Studies on Electrochemical Corrosion Resistance of HVOF Coating For Boiler Material

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Abstract- Thermal spraying process is used to deposit coatings for many industrial high-temperature applications such as in power plants etc, High-Velocity Oxy-Fuel (HVOF) is one of the widely used and recent trends in thermal spraying techniques due to its viability to produce dense deposits, with relatively low porosity. After a thorough review, Ceramicmetallic coating powders were selected to be coated on the substrate material due to their better resistance to corrosion over other coatings like cermet coatings, metallic coatings etc. In order to assess the electrochemical corrosion behavior, tests such as Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) were conducted to examine the potential change as well as the formation of a passive layer in various electrolytic solutions. The boiler tube material (Stainless steel 300 series) was immersed in 1M KOH and KOH+V₂O₅ solutions at various intervals of time to electrochemically characterize the behavior of the coated and uncoated specimens in the solutions.

Keywords- High-Velocity Oxy-fuel (HVOF), Open Circuit Potential, Electrochemical Impedance Spectroscopy.

I. INTRODUCTION

Thermal spray techniques are one of the widely used methods to improve various parameters of a material such as hardness, thermal resistance as well as corrosion and erosion. In thermal spray technique the coating materials are heated to their molten or sub-molten temperature and are deposited on the substrate by high velocity jets, as a result of which the coating material gets impinged and embedded onto the substrate material. Therefore, thermal spray coatings can provide protection against corrosion and wear failures. In this regard, high velocity oxy-fuel (HVOF) coatings are extensively used in industry to improve the corrosion and wear resistance of metallic surfaces[1,2]

HVOF process is widely used and more dominant over other thermal spray techniques such as electric arc, plasma spray because of its ability to produce dense coatings with relatively low porosity. HVOF uses liquid kerosene or other gases such as hydrogen, propane as a fuel for combustion of oxygen in the combustion chamber. The high energy combustion in the chamber produces a flame with high velocity and temperature reaching upto 3000ms⁻¹ and upto 4500° Celsius respectively. This high temperature strongly expanding flame melts the feedstock powder and accelerates it onto the substrate at very high speeds. This results in very dense coating which adhere to the substrate strongly and enhance the substrate properties. Consequently, coatings with high corrosion resistance can be obtained by using HVOF [3]

MA Zavareh et al (2016) has studied on Electrochemical Corrosion Behavior of Carbon Steel Pipes Coated with a Protective Ceramic Layer Using Plasma and HVOF. Ceramic composite Cr3C2-25%NiCr powder was chosen due to its high corrosion resistivity (up to 900°C) and was applied on carbon steel (SC45) pipes by two different thermal spray-coating techniques: HVOF and Plasma. The corrosion behavior of coated samples was investigated in crude oil solution at 60°C and 3.5% NaCl solution at 30°C for 30 days. The case study concluded that Potentiodynamic polarization and EIS results have shown that the HVOFcoated samples exhibit better corrosion resistance than the plasma-coated samples. However, both coating techniques protect carbon steel from a corrosive environment.[4]

Electrochemical corrosion, erosion and fatigue are one of the main mechanisms which happen to the cause of gradual breakdown of boiler tubes and its components. These changes appear due to the effect of chemical and electrochemical reactions.[5] Electrochemical corrosion can be briefly described as a phenomenon which occurs when two different metals are presented together in a conductive corrosive electrolyte. As a result of which a potential forms between the two metals, where one metal becomes the anode and the other the cathode. The anode, or sacrificial metal, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly than it would otherwise.

The necessity of proper protection of the base material by coatings is now a modern method and is extensively used in diverse applications: in the automotive industry, aviation industry, petrochemical and chemical industry, energy, construction, medical devices, internet and

IJSART - Volume 4 Issue 5 - MAY 2018

telecommunications as well as in the consumer goods industry.[5]. To prevent the corrosion mechanism special metallic composites (WC-NiCr and Cr_3C_2 -NiCr) were chosen for the research work as these coatings are economic and change the surface characteristic of the metal by forming a composite with the metal surface. This enhances various properties like hardness, corrosion resistance as well as load bearing capacity.

Cr3C2-NiCr and WC-Ni coatings are widely used for wear applications at high and room temperature, respectively. Due to the high corrosion resistance of NiCr binder, Cr3C2-NiCr coatings are also used in corrosive environments. Erosion-corrosion performance of thermal spray coatings is widely influenced by ceramic phase composition, the size of ceramic particles and also the composition of the metallic binder. In the present work, two types of HVOF thermal spray coatings (Cr3C2-NiCr and WC-Ni) obtained with different spray conditions were studied and compared with conventional micro-cracked hard chromium coatings. Both as-sprayed and polished samples were tested under two erosion-corrosion conditions with different erosivity. Tungsten carbide coatings showed better performance under the most erosive condition, while chromium carbide coatings were superior under less erosive conditions. Some of the tungsten carbide coatings and hard chromium showed similar erosion-corrosion behavior under more and less erosive conditions.[6]

The presence of Carbide in the coatings increases the hardness of the substrate (about 2200HV) and the melting temperature to (about 2800° C) hence coatings containing carbide are preferred due to their good hardness and thermal resistance respectively. Overall it can be said that Tungsten Carbide and Nickel based metallic alloy powders have better resistance to electro-chemical corrosion in various environments such as salt water. High densities with relatively low porosity of these coatings using HVOF thermal spray technique have proved to be a better solution for prevention of corrosion in boiler applications.[7].

II. EXPERIMENTAL PROCEDURES

A. Materials

The substrate material of Stainless Steel was cut in small rectangular pieces of dimension 5mm x 5mm x 25mm strips which was suitable for further electro-chemical tests. The small strips were obtained using wire cut Electro-discharge Machining (EDM) method as it gives accurate dimension as well as good surface finish without changing much of the surface morphology. For the coated samples we coated the

Page | 1748

same specimens with Ceramic-metallic coatings of 300 microns(μ) each for electro-chemical characterization.



Fig 1. Materials used for experimentation

B. Solution Preparation

The electrochemical corrosion tests were performed in 1M KOH(Potassium hydroxide) and 0.5M H2SO4 solution. The salts were dissolved in distilled water and the characterization was conducted under ambient temperature and pressure(25° C).

Potassium Hydroxide (basic):-

Molecular weight:- 56.1056g/mol. Required volume of solution:- 50ml. (Molecular weight / 20) = 56.1056 /20 = 2.805 g/mol 2.805 g + 50 ml= 1 molar solution of 50ml volume.

Sulphuic acid:-

0.5 Molar solution of sulphuric acid was already available in the lab which had already been prepared as a standard for using in other experiments.



Fig 2. The solutions used for analysis.

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C. Specimen Preparation

Before proceeding onto the tests, the specimens had to be prepared in order to avoid any irregularities or ambiguity in the results been obtained.

The sample of 25mm x 5mm x 5mm had to be prepared for electrochemical analysis. The sample was first cleaned with distilled water to remove all the foreign particles and impurities such as dust, grease, oil.etc. Prior to the electrochemical test three specimens of the above dimensions were prepared by polishing one end of the rectangular strips on emery paper of grade 202 and then smooth finishing the surfaces on silica paper using small quantity of Alumina(Al2O3) as an abrasive and washing them with deionized water



Fig 3. Specimen preperation prior to analysis

D. Experimental Setup

In this research all the electrochemical measurements were carried out using conventional three electrode system. Electrochemical analyzer from CH instruments was used to conduct the electrochemical characterization and the results were computed on a standard PC operated by Windows® 7 operating system.



Fig 4. The Electro-chemical analyzer

The three cell electrode mainly consisted of a Counter electrode here a cylindrical platinum wire was used as a counter electrode. As the tests involve using aggressive solution for the electrochemical characterization it was suitable to use inert metals such as platinum as a counter electrode because platinum is one of those few metals which prevents the contamination of the solution. Silver/Silver Chloride(Ag/AgCl) was used as a reference electrode whose potential is +0.222V vs Standard Hydrogen electrode(SHE). This reference potential was used for comparison with the working electrode in our tests. And lastly SS304 was used as our working electrode.



Fig 5. Three cell electrode setup.

III. RESULTS AND DISCUSSION

The understanding of the electrochemical phenomena underlying corrosion processes provides a basic understanding of the mechanisms taking place as well as forms a basis for experimental techniques that allow simple and accurate measurements of the corrosion taking place. During recent years with the advancement of technology we can take advantage of the modern instrumentation, to utilize feedback control and measure very small currents. These highly sensitive instruments allow us to measure small changes in current and potential along with various other factors which help us in determining the underlying corrosion mechanisms which are far more superior to the capabilities of most nonelectrochemical and conventional techniques such as for instance weight loss method or appearance.[9] In this research tests such as Open Circuit Potential(OCP) and Impedance Spectroscopy were performed to study the corrosion mechanisms and its effect on the boiler tube materials.

A. Open Circuit Potential

Open Circuit Potential or also known as polarization is one of the important and preliminary test required in any

IJSART - Volume 4 Issue 5 - MAY 2018

electrochemical characterization as it gives the long term change of corrosion potential which is directly proportional to the corrosion change in the system because corrosion in a system causes a change in either anodic or cathodic reactions which can be measured in Open Circuit Potential test. The electrochemical measurements are highly sensitive to the surface modification by corrosion which is reflected in the change of electrochemical parameters.

In the Open Circuit Polarization tests the specimens to be tested where taken as the working electrode in three-cell electrode setup. The working electrode were dipped in the electrolyte solution exposing about 1-cm² area with a sample interval of 0.1 seconds with an average runtime of about 300 seconds which was enough for the results to be clearly interpreted.

Firstly two environments and their behavior on the boiler tube materials were electrochemically characterized. That is 1M KOH which was chosen as a medium for attack in basic water and second media consisting of 0.5M H2SO4 which was a corrosive species and was found to be a byproduct in coal fired hot gases or coal ash.[8]



Fig 6. OCP plot for SS in 1M KOH and 0.5M H2SO4 slolutions.

The above figure shows OCP plot for SS304L in 1M KOH and 0.5M H2SO4 slolutions. It is observed that in acidic conditions(0.5M H2 SO4) the substrate material is continuously and at uniform rate, but in basic conditions(1M KOH) the material corrodes rapidly and after some time the corrosion reduces due to passivation on substrate.

B. Electrochemical Impedance Spectroscopy.

A method of measuring the electrical impedance of a substance as a function of the frequency of an applied electrical current. Impedance is a measure of the resistance to the flow of an alternating current (AC).



Fig 7. Plot for SS in 1M KOH at a potential of 0.5V

The above diagram shows EIS plot for for SS304L in 1M KOH at a potential of 0.5V. It can be observed that the material is offering less resistance to corrosion in basic medium at lower voltage(0.5V) than in acidic medium



Fig 8. Plot for SS in 0.5M H2SO4 at a potential of 0.5V

The above plot it can be obsered that the impedance at a potential of 0.5V in 0.5M H2SO4 is very high sugesting that the material is offering very high resistance to corrosion in the above conditiions ,(the impedance is in Kohm)

IV. CONCLUSION

The experiments were conducted at Room temperature on the substrate material without any coating using the above stated tests and the results were concluded as given below:-

- As analyzed in the above experiments it was found that the substrate material(SS304L) corroded at a faster rate and there was continuous corrosion in acidic medium(H2SO4 solution).
- And when the substrate was analyzed in a basic medium (KOH) initially the corrosion started at an early phase and then remained constant due to the formation of passive layer.protect the substrate(boiler material) and provide better corrosion resistance.

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