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ORIGINAL ARTICLE

Corrosion behavior of duplex coatings

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Abstract The titanium alloys are used in defense, aerospace, automobile, chemical plants and biomedical applications due to their very high strength and lightweight properties. However, corrosion is a life-limiting factor when Ti alloys are exposed to different chemical environments at high temperatures. In the present paper, duplex NiCrAlY/WC–Co coating is coated onto Ti6Al4V substrate to investigate the corrosion behavior of both coated samples and the substrate. The duplex coating was performed with NiCrAlY as the intermediate coat of 200 μm thickness deposited by HVOF process and WC–Co ceramic top coat with varying thicknesses of 250 μm, 350 μm and 450 μm deposited by DS process. Potentiodynamic polarization tests were employed to investigate the corrosion performance of duplex coated samples and substrate in Ringer's solution at 37 °C and pH value was set to 5.7. Finally the results reveal that 350 μm thick coated samples showed highest corrosion resistance compared to 250 μm thick samples as well as bare substrate. However, the 450 μm thick coated sample showed poor corrosion resistance compared to the substrate. The scale formed on the samples upon corrosion was characterized by using SEM analysis to understand the degree of corrosion behavior.

1. Introduction

Titanium alloys are widely sought after materials for biomedical applications, as they possess better corrosion resistance and biocompatibility as compared to stainless steel, Co–Cr alloys. Among various titanium alloys, Ti6Al4V is extensively used due to its useful mechanical and electrochemical properties (Goldberga and Gilbertb, 2004). A thorough understanding of high temperature corrosion behavior of Ti–6Al–4V is very essential for its viable applications in gas turbine components. It is essential to understand the degradation mechanism of titanium alloys under hot corrosion conditions and, subsequently, to apply appropriate coatings to effectively combat hot corrosion. Also, various surface modification methodologies such as plasma ion implantation (Mandl and Rauschenbach, 2002), laser melting (Singh et al., 2006) and laser surface alloying (Man et al., 2005), thermal oxidation (Garcia-Alonso et al., 2003), have been tried out to improve wear, corrosion, and fretting resistance of orthopedic implant materials including Ti6Al4V. Raghu Ram Mohan Reddy et al. (2013a,b) studied

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the tribological behavior of duplex coatings on Ti6Al4V alloy using HVOF and DS.

In general, the corrosion/erosion/wear resistance of thermal spray coatings depends on the chemistry and morphology of coatings. Microstructural features which enhance the coating performance include high density and low porosity, small grain size, good adhesion and absence of cracks (Wang and Lee, 1997). Wang et al. (2013) deposited WC coatings consisting of different binders by HVOF and found that the corrosion resistance of WC–Co–Cr coating was superior to that of WC–Co coating. Also Jafari et al. (2013) investigated the oxidation behavior of HVOF-sprayed WC–12Co and WC–10Co–4Cr coatings. The authors reported that the higher oxidation resistance of WC–10Co–4Cr coating probably results from the formation of compact chromium oxide layers and higher MWO_4 type tungstate (M: Co and/or Cr) to tungsten trioxide (WO_3) ratios which provide lower porosity.

In the present investigation duplex coatings were employed on the Ti6Al4V substrate to enhance the corrosion resistance. The NiCrAlY bond coat was deposited with 200 μm thickness by using HVOF and WC–Co top coat was deposited with varying thicknesses (250 μm, 350 μm and 450 μm) by using DS.

2. Experimentation

2.1. Coating deposition

Thermal spray duplex coatings were deposited on Ti6Al4V substrate. NiCrAlY and WC–Co were used as coating materials. The chemical compositions of NiCrAlY powder and WC–Co powder are presented in Tables 1 and 2 respectively with an average particle size of 30 μm. In the present investigation, duplex coating was performed with NiCrAlY as the intermediate coat of 200 μm thickness deposited by HVOF process and WC–Co as the top coat with varying thicknesses of 250 μm, 350 μm and 450 μm deposited by DS process. Prior to deposition the substrate surfaces were grit blasted with alumina grits, followed by an ultrasonic cleaning in acetone. The grit blasting was performed to get an optimum surface roughness and promote the best attainable adhesion between coating and substrate. The standard spraying process parameters are followed for HVOF and DS (Raghu Ram Mohan Reddy et al., 2013a,b). JSM-6610LV Scanning electron microscope (SEM) equipped with energy dispersive X-ray analyzer (EDX) is used to study the microstructure of the samples. X-ray diffraction patterns of the powders and coatings were taken using an Ultima IV X-ray diffractometer with CuKa radiation and Ni filter.

Table 1 Chemical composition of NiCrAlY powder.

Constituent	%
Cr	22
Al	10
Y	1
Ni	Bal.

Table 2 Chemical composition of WC–Co powder.

Constituent	%
WC	88
Co	12

2.2. Residual stress measurements

Residual stress measurements are made using PANalytical X-Pert Pro MRD system for untreated and heat treated samples.

2.3. Microhardness test

Microhardness tester model VMHT auto was used to find microhardness of substrate and coated material. Microhardness tests were performed by using the Vickers Microhardness tester (model VMHT auto) on a cross section of coatings with a load of 300 g and dwell period of 10 s. An average of three readings is reported.

2.4. Pull-out test

The pull-out tests were performed to those coated specimens under an increasing load with a stretching rate of 2 mm/min using a tensile test machine (Instron materials tester – Model 1121) until the shearing failure occurred. The failure mode is recorded gradually, and the bonding strength is calculated as the load at failure divided by the coated bonded area.

2.5. Potentiodynamic polarization test

The corrosion behavior of duplex coatings and uncoated samples was investigated by potentiodynamic polarization technique. All the electrochemical measurements were carried out in accordance with ASTM standard of G107-95 A. The electrochemical behaviors of the materials have been analyzed in deaerated Ringer's solutions (NaCl = 8.60 g/L, $CaCl_2{\cdot}2H_2O$ = 0.33 g/L and KCl = 0.30 g/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 (0.785) cm^2. The corrosion tests were performed by using a GILL AC electrochemical apparatus (ACM instruments, United Kingdom). The solution was deaerated to remove oxygen with nitrogen (N_2), and the process was started 1 h 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 1 mV/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 1 mA/cm^2. After polarization, the examinations of the corroded surfaces were carried out by using a JSM-6610LV model SEM.

3. Results and discussion

3.1. Characterization of coatings

Fig. 1 shows the SEM microstructure of powder samples and Fig. 2 shows the SEM micrographs of cross sectional duplex