Investigation on Corrosion Behaviour of Mild Steel Using Al, Zn, Ni-Cr Coatings by Thermal Spray Technique

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Abstract: - **Mild steel is the base material most commonly and widely used in ship and pipe building material. The purpose of this project is to analyse the different coating material like aluminium, zinc and Nichrome using thermal spray process and to select the suitable coating material for mild steel which resists corrosion better. The main aim of this research is to analyse the corrosion of coated mild steel in its first stages, in order to determine its corrosion rate and to select the suitable coating material for corrosion resistance of mild steel.**

Keywords: **Mild Steel, Thermal Spray, Corrosion resistance**

I. INTRODUCTION

The main aim of this research is to analyze the corrosion of coated mild steel in its first stages, in order to determine its corrosion rate and to select the suitable coating material for corrosion resistance of mild steel. The coating materials used in this project is aluminium, zinc and nichrome.

1.1 Mild Steel

Mild steel is the most common form of steel and because of its low cost it is chief material of construction. Mild steel has superior strength, hard and can be bent, worked or can be welded into an endless variety of shapes for uses from vehicles (like cars and ships) to building materials. Because of its unique properties such as economically cheap, high strength, hardness and easy availability, it has wide range of applications in nut bolt, chains, hinges, knives, armour, pipes, magnets, military equipment's etc.

Mild steel, also known as plain-carbon steel, is now the most common form of steel because its price is relatively low while it provides material properties that are acceptable for many applications. Low-carbon steel contains 0.05–0.15% carbon making it malleable and ductile. Mild steel has a relatively low tensile strength, but it is cheap and easy to form. Surface hardness can be increased through carburizing. Low-carbon steels contain less carbon than other steels and are easier to cold-form, making them easier to handle.

The major drawback in using the mild steel is the corrosion behaviour to the environment. Mild steel easily reacts with the atmospheric oxygen and moisture which results in the degradation of their properties, the corrosion occurs is referred to as Atmospheric corrosion which is also known as vapour phase corrosion (VPC) is due to the individual and combined action of oxygen, moisture, and atmospheric pollutants. Additional contributors to VPC are rain, snow, dust, soot, ash, wind, and radiation (light, heat, etc.). The rate of VPC may be accelerated by both acids and bases, depending upon the metal.

1.2 Metal Coating

Coatings have historically been developed to provide protection against corrosion and erosion that is to protect the material from chemical and physical interaction with its environment. Various technologies can be used to deposit the appropriate surface protection that can resist under specific conditions. They are usually distinguished by coating thickness: deposition of thin films (below 10 to 20μm according to authors) and deposition of thick films. The latter mostly produced at atmospheric pressure have a thickness over 30 μm, up to several millimetres and are used when the functional performance and life of component depend on the protective layer thickness. Both coating technology can also be divided into two distinct categories: "wet" and "dry" coating methods, the crucial difference being the medium in which the deposited material is processed. The former group mainly involves electroplating, electro-less plating and hot-dip galvanizing while the second includes, among others methods, vapour deposition, thermal spray techniques, brazing, or weld overlays. This chapter deals with coatings deposited by thermal spraying. Thermal spraying comprises a group of coating processes in which finely divided metallic or non-metallic materials are deposited in a molten or semi-molten condition to form a coating. The processes comprise: direct current (d.c.) arcs or radio frequency (r.f.) discharges-generated plasmas, plasma transferred arcs (PTA), wire arcs, flames, high velocity oxy-fuel flames(HVOF), high velocity air-fuel flames (HVAF), detonation guns (D-gun). Another spray technology has emerged recently; it is called cold gas-

dynamic spray technology, or Cold Spray (CS). It is not really a thermal spray technology as the high-energy gas flow is produced by a compressed relatively cold gas (T < 800°C) expanding in a nozzle and will not be included in this presentation. Most processes are used at atmospheric pressure in air, except radio frequency plasma spraying, necessarily operated in soft vacuum. Also, direct current plasma spraying can be carried out in inert atmosphere or vacuum and Cold Spray is generally performed at atmospheric pressure but in a controlled atmosphere chamber to collect and recycle the spray gas (nitrogen or helium) because of the huge gas flow rates used (up to 5 m³/min). In the following only processes, Advanced Plasma Spray Applications operated in air at atmospheric pressure will be considered, except when the coating material is very expensive, such as platinum that must be sprayed in a chamber to recover the overspray.

The coating material may be in the form of powder, ceramic rod, wire or molten materials. The central part of the system is a torch converting the supplied energy (chemical energy for combustion or electrical energy for plasma- and arc-based processes), into a stream of hot gases. The coating material is heated, eventually melted, and accelerated by this high temperature, highvelocity gas stream towards a substrate. It impacts on the substrate in the form of a stream of droplets that are generated by the melting of powders or of the tips of wires or rods in the high-energy gas stream. The droplets flatten or deform on the substrate and generate lamellae called "splats". The piling up of multiple layered splats forms the coating.

Thus, depending on the spray conditions and materials sprayed, the coatings are more or less porous and for certain applications must be sealed by appropriate means.
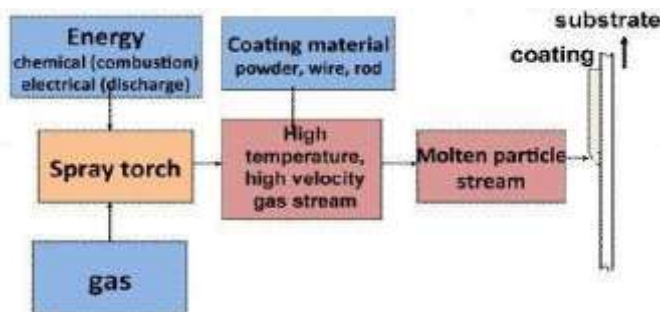
II. THERMAL SPRAY

Fig.2.1 Schematic of the thermal spray concept

Figure 2.1 shows the general concept of thermal spray. The coating material can be fed in the hot gas stream as powder or wire or rod. Coatings are built by the flattening and solidification of droplets impacting onto the part to be covered. These droplets can be partially or totally melted when they are issued from powders or totally melted when

they result from the atomization of melting wires or rods. The microstructure of the coating formed by the piling up of these particles depends on (i) particle impact parameters (particle temperature, molten state, velocity and size), (ii) substrate conditions (shape, roughness, surface chemistry…), (iii) the temperature control of substrate and coating before (preheating) during and after (cooling) spraying and (iv) the spray pattern.

2.1Thermal Spray Processes

2.1.1 Plasma-Based Processes

They comprise D.C. plasma spraying, plasma transferred arc and wire arc spraying.

2.1.2 Combustion-Based Processes

They mainly comprise flame spraying, High Velocity Oxy-fuel Flame (HVOF) or High Velocity Air-fuel Flame (HVAF) and Detonation gun (Dgun).

2.1.2.1 High Velocity Oxy-Fuel Flame (Hvof) and High Velocity Air-Fuel Flame (Hvaf)

These processes use significantly higher upstream pressures than flame spray processes and a de Laval nozzle; they are characterized by supersonic speeds of gas flow. The combustion of a hydrocarbon molecule (C_xH_y) either as gas or liquid (kerosene) is achieved with an oxidizer, either oxygen or air, in a chamber at pressures between 0.24 and 0.82 MPa or slightly more for high-power guns. A convergent-divergent de Laval nozzle follows the combustion chamber achieving very high gas velocities (up to 2000 m/s). The last trend is to inject nitrogen (up to 2000 slm) in the combustion chamber to increase the gas velocity and decrease its temperature. Mostly powders are used, which are injected either axially or radially or both, depending on the gun design. Few guns have been designed to use wires or cored wires. Also, recently liquid feedstock injection (suspensions or solutions) has been developed, mainly for axial injection. The particle velocities and temperatures achieved with different guns are presented in Figure 2.1. Substrate and coating must be cooled during spraying.

Power levels for HVOF guns working with gases is about 100-120 kW, while they can reach 300 kW for guns working with liquid. Globally this process, working mainly with metals, alloys and cermets (one of the most successful applications) has deposition efficiencies of about 70% for powder flow rates up to 7.2 kg.h-1 for gas-fuel guns and up to 12 kg.h-1 for liquid-fuel guns. Resulting coating porosities are a few %, with a good adhesion to substrate (roughly 60 to 80 MPa) and low oxygen content (between 0.5 and a few %). The process is rather noisy, dusty with large quantities of explosive gases. As for detonation-gun, the main applications of coatings are protection against abrasion and adhesion (friction) under low load as well as protection against corrosion.

III. MATERIAL SELECTION

3.1 Aluminium [1] [2]

Aluminium is a relatively soft, lightweight, ductile and malleable metal with appearance ranging from silvery to dull gray, depending on the surface roughness. It is nonmagnetic and does not easily ignite. A fresh film of aluminium serves as a good reflector of visible light and an excellent reflector of medium and far infrared radiation. Corrosion resistance can be excellent due to a thin surface layer of aluminium oxide that forms when the metal is exposed to air, effectively preventing further oxidation. In this project, we are using aluminium in the form of wire with gauge thickness.

Elements	Composition %maximum
Silicon (Si)	0.10
Iron (Fe)	0.20
Zinc (Zn)	0.03
Gallium (Ga)	0.04
Vanadium(V)	0.03
Aluminium	Reminder

Table 3.1 Chemical composition of Aluminium

Physical Properties	Values
Density	2.70 g·cm^{-3}
Melting point	1200°C
Thermal Expansion	23.1 μm·m^{-1}·K^{-1} (at 25 °C)
Thermal Conductivity	237 W·m^{-1}·K^{-1}
Electrical Resistivity	28.2 nΩ·m (at 20 °C)

Table 3.2 Physical property of Aluminium

Mechanical property	Values
Young's modulus	70GPa
Shear Modulus	26GPa
Bulk Modulus	76Gpa
Poisson ratio	0.35
Vickers Hardness	160 – 350 MPa

Table 3.3 Mechanical property of Aluminium

3.2 Zinc [1][2]

Zinc, also referred to in non-scientific contexts as spelter, is a bluish-white, lustrous, diamagnetic metal, though most common commercial grades of the metal have a dull finish. The metal is hard and brittle at most temperatures but becomes malleable between 100 and 150 °C. Its melting point is the lowest of all the transition metals aside from mercury and cadmium**.**

Elements	Composition, %maximum
Lead	0.025
Cadmium	0.02
Iron	0.01
Tin	0.001
Copper	0.002
Total impurities	0.05
Zinc, Min	99.95

Table 3.4 Chemical composition of Zinc

Physical property	Values
Density	7.14g·cm^{-3}
Melting point	800°C
Thermal Expansion	30.2 μm·m-1·K-1 (at 25 °C)
Thermal Conductivity	116 W·m-1·K-1
Electrical Resistivity	59.0 nΩ·m (at 20 °C)

Table 3.5 Physical property of Zinc

Mechanical property	Values
Young's modulus	108GPa
Shear Modulus	43GPa
Bulk Modulus	70Gpa
Poisson ratio	0.25
Brinell Hardness	327 – 412 MPa

Table 3.6 Mechanical property of Zinc

3.3 Nichrome [1][2]

A common alloy is 80% nickel and 20% chromium, by mass, but there are many others to accommodate various applications. It is silvery-grey in colour, is corrosion-resistant, and has a high melting point of about 1,400 °C

(2,550 °F). Due to its resistance to oxidation and stability at high temperatures, it is widely used in electric heating elements, such as in appliances and tools. Typically, nichrome is wound in coils to a certain electrical resistance, and current is passed through it to produce heat.

Material property	Values
Modulus of elasticity	2.2×10^{11} Pa
Density	8400 kg/m^3
Melting point	1400 °C
Electrical resistivity at room temperature	$(1.0—1.5) \times 10^{-6} \, \Omega \cdot m$
Specific heat	450 J/(kg·K)
Thermal conductivity	11.3 W/(m·K)
Thermal expansion	14×10^{-6} K^{-1}

Table 3.7 Material property of Nichrome

IV. COATING PROCESS

The mild steel coating can be done on any of the given thermal spray method, but according to the coating material selected and economic consideration, High velocity oxy fuel spraying is preferable than the other methods.

4.1 Specimen Preparation

Mild steel is chosen as a base metal, which has been already discussed above. Mild steel plate was cut to our requirement of 4×4 inch² with a thickness of 10mm, since the thermal spray has to be done on a large surface and the minimum dimension being 3×3 inch². The minimum thickness of the mild steel plate has to be 8mm or else there will be deformation of the plate at high temperature.

For the coating process, the wire feed system is used for thermal spray method. Since it is essential to have a close match between the thermal spray gun set-up and the wire size, it is recommended that wire size be specified in mm or inches as opposed to gauge. So, we selected the wire size of 10 gauge or 3.25mm diameter, which suites the path way of the spray gun.
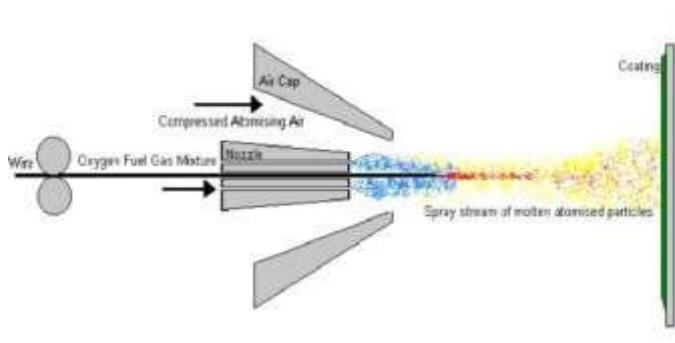
4.2 Coating Operation [3]

Fig. 4.1 High velocity oxy fuel setup

For the purpose of coating, high velocity oxy fuel method is used. In this method, the coating material is heated at the determined temperature and is sprayed on to the base material through spray gun at a particular velocity and it is widely used for many operations which has large surface areas. The fuel used in this method of thermal spray is acetylene and oxygen, which enhances the coating material to adhere to the base material. This coating is done in room temperature; it cannot be done at very high temperature or very low temperature. The coating thickness for each of the base material is around 200-230μm. According to British Standard, each coating has a specific film thickness, but for comparison of different coatings of different thickness it is very complicated. Hence the different coatings to base materials were given at the required thickness i.e. 200-230

Parameters	Unit	Value
Fuel used	-	Acetylene and Oxygen
Wire feed rate	m/min	2.54
Spray distance	Mm	300
Torch velocity	mm/s	600
Film thickness	μm	220±40

Table 4.1 Thermal spray test parameters

Fig.4.2(a)Aluminium coated   Fig 4.2 (b) Nichrome Coated

Fig4.3 (c) Zinc Coated

V. MATERIAL TESTING

Testing is an essential part of any engineering activity. Testing is applied to coating materials. It consists of measurement of fundamental properties like roughness, scratch, and corrosion. The engineer and designer need to know the hardness, strength, and other characteristics of the materials they use. The engineer and designer should know about the way in which the properties are determined. It can be noted that the tests need to be conducted according to

standard procedures so that one can have confidence in publish the test results.

5.1 Salt Spray Test [4]

The salt spray test is a standardized and popular corrosion test method, used to check corrosion resistance of materials and surface coatings. Usually, the materials to be tested are metallic and finished with a surface coating which is intended to provide a degree of corrosion protection to the underlying metal. Salt spray testing is an accelerated corrosion test that produces a corrosive attack to coated samples in order to predict the suitability of the coating in use as a protective finish. The appearance of corrosion products (oxides) is evaluated after a period of time. Test duration depends on the corrosion resistance of the coating; generally, the more corrosion resistant the coating is, the longer the period of testing before the appearance of oxides. The salt spray test is one of the most wide-spread and long established corrosion tests. In this project, we have conducted Salt spray test as per ASTM B 117.

TEST PARAMETERS	VALUES
Chamber temperature	34.5 – 35.5 °C
pH Value	6.65 – 6.85
Volume of salt solution collected	1.0 – 1.5 ml/hr
Concentration of solution	4.80 – 5.30 % of NaCl
Air pressure	14 – 18 Psi
Components loaded in chamber position	30-degree angle

Table 5.1 Salt spray chamber test parameter

5.2 Roughness Test [5]

Profilometer is a measuring instrument used to measure a surface's profile, in order to quantify its roughness. A diamond stylus is moved vertically in contact with a sample and then moved laterally across the sample for a specified distance and specified contact force. A profilometer can measure small surface variations in vertical stylus displacement as a function of position. A typical profilometer can measure small vertical features ranging in height from 10 nanometers to 1 millimeter. The height position of the diamond stylus generates an analog signal which is converted into a digital signal stored, analyzed and displayed. The radius of diamond stylus ranges from 20 nanometers to 50 µm, and the horizontal resolution is controlled by the scan speed and data signal sampling rate. The stylus tracking force can range from less than 1 to 50 milligrams.

5.3 SEM (Scanning Electron Microscope)

A Scanning Electron Microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a scan pattern, and the beam's position is combined with the detected signal to produce an image.

SEM can achieve resolution better than 1 nanometer.

Specimens can be observed in high vacuum, in low vacuum, in dry conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

The SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown above. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes.

VI. RESULTS AND DISCUSSION

6.1 Roughness

The roughness test was conducted using roughness tester equipment, the average

Roughness value (Ra), for all the coatings have been found out and the results are follows as,

ALUMINIUM	ZINC	NICHROME	ATED MILD STEEL
8.2, 10.74, 12.1, 13.34	8.37, 10.32, 8.56, 9.26	11.54, 13.54, 11.17, 13.86	2.44, 4.43, 3.67, 5.86

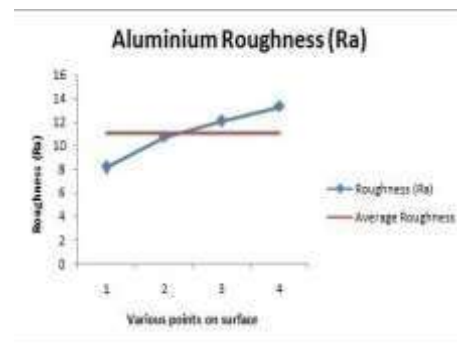Table 6.1 Roughness test results

Fig.6.1 Graph for Roughness test on Aluminium

The above graph represents the Roughness value (Ra) at four different points on the Aluminium coated mild steel, the roughness (Ra) and the points are marked in X-axis and Y-axis respectively.

The Roughness value (Ra) for Aluminium at different points are 8.2, 10.74, 12.1, 13.34. The red line indicates the average roughness value of the material and it was found to be 11.
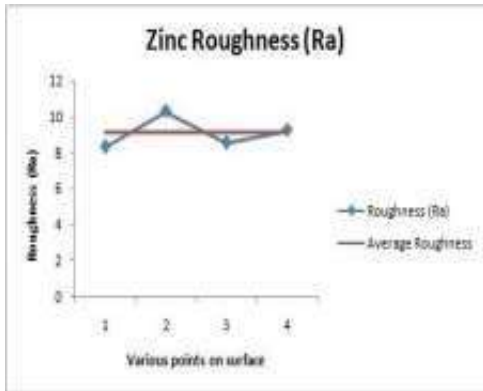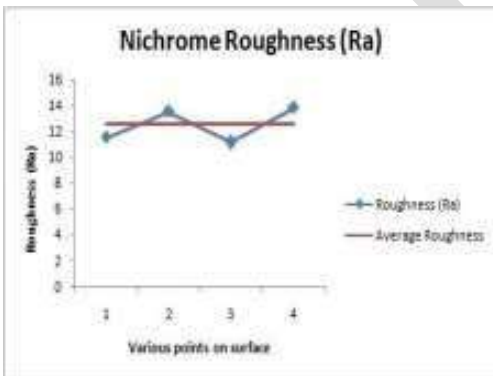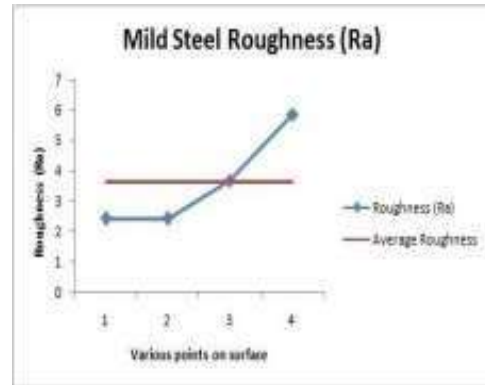

Fig.6.2 Graph for Roughness test on Zinc

The above graph represents the Roughness value (Ra) at four different points on the Zinc coated mild steel, the roughness (Ra) and the points are marked in X-axis and Y-axis respectively.

The Roughness value (Ra) for Zinc at different points are 8.37, 10.32, 8.56, 9.26.The red line indicates the average roughness value of the material and it was found to be 9.

Fig.6.3 Graph for Roughness test on Nichrome

The above graph represents the Roughness value (Ra) at four different points on the Nichrome coated mild steel, the roughness (Ra) and the points are marked in X-axis and Y-axis respectively.

The Roughness value (Ra) for Nichrome at different points are 11.54, 13.54, and 11.17, 13.86. The red line indicates the average roughness value of the material and it was found to be 12.

Fig.6.4 Graph for Roughness test on Mild Steel

The above graph represents the Roughness value (Ra) at four different points on the Uncoated mild steel, the roughness (Ra) and the points are marked in X-axis and Y-axis respectively.

The Roughness value (Ra) for uncoated mild steel at different points are 2.44, 4.43, 3.67, 5.86.The red line indicates the average roughness value of the material and it was found to be 3.
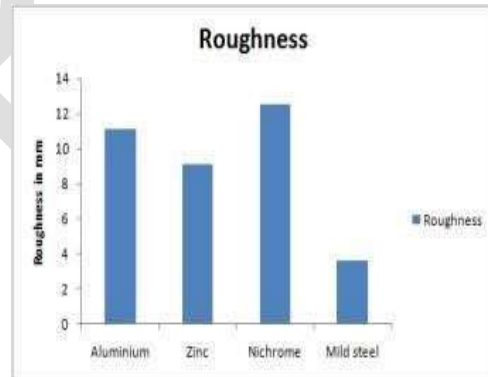
Fig.6.5 Graph for Roughness vs Materials

The average roughness value of the coated materials and the uncoated material are measured and the roughness value are compared using a bar graph, minimum and the maximum value for the coating thickness of 200-230 µm among the three-coated material was found to be zinc and Nichrome. Effect of surface roughness play a major role in the corrosion, the increase in surface roughness value increases the rate of corrosion, so the roughness value should be minimum, though uncoated material has a minimum surface roughness, the direct contact of the base material to the atmosphere causes increased rate of corrosion. Hence Zinc which has the minimum surface roughness value is considered to be less corrosive from the above results.

6.2 Salt Spray Chamber (Corrosion test):

The salt spray chamber test provides the corrosion rate of the material, the maximum time taken for a material to corrode in the chamber has a maximum corrosion resistance

on sea water and other harsh environment. Coated materials and the uncoated mild steel are tested in the salt spray chamber and the test result are given below,

ALUMINIUM	ZINC	NICHROME	UNCOATED STEEL MILD
White rust at 16 hours	White rust at 20 hours	Red rust at 24 hours	Red rust at 4 hours

Table. 6.2 Salt Spray Test results

The table represents the time taken by the material for the formation of rust, two types of rust formation occurs during the process, red rust and white rust. The white rust represents the formation of rust on the coating surface leaving the base material free of corrosion, whereas the red rust formation represents the rust on coating surface and base material. The red rust corrosion increases the corrosion rate on the base metal.

Fig 6.6(a) Aluminium Corroded   Fig 6.6(b) Nichrome Corroded

Fig 6.6(c) Zinc Corroded

From the above results a bar graph is plotted, with materials on X- axis and time taken for the corrosion on Y-axis to compare the corrosion rate of the coated materials.
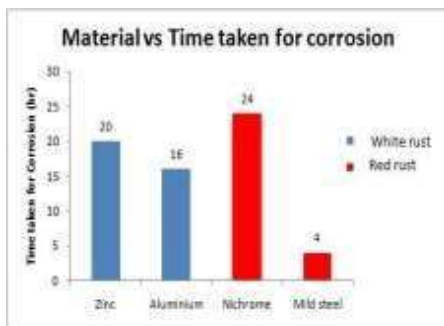
Fig.6.7 Graph for Material vs Corrosion time

The result shows that the uncoated mild steel corrodes in 4hrs, with red rust formation. It indicates that mild steel without coating corrodes at a very faster rate and so it cannot be used in corrosive environment.

Among the three-coated material, nichrome corrodes in 24hrs, which has a maximum life. Though corrosion starts after 24hrs there is a formation of red rust, which causes the base material to corrode away easily. Nichrome have a higher disadvantage that, if the porosity is intense it increases the corrosion rate of the base metal. A small scratch can also cause increase in corrosion rate, so nichrome coating though it has a higher corrosion resistance, the formation of red rust directly makes it not suitable for corrosive environment.

While the aluminium and zinc coated material shows the formation of white rust. White rust formation occurs on the coating surface, so that the corroded coating can be removed by blasting methods, and new coating surface can be sprayed over the metal. From the results above, aluminium corrodes in 16hrs, with white rust formation, whereas Zinc corrodes in 20hrs, with white rust formation. Since the zinc has the maximum life of 20hrs with white rust formation, zinc is suited for the coating on the mild steel to minimize corrosion.

6.3 Scanning Electron Microscope (SEM) Analysis:

Figures 6.8, 6.9, 6.10, 6.11 shows the scanning electron microscope (SEM) photomicrograph of Nichrome, Zinc, Aluminium and Mild Steel respectively.
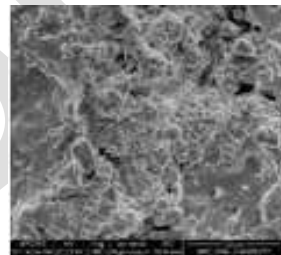

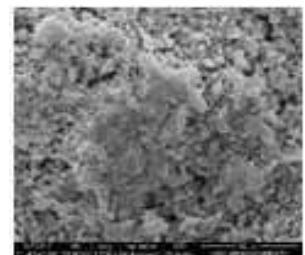Fig 6.8(a) Ni-Cr before corrosion   Fig6.8(b) Ni-Cr after corrosion
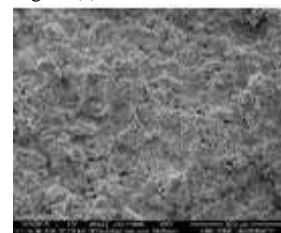

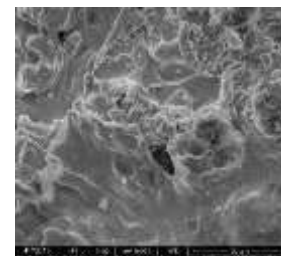Fig 6.8(c) Ni-Cr before corrosion   Fig 6.8(d) Ni-Cr after corrosion

Fig 6.9(a) Zinc before corrosion   Fig 6.9(b) Zinc after corrosion
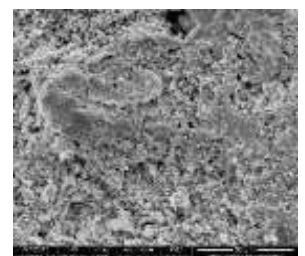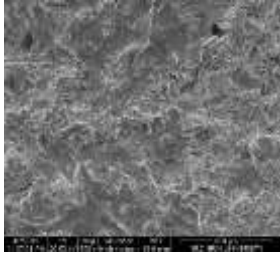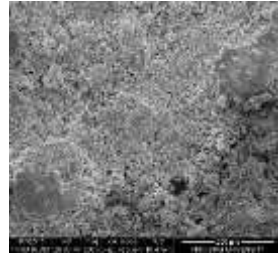
Fig 6.9(c) Zinc before corrosion
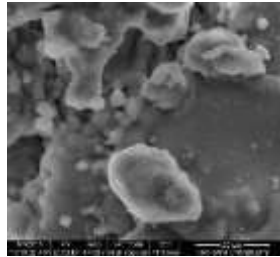

Fig 6.9(d) Zinc after corrosion
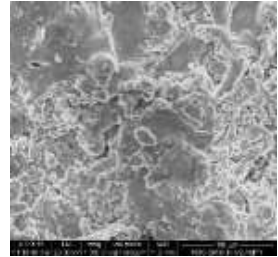

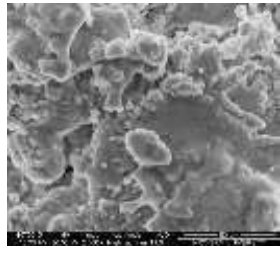Fig 6.10(a) Al before corrosion

Fig 6.10(b) Al after corrosion

Fig 6.10(c) Al before corrosion
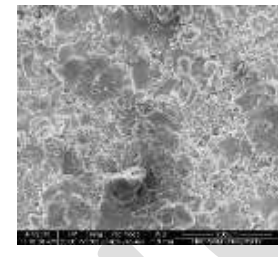

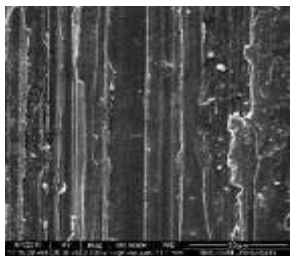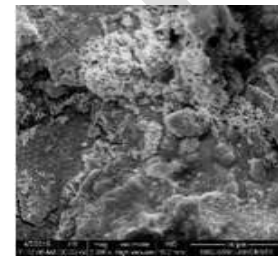Fig 6.10(d) Al after corrosion

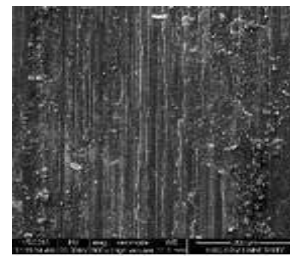Fig 6.11(a) M.S before corrosion

Fig 6.11(b) M.S after corrosion

Fig 6.11(c) M.S before corrosion

Fig 6.11(d) M.S after corrosion

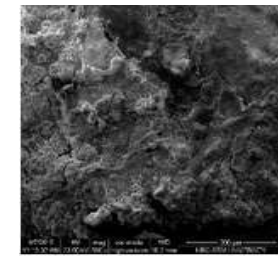Therefore, the above SEM micrograph reveals the grain structure of before and after corrosion of the specimen

.

VII. CONCLUSION

From the corrosion analysis conducted for mild steel with various coatings such as nichrome, zinc, aluminium by thermal spray method,

i. The mild steel specimen coated with zinc was found to be more corrosion resistant when compared to nichrome and aluminium which can be seen from the salt spray test results.

ii. Cost can be reduced when thermal spray method is employed over large area, while the electroplating method cannot be used for coating larger surface areas.

iii. Also in the electroplating method, the maximum coating thickness can be only in the range of 20μm whereas in thermal spray method, the coating thickness can be given to the requirements accordingly.

Thus, we can conclude that Zinc was found to be the better coating material for mild steel in order to prevent corrosion in terms of corrosion rate, cost and the method of coating.

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