

“Laboratory method to study the surface corrosion of $ZrO_2.5CaO + Al_2O_3$ coatings applied on Gray Cast Iron substrate”

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Abstract— A systematic investigation on surface corrosion of Calcia Stabilised Zirconia, top coat applied to Gray cast iron substrates were examined. To achieve coatings Air plasma spray technique was adopted. A total of nine specimens were prepared for different top coat thickness 100, 200 and 300 μm . The samples were tested for different concentration of 5, 7, & 10% in the aqueous nitric acidic (HNO_3) medium and continuously examined for weight loss and surface corrosion at an interval of 8, 16 and 24 hours. Surface corrosion tests were conducted with liquid immersion technique to examine the surface oxidation. In this investigation, it has been found that the 100 μm top coat specimens undergoes non uniform corrosion at all the concentration, relatively more compared to 200 and 300 μm coated specimens. Spallation of the top coat realised in case of 100 μm top coat specimens at higher concentration reason attributed to less coat thickness and porosity, facilitating nitric acid to diffuse easily to the underlying bond coat (Fe38Ni10Al) leads to accelerate corrosion of the top coat. All the results of the present investigation were presented in detail.

Index Terms— Corrosion, Nitric Acid (HNO_3), Thickness, Porosity.

1 INTRODUCTION

Ceramics are considered as one of the competitive material candidate, protects the specimens from corrosion. An aqueous nitric acid considered as extremely corrosive medium and used to measure the corrosiveness to the range of materials. There are several ways to examine the corrosion resistance of the materials using range of acids and alkaline solutions. However testing method heavily depends on industrial requirements and its application.

Over the last few decades, several efforts have gone into developing various alloys and coating techniques to control the degradation of magnesium [1]. Most researchers reported improved corrosion properties of coated specimens compared to uncoated magnesium [2,3]. Ruben Kotoka et al. have done study on corrosion behaviour of reactive sputtered Al_2O_3 and ZrO_2 thin films on Mg disk, immersed in saline solution and found that increasing the thickness of the Al_2O_3 coating improved the corrosion resistance of the Mg disk also suggested that Al_2O_3 and ZrO_2 coating can be used effectively to control the fast degradation of magnesium, for medical implant applications[4]. Wu et al. showed that Al_2O_3 and TiO_2 developed

using electron beam evaporation can significantly improve the corrosion resistance of AZ31[5].

In the present exploration we have considered, specific weight percentage of alumina Al_2O_3 along with 5% of Calcia stabilized Zirconia (CAZ) blended together in 50:50 proportions long with specific weight percent of Fe38Ni10Al act as bond coat applied on gray cast iron substrates to investigate the cause of chemical instability against aqueous nitric acid (HNO_3) medium at different concentration of 5%, 7% and 10%, for the duration of twenty four hours.

2 Experimentations:

2.1 Sample preparation

A cylindrical specimen of sizes 2.5 cm^2 was prepared. Electrical insulation Teflon tape was used to isolate the coating from all the remaining sides. Wrapping of the uncoated sides shown in figure no. 1. Air plasma spray coating technique was adopted for coating applications. Detail study of the coating, coating thicknesses, parameter adopted during the coating, porosity and machine specifications has been discussed and

mentioned in the previous published paper refer[6,7].

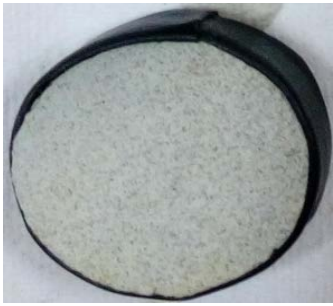


Fig -1: Electrical insulated Teflon tape wrapped around the circumference of the specimen.

2.2 Corrosion Test

Surface corrosion studies were done using liquid immersion and weight loss technique. The test was performed at 5%, 7% and 10 % concentrated aqueous nitric acid HNO₃ medium. A cylindrical specimen of size 2.5 cm² was prepared for the test applications. 5ml, 7ml and 10ml of HNO₃ was taken in 100ml volumetric flask and make up to the mark with distilled water. The specimens were immersed completely in the beaker shown in fig no.2. Total emersion time was approximately twenty four hours of each concentration. pH of the aqueous solution was measured using litmus paper and found 5 ,8 & 2 for the corresponding concentration of 5%,7% & 10% respectively. Initially weight of each sample along with Teflon tape and without tape was measured ensuring accuracy in the weight loss. After every eight hour the specimens were taken out and kept under dryer and rust were removed followed by net weight losses were measured using digital measuring device. Total three readings were recorded at an interval of eight hours of each concentration. Material losses on the samples were measured in milligram. Superficial corrosion images were captured using optical microscope. The optical microscope specifications are given in the Table 1

Table 1: Optical microscope specifications

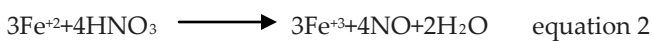
Specifications	Parameters
Binocular co-axial microscope vision plus	5000 BM
Observation Head	Binocular or Trinocular 45°, 360° rotatable
Magnification Range	40x to 1000x.
Illumination	Built in base 6V - 20W Halogen lamp with light intensity control system

3 Results and Discussion

It has been found that at 5% and 7% concentration there was no noticeable mark of oxidation on 200 and 300 μm but localised red rust appeared on 100 μm top coated specimens at all the concentration refer figure no. 3 to 5. In the present investigation weight loss and corrosion study has been done only at 100 μm top coat specimens reasons allied to visible mark of oxidation only at the aforesaid coating thickness. It has been realised from the figure no 2 to 5 that 100 μm top coat specimens are more prone to red rust at all the concentration. At 10% concentration it has been found that the 100 μm top coat along with bond coats peel out from the Gray cast iron substrate after 24 hours of experimentation. In the exploration it has been found that as the concentration increases in 5% to 7% followed by 10% the rate of oxidation increases exhibiting instability in the 100 μm top coated specimens compared to other coated specimens reasons attributed to less coat thickness and non-uniform porosity. The detailed discussion on coating thickness and porosity has been done in the previous published papers [6, 7]. Corrosion at the top coat realised and also can be clams due to bubble formation with release of NO, Nitric oxide during the experimentations, which gives the clear

clue to the oxidation. Other reasons attributed to the corrosion of the top coat are due to higher content of iron in the alloy mixture of bond coat which easily gets exposed to oxygen due to less coating thickness. It is also suspected that small particle size and porosity in the local region of the top coat provides large surface area leads HNO₃ solution diffuse easily to the substrate interacting faster to the Iron content refer fig.no. 3, 4 and 5. The corrosion reactions can be understood by the chemical reactions shown in equation no 1 & 2.

Fe²⁺ ions loses electrons and undergoes oxidation followed by reduction of H⁺ ion to water



In the corrosion study it has been observed that different coating thicknesses behave differently at different concentration. As the coating thickness increases corrosion resistance increases refer [6,7]. Weight loss measurement was done only on 100 μm top coat thicknesses and was observed very minimal weight loss in milligrams at 5 and 7% compare to 10% concentration. Weight loss measurement is shown in Table no. 2 at all the concentration. In the exploration it has been found that 300 μm coating is more resistance to corrosion and chemically more stable compared to 100 and 200 μm coating system at all the concentration. From the earlier investigation and published journal papers it has been found that 100 μm coating exhibit maximum porosity compared to the other coating systems refer [6,7]. After extensive literature reviews it has been found that sprayed ceramic coating always contains open porosity which may reduce the cohesion strength of top coat with bond coat which could be also one of the reasons for spallation of the coat of the present study. It was reported that aluminium phosphate sealing treatment improves the corrosion resistance of oxide based coatings [8, 9].

Weight of the sample with tape (W1): 18.751gms

Weight of the sample without tape (W2): 18.209gms

Weight of tape (W3) => 18.751-18.209=0.542gms

Table 2: Weight loss of 100 μm top coat specimens at 5%, 7% & 10% concentration measured at an interval of 8 hours.

SL. No.	Concentration of solution	Weight loss in gms after drying including weight of the tape (W4) At an interval of eight hours.	Net weight loss (W1-W4)
1	5%	18.746 gms	5mg (100 μm top coat, after 8 hrs.)
		18.740 gms	11mg (100 μm top coat, after 16 hrs.)
		18.692 gms	59mg (100 μm top coat, after 24 hrs.)
2	7%	18.626 gms	125mg (100 μm top coat after 8 hrs)
		18.432 gms	319mg (100 μm top coat, after 16 hrs.)
		18.395 gms	356mg (100 μm top coat, after 24 hrs.)
3	10%	18.289 gms	462mg (100 μm top coat, after 8 hrs.)
		18.055 gms	699mg (100 μm top coat, after 16 hrs.)
		18.029 gms	722mg ((100 μm top coat, after 24 hrs.)

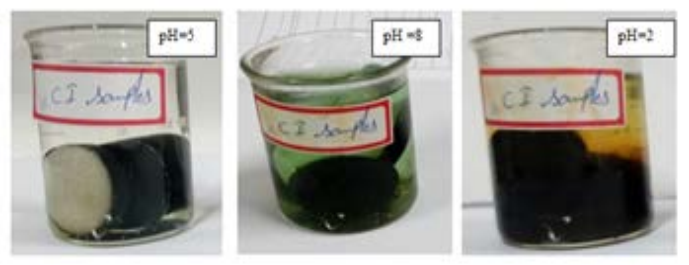


Fig. 2: illustrating coated samples immersed in 5%, 7% & 10% in aqueous nitric acid HNO₃ solution for duration of 24 hours from left to right respectively.



Fig-3: Images of the top coat samples under 5 % diluted HNO₃ solution after 24 hours.

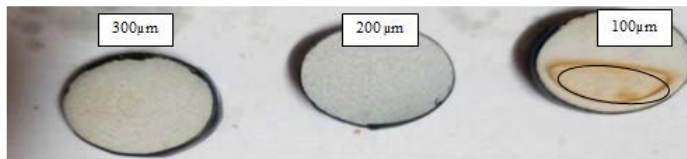


Fig-4: Images of the top coat samples under 7 % diluted HNO₃ solution after 24 hours.



Fig-5: Images of the top coat samples under 10 % diluted HNO₃ solution after 24 hours.

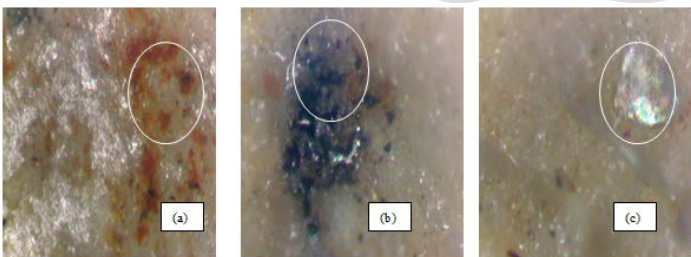


Fig. 6 a, b & c: Mark of oxide formation along with impurities on the top coat of ZrO₂.5CaO + Al₂O₃

4 CONCLUSION

Localise corrosion along with unknown impurities shown in fig. 6 a, b and c. From the study it can be concluded that oxide based ceramics, can undergo corrosion even at room with little porosity less than 2% refer [6,7]. Increase in concentration, 5% to 10% can also transport oxidation and specific percentage of Fe in alloy mixture of Fe38Ni10Al directly exposed to acidic medium along with less coating thickness can be the cause of corrosion of the pure ceramic and cermet in the present case.

The summary of the present experimentations has been enumerated in the following points:

1. In this investigation into all specimens 200 and 300 μm specimens does not show any noticeable mark of oxidation at all concentrations, however only 100 μm top coat specimens at 10% concentration shows severe chemical instability.
2. A net weights loss of 0.059, 0.356 & 0.722 milligrams at different of 5%, 7% and 10% concentration respectively in case of 100 μm top coat specimens in 24 hours.
3. With the increase in time may be due to the enhancement of the porosity 100 μm coating come out.
4. From all the studies it has been concluded that less thicknesses, high porosity & high chemical concentration with increase in time, leads to high corrosion/failure of the coatings. In view of this, above 100 μm thickness of ZrO₂.5CaO + Al₂O₃ coatings is more desirable for anti-corrosion related applications.

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