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Study of Nano Coating on Zirconium by Sol-Gel Process

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Abstract : There are several cladding techniques such as hard facing, coating and surfacing to improve corrosion and wear properties of base materials. Cobalt base alloys / Nickel based alloys are the most common clad materials used to improve the corrosion and wear properties of the base materials, Nano-coating of these valve material by Zirconium using sol-gel process and validating the same with the Electrophoretic deposition processes is executed. Conventionally research studies indicates the various methodologies adopted for the Nano coating of Zirconium are spin coating ,sol-gel dip coating method, plasma sputtering, Ion beam assisted deposition (IBAD) etc. The results proved the uniform distribution with good penetration and significant improvement in other properties. It has been established that there is an 84% increase in corrosion resistant and 30% improvement in wear resistance properties.
Keywords : Nano-coating, sol-gel, wear resistance, Zirconium.

1 Introduction

Steel is an alloy of iron and carbon, though which other alloying elements are also found in a many steels. Perhaps the most of dramatic property of steel is that some allo ys can be strengthened b y quench hardening. Red hot is metal is rapidly cooled by a n plunging it into a liquid. These a l l o y s can be ductile for fabrication of much stronger as a finished product. Steels are loosely grouped by carbon content into form of steel to obtain a Steels are loosely grouped by carbon content into form of steel to obtain a these a l l o y s can be ductile for fabrication of much stronger as a finished product. Steels are loosely grouped by carbon content into form of steel to obtain a low carbon steels (<0.35% carbon by weight, approximately), medium carbon steels (0.35%–0.5% carbon by weight, approximately), and high carbon steels (0.5%–1.5% carbon by weight, approximately). These numbers may seem to be small, but they reflect the fact that carbon is a small, light element, iron formation of much larger to heavier atom. When they l o o k at the detailed structure of steels. They are obtain to maintained the corrosion way of substance to change the view of ratio to be increase the efficiency process of both rate view by wear and corrosion process.In either case(discrete particles or continuous polymer network) the sol evolves then towards the formation of an inorganic network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

Presence, and particularly the shape, of the carbide F e 3 C. This compound i s a 25% carbon by atom by fraction, but only 67% Carbon by weight.A105 steel is a commonly used valve material grades which are used under high pressure and temperature of operating conditions. These are materials have a moderate w e a r of r e s i s t a n c e but an often subjected to pitting corrosion.

1.1 ASTM A216

WCB (UNS Code J03002) is covered by an ASTM A216 standard, which is specification covers carbon steel is castings for valves, fittings, flanges and other pressure-containing parts of a high temperature service and the quality is required for assembly with other castings or wrought steel parts by a fusion welding. These grades are all "cast" grades meaning is made through "casting" which is a manufacturing process by where a liquid material is poured into a mold and allowed to harden.

ASTM A216/a216M Standard

Specification for Steel Castings

Table 1.1(a) ASTM Standard

CO	Si	Su	Cu	Ni	Cr	Mo
0.30 max	0.60 max	0.045 max	0.30 max	0.50 max	0.50 max	0.20 max

All total of those specified residual elements 1.00max

Materials view by process by change the residual way by incasing the substances formation through each element by tensile strength, yield strength, hardness. A clear distinction has to be made between those which have an effect due to their presence in solid solution, such as Mo, Cr, Ni, and Cu, and those which have an effect due to their segregation at organization by element can be appraised either as an alloying element or as a tramp element depending. The most important residual elements are:

Cu, Sn, Zn, Pb, Bi, Sb, As, Ni, Cr, Mo and V.

Table 1.1(b) specified residual elements 1.00max

Tensile Strength	70-95 ksi(485-655Mpa)
Yield Strength	36ksi (250Mpa) min
Elongation in 2in. or 50mm	22.0% min
Reduction of area	35% min
Hardness	137HB min.

1.2 Anti-Corrosion Coating Method i) Chemical vapour deposition

A) Metal organic vapour phase epitaxy

It is organometallic vapour phase epitaxy (OMVPE) or metal organic chemical vapour deposition (MOCVD) form of chemical vapour deposition method used to produce single or polycrystalline thin films. It is a highly complex as process of growing crystalline layers to create a complex semiconductor of multilayer structures. This takes place not in a vacuum, but from the gas phase at moderate pressures (10 to 760 Torr).

B)Electrostatic spray assisted vapour deposition

Electrostatic spray assisted vapour deposition by developed by a company to deposit both thin and thick layers of a coating onto various substrates. Terms chemical precursors are sprayed across an electrostatic field towards a heated substrate, the chemicals undergo a controlled chemical reaction and are deposited on the substrate as the required coating.

C) Sherardizing

Sherardizing is a process galvanization of ferrous metal surfaces as called vapour galvanizing and dry galvanizing. It is ideal for small parts that require coating of inner surfaces, such as batches of small items. Part size is only limited by the drum size.

D) Pulsed laser deposition

Pulsed laser deposition(PLD) is a laser- based technique used to grow high quality thin films of complex materials on substrates like Silicon wafers.

ii) Physical vapor deposition

A) Electron beam physical vapor deposition

Electron Beam Physical Vapor Deposition or EBPVD is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. The electron beam causes atoms from the target to transform into the gaseous phase.These atoms then precipitate into solid form, coating everything in the vacuum chamber (within line of sight) with a thin layer of the anode material.

B) Ion plating

Ion plating is a physica vapor deposition (PVD) process that is form is Called ion assisted deposition (IAD) or ion vapor deposition (IVD) and is a version of vacuum deposition. Ion plating utilizes concurrent or periodic bombardment of the substrate and depositing film by atomic-sized energetic particles. Bombardment prior to deposition is used to sputter clean the substrate surface. During deposition the bombardment is used to modify and control the properties of the depositing film.

C) Magnetron sputtering

Magnetron sputtering is somewhat different from general sputtering technology. The difference is that magnetron sputtering technology uses magnetic fields to keep the plasma in front of the target, intensifying the bombardment of ions. Highly dense plasma is the result of this PVD coating technology, be deposited (target) is vaporized by short and intense laser pulses and forms a plasma plume. Then, the vaporized target material from the plasma bombards the substrate and – under the right conditions – creates a thin homogenous layer on this substrate.

D) Sputter deposition

Sputter deposition is a physical vapor discharge method by thin film deposition by sputtering. This involves ejecting material from a target that is a source onto a "substrate" such as a silicon wafer. Sputtering is re-emission of the deposited material during the deposition process by ion or atom bombardment. Sputtered atoms ejected from the target have a wide energy.

distribution, typically up to tens of eV.

Table1.2 (ii) Process Parameters

Parameters	**Operating condition**
In put voltage	220-240 volts
Current	0.5 Amps
Time	20 mins
Gas used	Argon (40 ml/min)

Other Methods

 Sol gel dip coating
 Plating
 Eletroless plating
 spraying
 High velocity oxygen fuel (HVOF)
 Plasma spraying
 Thermal spraying

1.3 Zirconium Dioxide i) Structure

Three phases are known: monoclinic <1,170 °C, tetragonal 1,170–2,370 °C, and cubic >2,370°C.The trend is for higher symmetry at higher temperatures, as is usually the case. A few percentage of the oxides of calcium or yttrium stabilize the cubic phase.

ii) Properties Of Zirconium Dioxide

 Use temperatures up to 2400°C.
 High density process
 Low thermal conductivity (20% That of alumina)
 Chemical inertness except hydrogen fluoride
 Resistance to molten metals
 Ionic electrical conduction

1.3 Problem Definition

Stainless steel is widely used in various industrial applications because of their Excellent corrosion resistance and their mechanical properties. However, the Corrosion resistance and the oxidation resistance of stainless steel need to be improved in order to increase their durability. The best stainless steels may fail in saline and environments, where once the process of corrosion begins it brings as consequence the loss of mechanical properties through deterioration of the passivation layer. Effect of heating temperature on the thickness of ZrOnano structure thin films was studied using SWE, SEM and AFM techniques. Resulting thickness values are the average values of the ten independent measurements performed at the same environmental. The average error between measurements within each series is shown by error bars on the plots These studies focused on the growth of a coating of an oxide, carbide, or ox nitride layer on a stainless steel surface. The properties of ZrO_2 and ZrO_xN_y, in particular, have attracted wide research interest, and this as a result has boosted their application in the creation of bulk components and coatings. Based on the literature, accounting of the disadvantages faced during hard facing of the valve seat rings with cobalt based or nickel based alloys and the work carried on phase 1 by coating steel with Zirconium coating process the problems were identified as.

 Secondary operations are necessary in case of hard facing operation.
 Proper heat treatment is necessary for these processes.
 Shielding gasses are necessary for the above processes since it leads to oxidation on surface.

1.4 Problem Statement

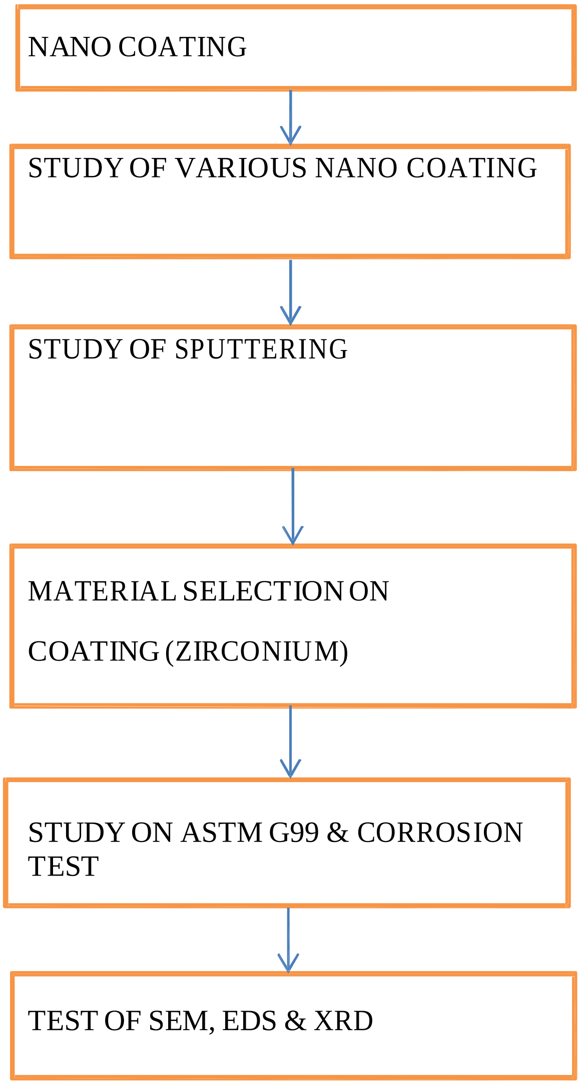
Nano coating of Zirconium is studied and experimented for the proposed problem, thereby increasing the corrosion resistance of A216 carbon steel.

1.5 Proposed Solution

Zirconium on A216 steel, the expected outcome of the proposed work is to increase the corrosion resistance and the wear resistance of the base metal mainly in the saline water that can be used in the underwater pipelines, valves and the marine applications. This also improves the structural and the optical properties of the base material It can be seen that after crossing the tip over the step and just before dropping into the stable thickness of the film

2. Experimental

View the terms of process by analysis the materials there are several cladding techniques such as hard facing, coating, and surfacing techniques, to improve corrosion and wear properties of base materials. Cobalt base alloys / Nickel based alloys are the most common clad materials used to improve the corrosion and wear properties of the base materials, Nano-coating of these valve material by Zirconium



Zirconia sol has been prepared by taking zirconium (IV)- n-prop oxide as a precursor 10 ml volume of precursor was diluted with 100 ml of n-propanol with continuous stirring, Thereafter, acetyl acetone was added within a few minutes of the addition of the n- propanol. A few drops of water were also added to the solution and the resultant solution was stirred up to 4 hrs with proper mixing. Once, solution becomes miscible the stirring was stopped and resultant solution was used for coating development. The viscosity of the synthesized sol was measured using Brookfield make remoter. The 9Cr1Mo ferritin steel sheet was cut to a dimension of 30 mm × 18 mm × 3 mm for oxidation/hot corrosion test under air/fused salt system. The cut samples were metal- graphically polished by grinding them with emery pa- per of 120, 600, 800 grit size followed by mirror polish with alumina suspension (size 3µm). The metallography-phially, polished specimens were degreased properly with acetone. In the next step polished specimens were kept in concentrated nitric acid for few minute to roughen the surface for a purpose of increased the coating adherence. Afterwards, the synthesized zirconia sol was coated on the polished substrate through dip coating technique with a constant withdrawal speed of 1 cm/sec (approx). The coated specimens were dried in air for 10 minutes. Further, the coated specimens were heated at 300˚C and kept at the desired temperature for half an hour. The heat treatment temperature was then raised to 600˚C for complete sintering of the coatings.

2.1 Sputtering

The ejection of atoms from the surface of a material (the target) by an bombardment with energetic particles is called sputtering. Sputtering is a momentum of transfer process in which atoms from a cathode/target are driven off by bombarding ions. Sputtered is atoms of travel until they strike a substrate, where is deposit to from the desired layer. The simplest source of ions for sputtering is provided by the well-known phenomenon of glow discharge due to an applied of electric field between two electrodes in a gas at low pressure of gas breaks down to conduct electricity when a certain by minimum voltage is reached. Such an ionized gas is called plasma of Ions plasma is accelerated at the target by a large electric field. When the ions impact the target of atoms (or molecules) are ejected from the surface of the target the plasma, where carried away and then deposited on the substrate. This type of sputtering is called "DC sputtering"

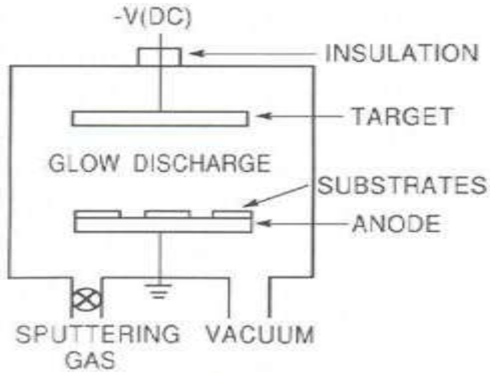


Fig 2.1 Sputtering

In order to increase the efficiency of the sputtering process, it is common for the sputtering source to have some magnetic confinement through a magnetron source. The effect of the magnetic field is to spiral the electrons so that they have more chance The use of electrons not only gives better resolution but, due to the nature electron beam specimen interactions there are a variety of signals that can be used to provide information regarding characteristics at and near the surface of a specimen. In scanning electron microscopy visual inspection of the surface of a material utilizes signals of two types, secondary and backscattered electrons. Secondary and backscattered electrons are constantly being produced from the surface of the specimen while under the electron beam however they are a result of two separate types of interaction of undergoing an ionizing collision thus enabling the plasma to be operated at a higher densit y.

2.2 Corrosion Of Metals And Its Prevention

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete the wood by generally refers t o metals. Widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion.

3. Discussion and Testing

3.1 SEM

The electrons are a result by an elastic collision of scattering event between the incident electrons and specimen nuclei or electrons. Backscattered electrons can be generated further from the surface of material to help resolve topographical contrast by atomic number contrast with a resolution of >1micron.While they several types of signals that are generated by specimen under an electron beam the x-ray signal is typically from only other signal that is used for scanning electron microscopy. The x-ray signal is a result of recombination of interactions between the free electrons and positive electron holes that are generated within the source of material. The x-ray signal can originate from further down into the surface of the specimen surface from the allows for the process by elevating the defects by material process.

3.2 Effect Of Working Distance

Besides the accelerating voltage one's choice of working distance and spot size will greatly influence the image quality. As with accelerating voltage there exists a give and take situation when choosing the most suitable settings for working distance and spot size. Generally speaking a working distance of 10mm should be used and will allow for a good depth of field while maintaining good resolution. In most cases one may want to reduce the working distance to achieve better resolution especially when using lower accelerating voltages.

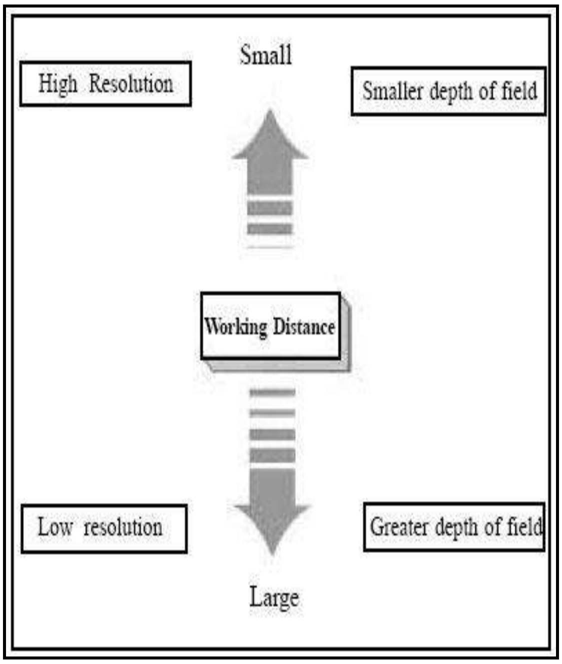
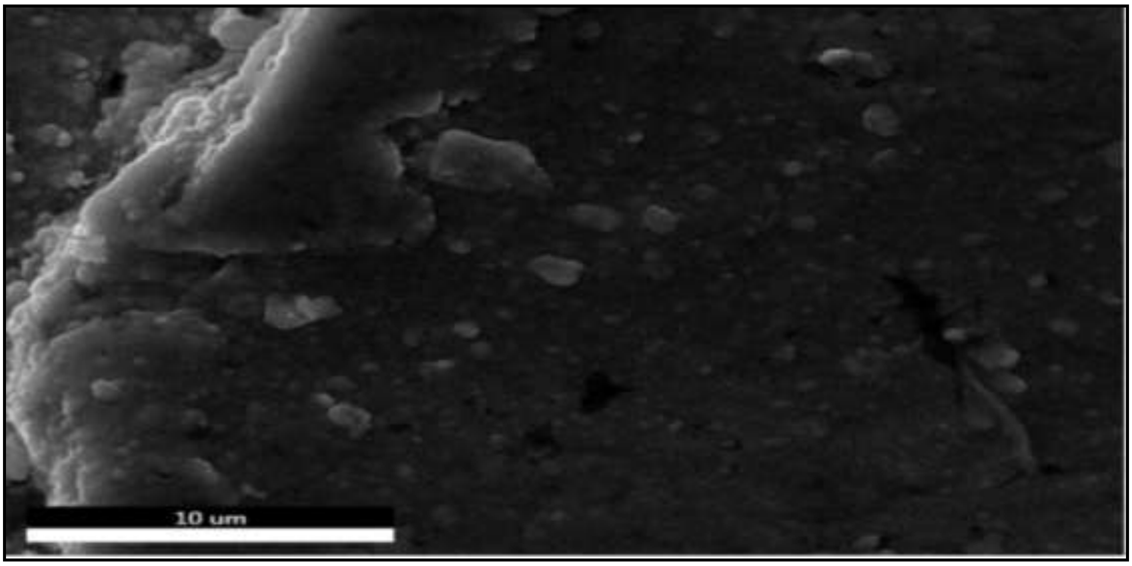


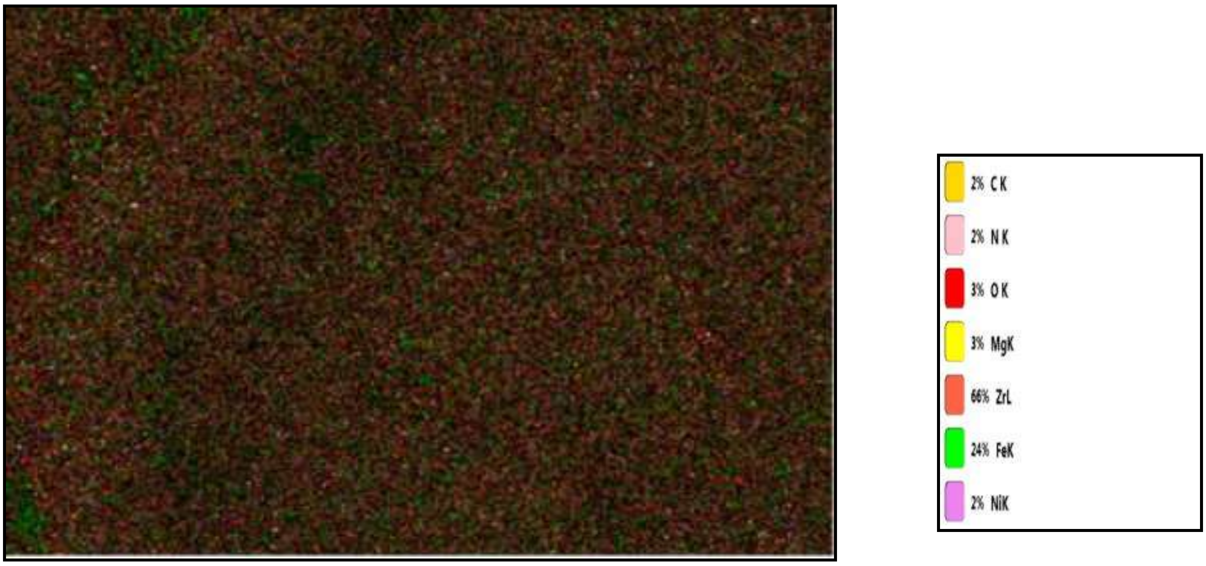
Figure 3.2 effect of working distance

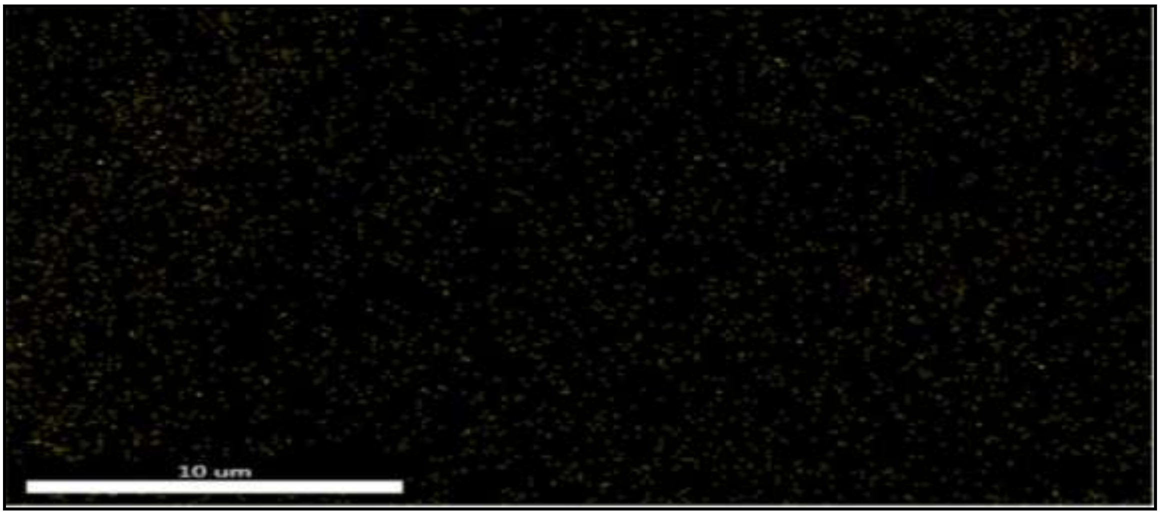
3.3 Energy Dispersive X-Ray Spectrometry

EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a Focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements (Z < 10). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity.X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition. By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can be produced. Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images, but can also be used for element mapping, and even point analysis, if an X-ray spectrometer is added. There is thus a considerable overlap in the functions of these instruments. The critical excitation energy (E_C) is the minimum energy which bombarding electrons (or other particles) must possess in order to create an initial vacancy its dependence of E_C on Z for the principal shells. In electron probe analysis the incident electron energy (E_0) must exceed E_C and should Preferably be at least twice E_C to give reasonably high excitation efficiency. For atomic numbers above about the usual to change from K to L lines to avoid the need for an excessively high electron beam energy (which has undesirable implications with respect to the penetration of the electrons in the sample, and in any case may exceed the maximum available accelerating voltage) The 'critical excitation energy' (E_C) is the minimum energy which bombarding electrons (or other particles) must possess in order to create an initial vacancy.

3.4 Image Of Zr Eds







3.5 Micro structural Evaluation using Scanning Electron Microscope Zr coated A216

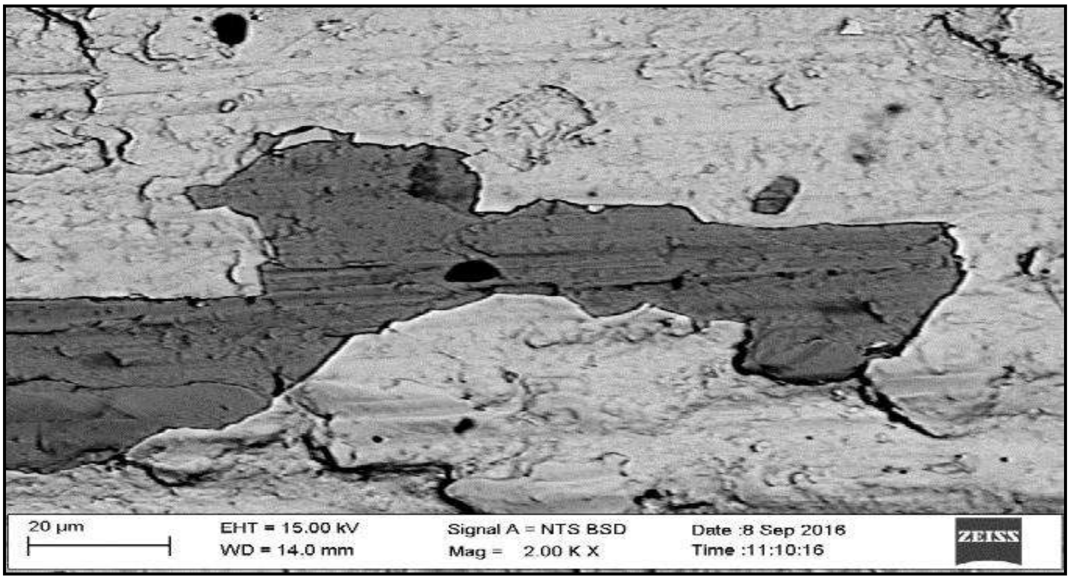


Fig.3.5 (A) Micro structure of Zr coated A216 at 2000X

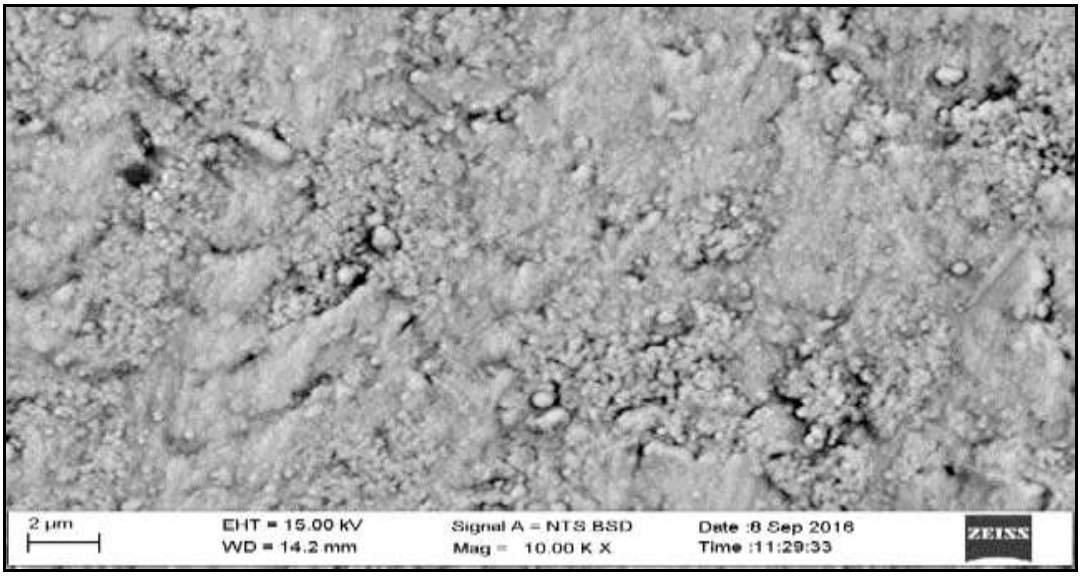


Fig. 3.5(B) Micro structure of Zr coated A216 at 10000X

3.6EDS IMAGES for Zr coated samples

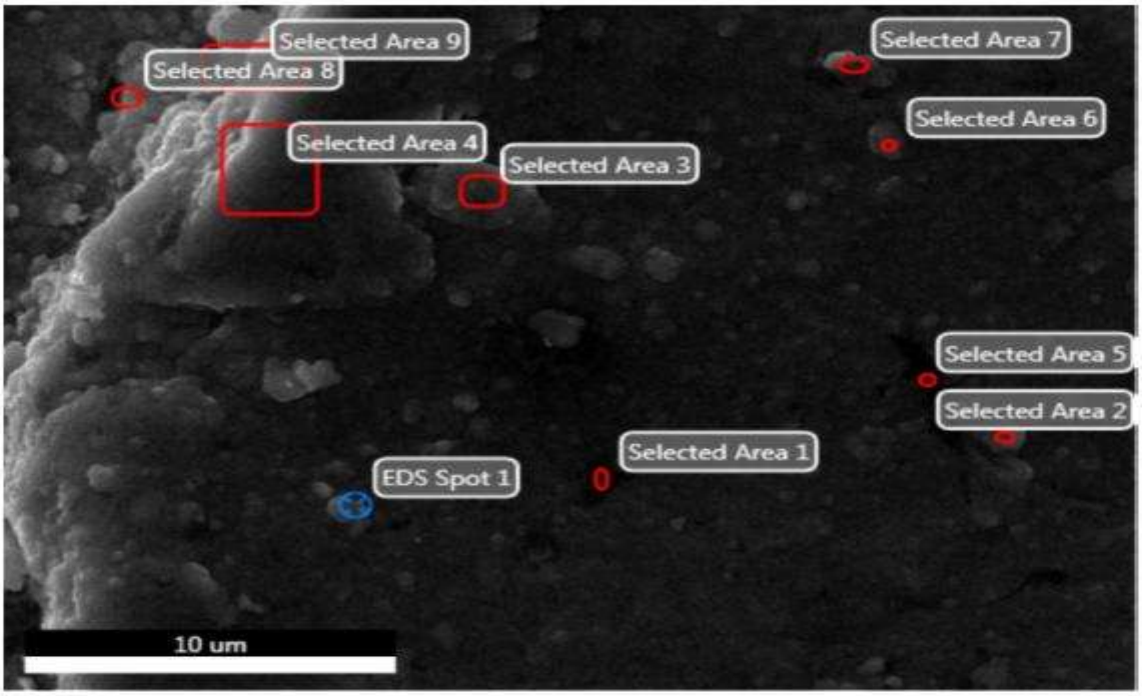
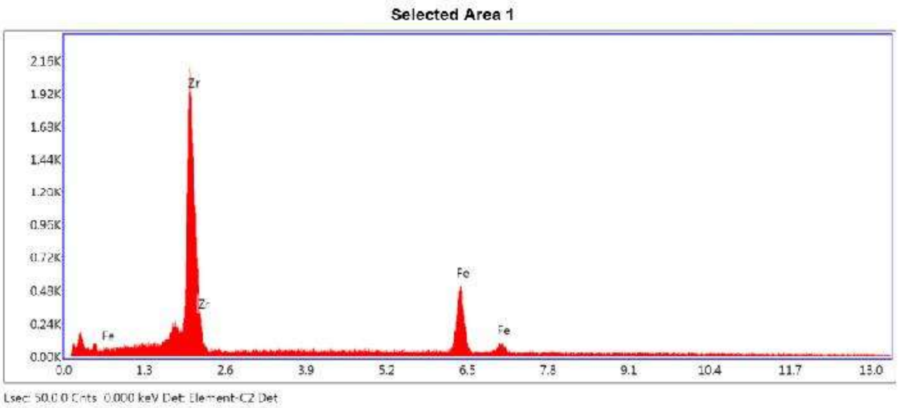
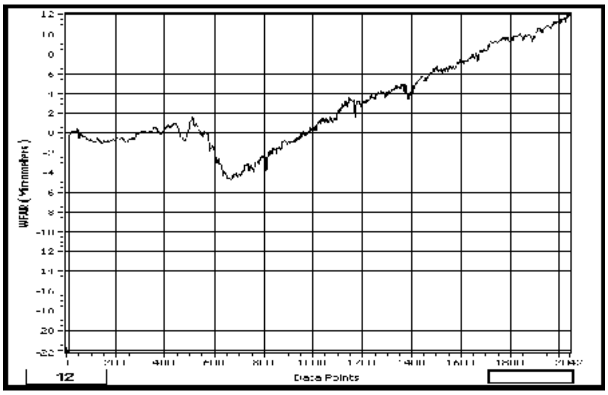


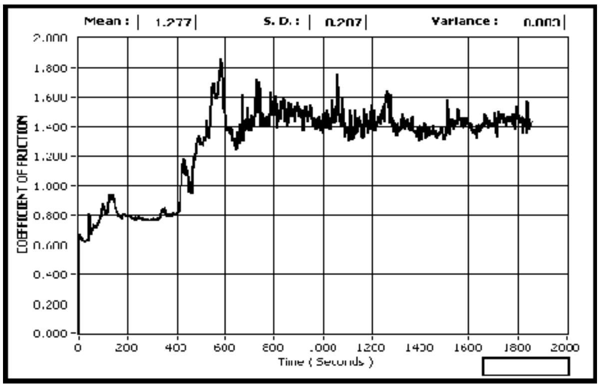
Figure 3.6 EDS IMAGES for Zr coated samples

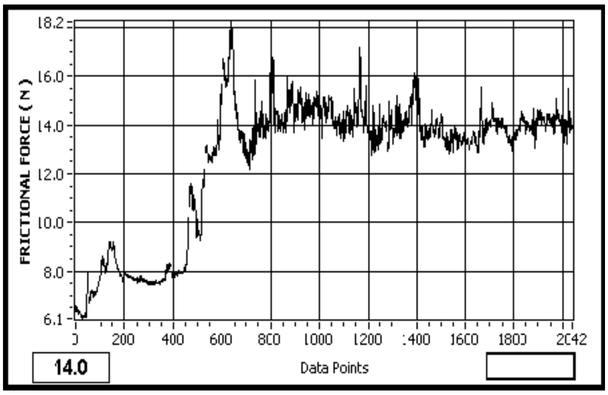


Spot Area	Zr %	Fe %
Area 1	66.36	33.64
Area 2	74.25	25.75
Area 3	70.19	29.81
Area 5	69.12	30.88

3.7 Zr Coated A216







4. Conclusion

Most of the research works related with coating techniques were carried out to optimize the coating parameters for controlling the wear, corrosion behaviors and thickness of the coating. It was observed that only a few attempts were made to restrain the causes of failure. A few researchers strongly are advocated to widen the research work towards the Nano coating techniques for controlling the wear and corrosion properties of the base materials. Analysis of failures of the material due to corrosion and wear involved the collection and analysis of Nano coating related data. A few researchers indicated that voluminous information available in paper form was difficult for handling, storing and analyzing. It was witnessed that lack of awareness of modern coating techniques on the base material to prevent the problems caused due to the corrosion and wear. Further, the Literature survey indicated that the use of modern coating techniques on the base material to prevent the problems caused due to the corrosion and wear. In-depth analysis of these cases in the literature revealed that corrosion and wear properties are improved by eliminating or minimizing the failures of coating. The study on the application of Nano coating in literature hinted that Nano coating could be applied for the reduction o f failures in coating d u e to coating methods of earlier period. The specimen was coated with zirconia using Sol gel dip coating process. From the mentioned process the ceramic materials with metals had been Nano-coated.

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