6]. The isothermal oxidation tests were performed at 650°C for 100h in ambient air, while the corrosion experiments were carried out at 600°C for 10h in O₂/H₂O mixture with NaCl deposit on the specimens. The Ni–Si coatings possessed excellent oxidation and corrosion resistances and eliminated the corrosion-induced crack which was observed in the uncoated Ti6Al4V specimens after 10h of corrosion.

A detailed evaluation on corrosion resistance of laser surface alloyed of AISI 304 stainless steel with WC+Ni+NiCr (in the ratio of 70:15:15) has been studied by J. D. Majumdar [7]. The corrosion property is measured using a potentiodynamic polarization testing unit in a 3.56 wt.% NaCl solution.

3.Experimental setup

This paper describes the materials (i.e. Ti6Al4V substrate, WC–Co powders and coatings), coating techniques employed, testing procedures, hardness, etc.) and corrosion effects. Examination and assessment of the coating microstructures in terms of surface morphology, porosity, cracks, chemical composition and phase constituents was carried out using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The hardness of the coatings and substrate was measured by using Vickers Microhardness Tester. The corrosion performance of the coatings was evaluated using potentiodynamic polarisation at room temperature. The corrosion morphology of coatings was observed using SEM.

3.1 Materials

In the present study, Table 1 shows the chemical composition of Ti6Al4V substrate. This alloy widely used in chemical plants, automobile, aerospace industries and medical applications (bone, dental). WC–Co powders with an average particle size of 30 and 35 μm are used as coating materials whose chemical compositions presented in Table 2. The feedstock powders were produced by an agglomeration method. In the present investigation, WC–Co powder was used with varying average coating thickness from 250 to 450 μm .

Table 1 Chemical composition of Ti6Al4V

Ti	Al	V	Fe	C	Mo	Cr	O	N	H
Bal	6.52	4.17	0.16	0.013	0.03	0.01	0.17	0.006	0.0011

Table 2 Chemical composition of WC–Co powder

WC	Co
94	6

3.2 Base Material Preparation



Figure 1 Grit blasting equipment

The substrate of size 25mm length and 10mm diameter bare specimens with one of its surfaces were grit blasted with alumina grits of grit size 70 and pressure about 90PSI, using pneumatic type grit blasting equipment shown in Figure1, followed by an ultrasonic cleaning in acetone to attain enough surface roughness for the best adhesion between coating and substrate.

3.3 Detonation Spray (DS) Technique

DS offers a controlled explosion of a mixture of fuel gas, oxygen and powdered coating material and is utilized to melt and propel the material onto the substrate. The "waves" are produced by igniting a mixture of acetylene and oxygen into the detonation chamber which is open to a 1m long tube and 2.5cm in diameter. The system consists a mixture of spray material, acetylene and oxygen is injected into the detonation chamber. Combustion gases can be neutral, reducing or oxidizing and can have their temperature controlled by the addition of an inert gas, for cooling, or hydrogen to heat it. The procedure is initiated by a gas/powder metering system that measures and delivers the mixture in the chamber where it is ignited. The resulting shock wave accelerates the powder particles to over 731m/sec and produces temperatures in excess of 4000°C. Pressures from the detonation close the controlling valves until the chamber pressure is equalized. When this occurs the cycle may be repeated either 4 or 8 times per second. There is a nitrogen purge between cycles. Each detonation deposits a dense and adherent layer of 30–500µm thick and about 2.54cm in diameter. The spray distance ranges 90mm to 500mm. The gun speed ranges 5mm/sec to 50mm/sec. The DS process set up is shown in Figure 2.



Figure 2 DS process set up

In the present study, DS technique was used to deposit WC-Co coat with varying coating thickness. The standard process parameters used for DS

Table 3 Process parameters for DS

Parameter	Quantity
Oxygen flow rate (l/min)	35
Gas flow rate (l/min)	15 (H ₂)
Spray distance (mm)	15 (N ₂)
Sample speed (m/s)	180mm
Gun speed	2.5 m/s

3.4 Testing and Characterization



Figure 3 Vickers digital hardness tester DHV-1000

Hardness test and wear test are carried out since the wear is the function of hardness. In order to characterize uncoated and WC-Co coated surface, hardness tests are performed by using Vickers digital hardness tester DHV-1000 as shown in Figure 3.

The corrosion tests were performed by using a GILL AC electrochemical apparatus (ACM instruments, United Kingdom) is shown in Figure 4. The solution was deaerated to remove oxygen with nitrogen (N₂), and the process was started 1h prior to the measurement. The specimens were immersed into the solution until obtaining a steady open circuit potential (OCP). After equilibration, polarization started at a rate of 1mV/s. The cycle began at the cathodic over potential, according to OCP, and the scan was stopped when the specimens reached the anodic current density of approximately 1mA/cm².

The corrosion behaviour coated and uncoated samples were investigated by potentiodynamic polarization technique. All the electrochemical measurements were carried out in accordance with ASTM standard of G107-95A. The electrochemical behaviours of the materials have been analyzed in deaerated Ringer's solutions (NaCl = 8.60g/L, CaCl₂·2H₂O = 0.33g/L and KCl = 0.30g/L) in a pyrex glass cell. The pH of the test solution was 5.7 at room temperature. The potentiodynamic polarization curves were obtained by an Ag/AgCl reference electrode and a platinum (Pt) counter electrode. The exposed area of the working electrodes was about 0.785cm².



Figure 4 Electrochemical system of GILL AC unit for corrosion test

In the present study, JSM-6610LV Scanning electron microscope (SEM). X-ray diffraction patterns of the as-coated samples were taken using an Ultima IV X-ray diffractometer with CuK α radiation and Ni filter.

4. Results and Discussion

The WC-Co coatings are deposited by melting, partially melting and un-melting of powder particles which are sprayed at high velocity on the substrate (Ti6Al4V), using a HVOF technique. Figure 5 a-c shows a typical cross sectional view of WC-Co coating with varying coat thickness. The coating thickness was measured on the SEM micrograph.

The mechanical bonding between the WC-Co coatings can be clearly seen.

The XRD pattern of HVOF sprayed WC-Co coatings are shown in Figure 6 a-c. Peaks corresponding to WC and W₂C are clearly seen in all the three cases i.e. 250 μ m, 350 μ m and 450 μ m thick coated samples. The presence of W₂C in HVOF coatings is due to undesired decarburisation of WC.

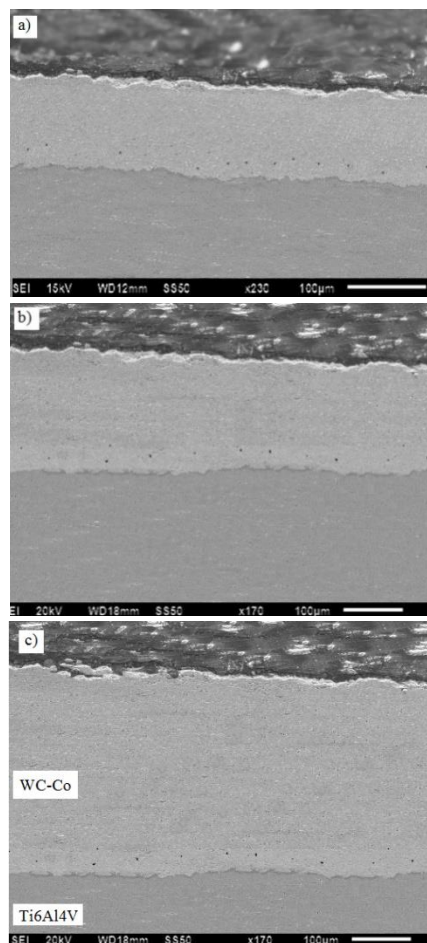


Figure 5 Cross sectional SEM micrographs with varying top coat thickness a) 250 μ m b) 350 μ m and c) 450 μ m

The micro hardness increased with increasing coating thickness, which can be attributed to reduction in porosity during deposition of coatings. The increase in wear resistance can be attributed to the increase in hardness which results from hard WC particles on the substrate.

The microhardness of the substrate is found to be 324HV and that of 250 μm , 350 μm and 450 μm coated sample is 1215HV, 1257 HV and 1294 HV.

The potentiodynamic polarization tests were undertaken in Ringer's solution, and the related curves of varying thick WC-Co coated and uncoated Ti6Al4V substrates, in comparison, are given in Figure 7

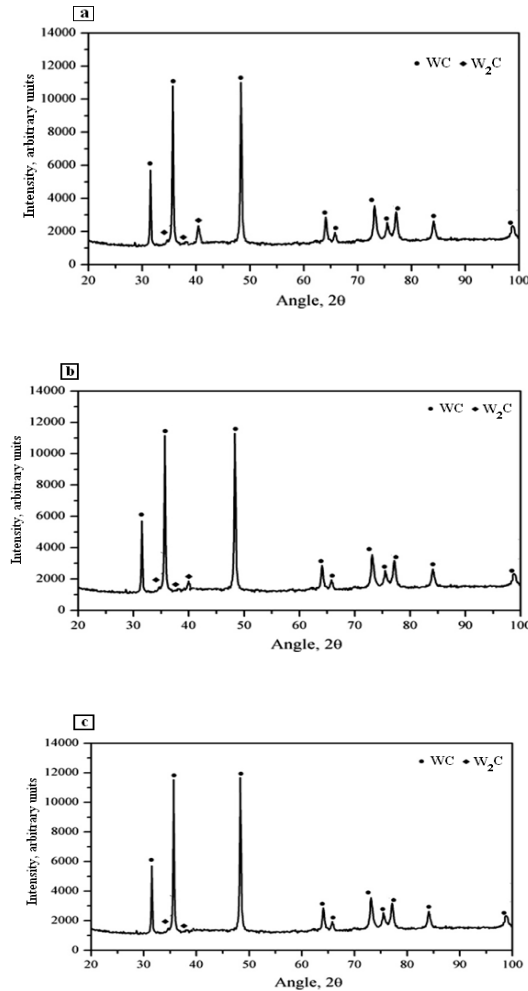


Figure 6 XRD patterns of WC-Co coatings a) 250 μm b) 350 μm c) 450 μm

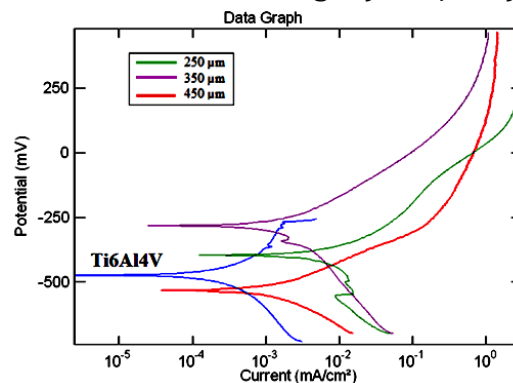


Figure 7 Potentiodynamic polarization curves for uncoated and coated samples

It can be clearly seen from Figure 7 that the highest corrosion resistance was exhibited by the 350 μm thick coated samples over the 250 μm thick coated samples in the Ringer's solution at

room temperature, which can be attributed to the decrease in porosity. However, 350 and 250 μm thick coated samples showed better corrosion resistance than Ti6Al4V substrate. But, surprisingly the 450 μm thick coated specimen exhibits lower corrosion potential compared to the substrate material, this can be due to increase in tensile stresses which causes spallation where the fluid medium stagnates and does not allow the oxygen content to the substrate surface. The E_{corr} value of 250 and 350 μm thick coated samples are -400.50 and -290.50mV respectively, which are higher than the value of Ti6Al4V. But the E_{corr} value is -540mV for 450 μm thick coated sample which was found to be lower than the value of Ti6Al4V. Also, it is obvious that the 350 μm thick coated samples are more positive E_{corr} value compared to all coated samples and substrate.

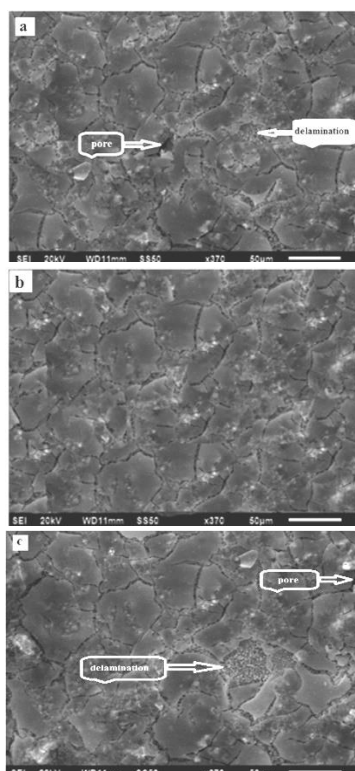


Figure 8 SEM graphs after corrosion test for a) 250 μm b) 350 μm c) 450 μm

In the present study it is clear that the hardness increases with increasing the coating thickness due to decrease in porosity. Figure 8 shows the SEM graphs after corrosion test for 250 μm , 350 μm and 450 μm thick coated samples and evident that the 250 μm thick samples having more pores and consequently the corrosive medium attacks into the substrate through the pores, which results in little delamination. Also the delamination of coating material increases with increasing coating thickness, the thicker coatings (450 μm) causes weakening of bond strength. Increasing the coating thickness, increasing tensile stress and reducing bond strength there by the corrosion can be initiated and so rendering the WC-Co coating liable to severe attack (Figure 8c). The passivation is high for 350 μm thick coating which can be attributed to delamination free coating structure as shown in Figure 8b and the passivation is moderate for 250 μm thick coating which can be attributed to only a little delamination of coating as shown in Figure 8a. But for 450 μm thick coating the passivation is very low which is lower than Ti6Al4V substrate because of significant delamination and it is clearly observed in Figure 8c.

5. Conclusion

The corrosion potential of Ti6Al4V is -470mV. The corrosion potential of 250, 350 and 450 μ m thick coated samples are -400.50, -290.50mV and -540mV respectively. So, 250 and 350 μ m thick coated samples exhibit more positive potential than Ti6Al4V, but 450 μ m thick coated samples exhibit negative potential than Ti6Al4V.

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Conflicts of interest

The authors have no conflicts of interest to declare.

Author's Contribution Statement

K. Raghu Ram Mohan Reddy: Conceptualization, formal analysis, methodology, validation and writing draft. **P N E Naveen:** Conceptualization, formal analysis, methodology.

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