Corrossion Behaviour of Ceramic Coated Stainless Steel in Aqueous Condition

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ABSTRACT:

Stainless steels are used today in a wide range of applications as a result of their combination of high corrosion resistance and good mechanical properties. In marine applications, corrosion resistance may need further improvement, and surface coatings may be applied for enhanced protection. The morphology, composition and corrosion protection has to be investigated using different techniques like optical and electron microscopes. The corrosion protection obtained on AISI 320 stainless steel by the application of this type of ceramic coatings proved to be very cost effective and suitable for corrosion prone region.

I INTRODUCTION

Due to its numerous properties and specifically, its corrosion resistance, stainless steel is used for many applications in the Industrial, Automotive or Domestic sectors. Stainless steel is steel with a chromium content of more than 10.5%

Corrosion can be viewed as a universal phenomenon, omnipresent and omnipotent. It is there everywhere, air, water, soil and in every environment, we encounter.

II FUNDAMENTALS OF CORROSION MECHANISMS

Corrosion is defined as the degradation of a metal when it undergoes an electrochemical reaction with the environment. This phenomenon has a potential to cause catastrophic failures to materials if the causes and prevention of corrosion are not well understood. There are many types of corrosion that can occur in the environment namely uniform, pitting, crevice, galvanic, intergranular and flow-induced. This section of the literature review will focus mainly on the general principles of corrosion. Schematic diagram showing the electrochemical process that occurs during corrosion

The schematic diagram shown in Figure describes a simple electrochemical reaction that occurs during corrosion. For corrosion to take place, a few essential elements have to be present to allow electrochemical reaction to occur. These elements are an anode, a cathode, an electrolyte and some form of connection between the anodic region and the cathodic region. The anode and cathode do not have to be from two separate metals, it could be from different regions of the same metal. Assuming the anodic and cathodic regions are from the same metal, we shall consider the reaction that occurs in Figure 1.2 using iron as the metal and an aqueous neutral or alkaline solution as the electrolyte.

III METHODOLOGY
Flame powder spray

Flame spraying is one of the several methods classified under the category of thermal spraying. This method is used to deposit coatings from ceramic, metallic and polymeric powders. It is primarily used to apply abradable coatings or nickel/chrome self-fluxing alloys which are subsequently heat treated to metallurgically bond them to the substrate (Fused coatings). Abradable coatings are used for machine element clearance in compressors. Fused coatings are extensively used in high wear applications such as mining and steel industries to prevent wear of rolls, pistons and other equipment in aggressive wear environments.

A Flame Spray gun uses oxygen and fuel gases to produce a flame into which powder is injected. The resultant molten particles of powder are projected on to the work piece to produce the coating. Many coatings sprayed by this process are then heat treated at around $1000°C$ to 'fuse' the coatings to the substrate surface. Fused coatings produced by this process are hard and corrosion resistant and are able to withstand wear by abrasion, fretting, cavitation and other hard surfaces. The addition of different proportions of carbon, silicon and boron to the basic nickel/chromium alloy.

They can be applied 1 - 5 mm thick; much thicker than hard ware coatings applied by the plasma or HVOF processes.

Of all the Cermet coatings, the Al_2O_3– TiO_2 coating containing 40 wt.% of TiO_2 showed the most excellent wear resistance.
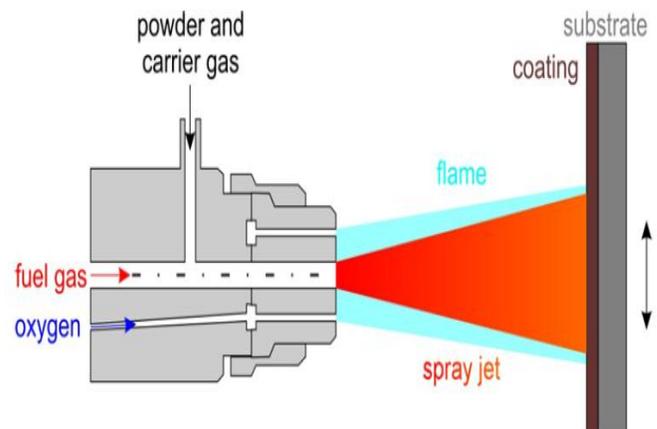
Principles of powder flame spray

Hence Al_2O_3– TiO_2 coating has been chosen for the study.

IV CORROSION STUDIES

Potentiodyamic polarization allows the measurement of the polarization behavior of a metal by continuously applying a potential and monitoring the subsequent current response at a dynamic varying potential. A standard method to perform this test is using a three electrode cell set-up, as shown in Figure.

The cell consists of a working electrode, reference electrode, counter electrode, current measuring device, potential measuring device and a source of potential. The working electrode is the material being investigated with known area, so that the resulting current can be normalized to current density (current per unit area, A .m-2). The counter electrode, normally an inert material, is used to carry the current created in the circuit, while the reference electrode should be a stable material used as a datum to measure the potential of the working electrode. The source of potential must be able to polarize the working electrode to the desired state.

A standard recommended guide for performing potentiostatic and potentiodynamic measurements has been developed by ASTM through ASTM standard G59. It provides a detailed description on the choice of test apparatus, electrodes, good practices on specimen test preparation, and potentiodynamic measurement. Both anodic and cathodic polarization curves can be determined with a single sweep rate by starting the measurement at a negative over potential and swept to a positive direction (above the corrosion potential). At negative over potentials, the counter electrode will act as the anode. Electrochemical Corrosion rate measurements were carried out using the conditions used for testing are listed below in Table.

Corrosion test conditions

Electrolyte	water (pH=2.5, 3.5, 4.5)
Reference electrode	Saturated calomel electrode(SCH)
Counter electrode	Platinum electrode
Working electrode	Stainless Steel (Bare and Al_2O_3-TiO_2 Coated)

Data obtained from the polarization behaviour of the metal can be used to determine the corrosion rate of a metal. Water samples with three different pH conditions (pH=2.15, 4.15, 5.30) were used as electrolytes. The samples made of stainless steel both coated and uncoated are subjected to polarization tests. For comparative purpose, corrosion tests were conducted in Stainless Steel samples as no published literature or data are available for such mining environment. Tafel plots for the different environments for the materials considered were drawn. These permit rapid and accurate corrosion rate measurements and gives broader ideas of corrosion rates which cannot be measured with conventional mass less methods or chemical analysis methods. To know the intensity of corrosion I_{Cor}, E_{Cor} values and Liner polarization resistance were plotted for all the tests.

Coating Equipement

All of the samples deposited by coating technique must be scientifically characterized either macro or microscopically to gain coating microstructural characteristics such as chemical composition, grain morphology, or the detection of large defects like cracks, adhesion failure and so on. A large indefinite number of optical techniques are available; such examples available in the Materials Processing Research Centre (MPRC) as Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Optical Microscope (OM) may be used.

X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive measurement technique that evaluates out detailed information about the crystalline phases present in materials, chemical composition of these phases and structural properties which include grain size, strain state, phase composition and orientation. Complex structures can also be analyzed by X-ray diffraction such as DNA and proteins. The thickness of thin films and multilayers, and atomic arrangements in amorphous materials can also be determined by XRD. The principle of the X-ray process is to measure relative shift of X-ray diffraction lines created on an irradiated surface by the use of a diffractometer. According to Bragg's law, diffraction occurs at an angle of 2θ which is given by this equation.

$$n\lambda = 2d \sin\theta$$

where, n = Integer
λ = Wavelength of X-ray beam
d = Lattice spacing of crystal plane
θ = The angle of diffraction

When a X-ray beam is applied onto a crystalline material at an angle θ with wavelength λ, diffraction occurs only if the distance between the rays received back or reflected from sequential planes differs by a complete number n of wavelengths. The Bragg's Law conditions are satisfied by different d-spacings if any change is made at the angle θ.

Scanning Electron Microscope

The scanning Electron Microscope (SEM) offers superior quality of resolution and depth of focus. SEM is a type of electron microscope which scans the sample surface with a high energy beam of electrons. A series of lenses detect the spot of electrons on the surface of the specimen. The emission of electrons and photons from the surface occur because the electrons emitted from the electron gun penetrate the surface. The detectors collect the output emitted electrons and this is used to modulate the brightness of a Cathode Ray Tube (CRT). An image of the sample is displayed onto a monitor when the electron beam collides on the sample and each of this strike established directly onto a corresponding point on the screen. The image can also be transmitted to a photographic plate for observation.

The scanning electron microscope used in this experimental work was the 'EVO LS 15' developed by Carl Zeiss, as shown in figure 3.23. It can be operated at magnifications from about 5X to 1,000,000X. Its X-ray analysis is 8.5mm analytical working distance and 350 take-off angle. The chamber is 365mm (φ) x 275mm (h) and a maximum specimen height of 145mm can be used.

V RESULT AND DISCUSSION
SCANNING ELECTRON MICROSCOPE

Scanning Electron Microscopy was performed on the corroded samples at optimum mass loss levels found to assess the corrosion mechanism that has occurred during corrosion.
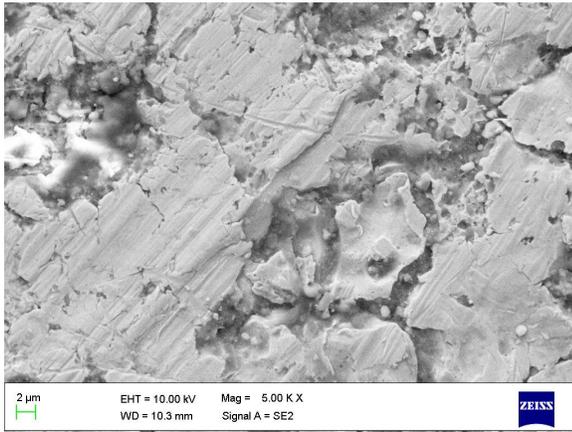
Cross section morphology uncoated sample
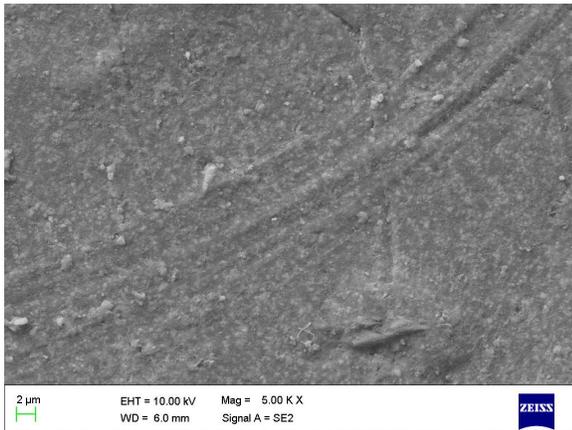
Cross section morphology of thermally sprayed coated sample

Based on the micrographs it can be understood that in the uncoated sample material degradation mainly occurs due to corrosion where the material is subjected to plastic deformation on impact by the silica particles in the jet. The materials undergo repeated plastic deformations before being detached from the surface. This leads to removal of material in layers leading to this type of corrosion process.

X-RAY DIFFRACTION

To investigate the phases present in the flame sprayed coatings, samples were analyzed using the X-Ray Diffraction technique. The XRD results show rutile as the prominent phase in the coating's structure. Rutile is produced after melting and resolidification of anatase, the prominent phase in the spray-dried Al_2O_3-TiO_2 powder, used to deposit the coating. It is also possible that the anatase peaks and the amorphous titania, which can be present in the coating's microstructure, and is probably the result of rapid resolidification of the same anatase from the powder feedstock,are covered by the humps formed from peak overlaps. An XRD pattern for the Al_2O_3-TiO_2 anatase powder has also been shown in Figure, which shows the anatase peaks.

The XRD analysis of the Al_2O_3-TiO_2 powders was confirmed in several previous studies that both powders are prominently α- Rutile phase of TiO_2. The XRD analysis of the thermal sprayed coatings are shown in Figure.
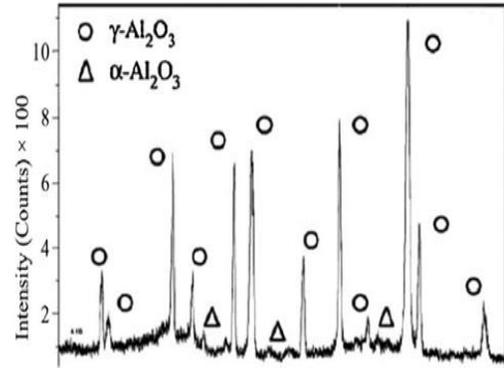
X-ray diffraction Al2O3-TiO2 thermally sprayed coating

The XRD patterns of the coatings show that most of α-alumina in the Al_2O_3-TiO_2 powder converted into $\gamma - Al_2O_3$ after flame spraying process, which was similar to that in commercial available powder. It is well established $\gamma - Al_2O_3$ tends to be nucleated from the melt in preference to α- Al_2O_3 due to the higher cooling rate.

POTENTIODYNAMIC POLARIZATION STUDIES

The potentiodynamic polarization test was conducted using the polarization equipment. From the above figure, E_{corr}, I_{corr} values are calculated using the Cathodic and Anodic polarization respectively. The corrosion rates are calculated from i_{corr} values using the following equation given below.

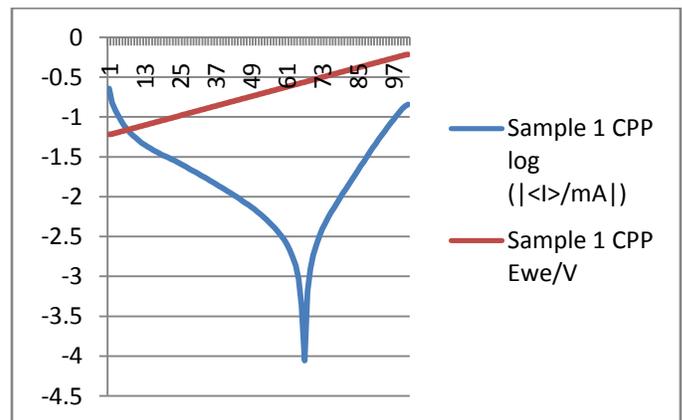$$\text{Corrosion Rate}, \mathbf{CR} = \frac{\mathbf{I_{corr} \times K \times EW}}{\mathbf{dA}}$$

where,

CR = the corrosion rate, units are given by the choice of K
Icorr = the corrosion current in amps
K = a constant that defines the units for the corrosion rate
EW = the equivalent weight in grams/equivalent
A = sample area in cm^2

The values obtained from the above equations are given below in Table.

	3.332 pH	5.087 pH	8.429 pH
E_{corr} Mv	-583.31	-732.79	-693.34
I_{corr} mA/cm^2	0.0078986	0.0038054	0.0038545
CR in penetration mm/year	0.11244	0.03722	0.03518

From the table it is inferred that the corrosion resistance is significantly higher at pH=3.332 for coated sample. With the decrease in pH the i_{corr} and Corrosion rate values show an increasing trend which indicates a significant decrease in the corrosion resistance of the material when compared to that of pH=.5.087 and pH=8.429.

The coating is found to have increased corrosion resistance than that of the uncoated sample by almost two times at pH=3.332.

VI CONCLUSION

The coating is found to have superior corrosion resistance than the uncoated sample. Corrosion resistance of the coating is higher than that of the uncoated substrate by about two times at pH=3.332.

The decrease in pH value of the electrolyte decreases the corrosion resistance of the stainless steel both coated and uncoated.

As the electrolyte becomes more and more acidie (low pH) there is a tremendous decrease in the corrosion resistance of the stainless steel where as only a minimal decrease is observed in case of the coating.

Coating is found to have a more noble E_{corr} value when compared to that of the uncoated substrate at all pH conditions.

VII REFERENCE

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