International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.14, pp 362-374, 2017

Study of Nano Coating on Molybdenum by Sol- Gel Process

Prince Sam Glytton.A*, David Rathnaraj.J, Sathis.S

Department of Mechanical Engineering, Sri Ramakrishna Engineering College
Coimbatore, India

Abstract : Nano coating are coating that produced by usage of some components at Nano scale to obtain desired properties. Nanostructured coatings offer great potential for various applications due to their superior characteristics that are not typically found in conventional coatings. In order for steel to be considered low carbon steel, there are certain characteristics it must meet. For instance, the steel has to have less than .3 percent carbon in its total makeup to be considered low carbon. Low carbon steel also contains pearlite and ferrite as major components. Low carbon steel is generally used straight from the forming process, whether that process is hot forming or cool forming, because that's when it's most workable and easiest to form. 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 Molybdenum. But since it is a material used for high temperature-pressure applications it is necessary to select a proper cost effective coating. Molybdenum being an apt material for corrosion resistance and high mechanical properties is synthesized and used for coating. The specimen was dipped in electrolyte and a potential of 4.1V. The specimen is coated in the electrolyte and the coating thus formed is characterized using XRD analysis, and then the coating is tested for its corrosion potential.

1. Introduction

Metals can be classified into two groups basically. Ferrous and Non ferrous metals are classified based on presence of iron in them. Ferrous metals are mainly composed of iron and have magnetic properties. Steel, an iron alloy containing carbon, is by far the most-recycled material in the world. In metallurgy, a non- ferrous metal is any metal, including alloys, that does not contain iron in appreciable amounts.

1.1 Astm A216 Wcb Cast Steel

WCB (UNS Code J03002) is covered by ASTM A216 standard, which specification covers carbon steel B castings for valves, fittings, flanges and other pressure- containing parts for high temperature service and the quality required for assembly with other castings or wrought steel parts by fusion welding. These grades are all "cast" grades meaning they are made through "casting.".

Anticorrosion coating methods

Vapour deposition

1.2 Chemical vapour deposition: Metal organic vapour phase epitaxy :

It is an organometallic vapour phase epitaxy (OMVPE) or metalorganic chemical vapour deposition (MOCVD),[1] is a chemical vapour deposition method used to produce single or polycrystalline thin films. It is a highly complex process for growing crystalline layers to create complex semiconductor multilayer structures. This takes place not in a vacuum, but from the gas phase at moderate pressures (10 to 760 Torr). As such, this technique is preferred for the formation of devices incorporating thermodynamically metastable alloys, and it has become a major process in the manufacture of optoelectronics

- **Electrostatic sprayassisted vapour deposition (ESAVD)** :

Electrostatic spray assisted vapour deposition (ESAVD) is a technique (developed by a company called IMPT) to deposit both thin and thick layers of a coating onto various substrates. In simple 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.

- **Sherardizing :**

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

1.3 Physical Vapor Deposition

Electron beam physicalvapor deposition (EBPVD) : 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.

Ion plating

Ion plating is a physical vapor deposition (PVD) process that is sometimes 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.

Ion beam assisted deposition (IBAD)

Ion beam assisted deposition or IBAD or IAD (not to be confused with ion beam induced deposition, IBID) is a materials engineering technique which combines ion implantation with simultaneous sputtering or another physical vapor depositiontechnique. Besides providing independent control of parameters such as ion energy, temperature and arrival rate of atomic species during deposition, this technique is especially useful to create a gradual transition between the substrate material and the deposited film, and for depositing films with less built-in strain than is possible by other techniques.

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. A highly dense plasma is the result of this PVD coating technology.

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. The material to 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 creates a thin homogenous layer on this substrate

Sputter deposition

Sputter deposition is a physical vapor deposition (PVD) method of thin film deposition by sputtering. This involves ejecting material from a target that is a source onto a "substrate" such as a silicon wafer. Resputtering 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.

Vacuum deposition

Vacuum deposition is a family of processes used to deposit layers of material atom-by-atom or molecule-by-molecule on a solid surface. These processes operate at pressures well below atmospheric pressure(i.e. vacuum). The deposited layers can range from a thickness of one atom up to millimeters, forming freestanding structures. Multiple layers of different materials can be used, for example to form optical coatings.

Vacuum evaporation, evaporation (deposition)

Vacuum evaporation is the process of causing the pressure in a liquid-filled container to be reduced below the vapor pressure of the liquid, causing the liquid to evaporate at a lower temperature than normal. Although the process can be applied to any type of liquid at any vapor pressure, it is generally used to describe the boiling of water by lowering the container's internal pressure below standard atmospheric causing the water to boil at room temperature.

1.4 Chemical and electrochemical technique

Conversion coating

Autophoretic coating

A method of application rather than a paint. An automated system of painting on a production line such as automotive manufacture. Involves the dipping of the whole item in an acidic solution containing diluted paint (5%) which etches and applies the paint. There is no electricity or charge involved, and in this way is similar to electroless plating. Used most often in high volume manufacturing, where the same colour is used for long periods.

Chromate conversion coating

Chromate conversion coating is a type of conversion coating used to passivatesteel, aluminum, zinc, cadmium, copper,silver, magnesium, and alloys. It is primarily used as a corrosion inhibitor,primer, decorative finish, or to retainelectrical conductivity. The process is named after the chromate found in chromic acid, also known as hexavalent chromium, the chemical most widely used in the immersion bath process whereby the coating is applied

1.5 Introduction To Coating Element

Molybdenum is a chemical element with symbol Mo and atomic number 42. Molybdenum minerals have been known throughout history, but the element was discovered (in the sense of differentiating it as a new entity from the mineral salts of other metals) in 1778 by Carl Wilhelm Scheele. The metal was first isolated in 1781 by Peter Jacob Hjelm. Molybdenum does not occur naturally as a free metal on Earth, but rather in various oxidation states in minerals. The free element, which is a silvery metal with a gray cast, has the sixth-highest melting point of any element. It readily forms hard, stable carbides in alloys, and for this reason most of world production of the element (about 80%) is in making many types of steel alloys, including high strength alloys and superalloys. Most molybdenum compounds have low solubility in water, but the molybdate ion MoO2−4 is soluble and forms when molybdenum-containing minerals are in contact with oxygen and water. Industrially, molybdenum compounds (about 14% of world production of the element) are used in high-pressure and high-temperature applications, as pigments, and as catalysts.Molybdenum-containing enzymes are by far the most common catalysts used by some bacteria to break the chemical bond in atmospheric molecular nitrogen, allowing biological nitrogen fixation. At least 50 molybdenum-containing enzymes are now known in bacteria and animals, although only bacterial and cyan bacterial enzymes are involved in nitrogen fixation. These nitrogenases contain molybdenum in a different form from the other molybdenum-containing enzymes, which all contain fully oxidized molybdenum incorporated into a molybdenum cofactor. Owing to the diverse functions of the various molybdenum cofactor enzymes, molybdenum is a required element for life in all higher eukaryote organisms, though it is not required by all bacteria

1.6 Characteristics physical properties

In its pure form, molybdenum is a silvery-grey metal with a Mohs hardness of 5.5. It has a melting point of 2,623 °C (4,753 °F); of the naturally occurring elements, only tantalum, osmium, rhenium, tungsten, and carbon have higher melting points. Weak oxidation of molybdenum starts at

300 °C (572 °F). It has one of the lowest coefficients of thermal expansion amongcommercially used metals. The tensile strength of molybdenum wires increases about 3 times, from about 10 to 30 GPa, when their diameter decreases from ~50–100 nm to 10 nm.

1.7 Chemical Properties

Molybdenum is a transition metal with an electronegativity of 2.16 on the Pauling scale and a standard atomic weight of 95.95 g/mol.[13][14] It does not visibly react with oxygen or water at room temperature, and the bulk oxidation occurs at temperatures above 600 °C, resulting in molybdenum trioxide: $2\ Mo + 3\ O_2 \rightarrow 2\ MoO_3$. The trioxide is volatile and sublimes at high temperatures. This prevents formation of a continuous protective oxide layer, which would stop the bulk oxidation of metal. Molybdenum has several oxidation states, the most stable being +4 and +6. The chemistry and the compounds show more similarity to those of tungsten than that of chromium. An example is the instability of molybdenum(III) and tungsten(III) compounds as compared with the stability of the chromium(III) compounds. The highest oxidation state is common in the molybdenum(VI) oxide (MoO3), whereas the normal sulfur compound is molybdenum disulfide MoS2. Molybdenum(VI) oxide is soluble in strong alkaline water, forming molybdates (MoO42−). Molybdates are weaker oxidants than chromates, but they show a similar tendency to form complex oxyanions by condensation at lower pHvalues, such as [Mo7O24]6− and [Mo8O26]4−. Polymolybdates can incorporate other ions into their structure, forming polyoxometalates.[17] The dark-blue phosphorus-containing heteropolymolybdate P[Mo12O40]3− is used for the spectroscopicdetection of phosphorus.[18] The broad range of oxidation states of molybdenum is reflected in various molybdenum chlorides

- Molybdenum(II) chloride $MoCl_2$ (yellow solid)
- Molybdenum(III) chloride $MoCl_3$ (dark red solid)
- Molybdenum(IV) chloride $MoCl_4$ (black solid)

The oxidation state 0 is possible with carbon monoxide as ligand, such as in molybdenum hexacarbonyl, $Mo(CO)_6$.

1.8 Structure Of Molybdenum Oxide

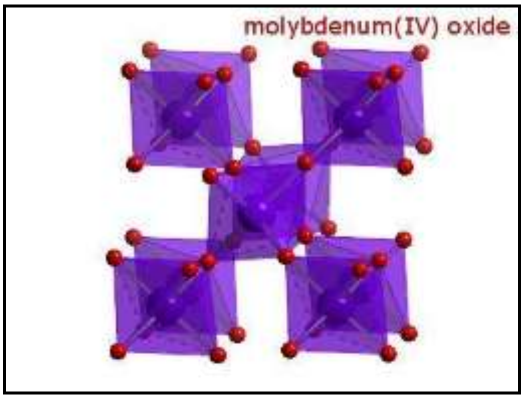


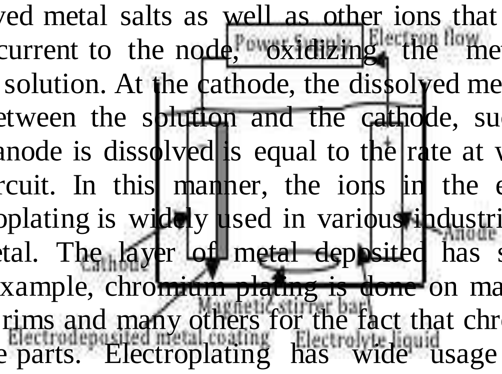
Figure: 1.0 Structure Of Molybdenum Oxide

Molybdenum dioxide is the chemical compound with the formula MoO_2. It is a violet- colored solid and is a metallic conductor. It crystallizes in a monoclinic cell, and has a distorted rutile, (TiO_2) crystal structure. In TiO_2 the oxide anions are close packed and titanium atoms occupy half of the octahedral interstices (holes). In MoO_2 the octahedra are distorted, the Mo atoms are off-centre, leading to alternating short and long Mo – Mo distances and Mo-Mo bonding. The short Mo – Mo distance is 251 pm which is less than the Mo – Mo distance in the metal, 272.5 pm. The bond length is shorter than would be expected for a single bond. The bonding is complex and involves a delocalisation of some of the Mo electrons in a conductance band accounting for the metallic conductivity.

1.9 Electrodeposition Coating Method

Electrodeposition is a process that uses electric current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode. The term is also used for electrical oxidation of anions onto a solid substrate, as in the formation silver chloride on silver wire to make silver/silver- chloride electrodes. Electroplating is primarily used to change the surface properties of an object but may also be used to build up thickness on undersized parts or to form objects by electroforming.

The process used in electroplating is called electrodeposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the node, oxidizing the metal atoms that it comprises and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.Electroplating is widely used in various industries for coating metal objects with a thin layer of a different metal. The layer of metal deposited has some desired property, which the metal of the object lacks. For example, chromium plating is done on many objects such as car parts, bath taps, kitchen gas burners, wheel rims and many others for the fact that chromium is very corrosion resistant, and thus prolongs the life of the parts. Electroplating has wide usage in industries. It is also used in making inexpensive jewelry. Electroplating increases life of metal and prevents corrosion.



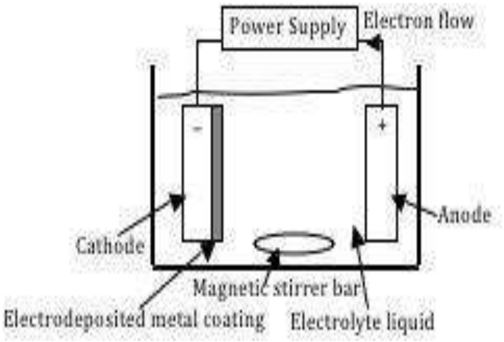


Fig 1.1: Electrodeposition Technique

2 Problem Definitions

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. These studies focused on the growth of a coating of an oxide, carbide, or oxynitride layer on a stainless steel surface.The main reason for the existence of the stainless steels is their resistance to corrosion. Chromium is the main alloying element, and the steel should contain at least 11 %. Chromium is a reactive element, but it and its alloys passivate and exhibit excellent resistance to many environments. Higher Cr contents may be necessary for to improve the corrosion resistance of stainless steels in more aggressive media. Among other alloying elements, Nickel is the most important: it is added to control the alloy microstructure and to improve the corrosion resistance in acidic or caustic media. The addition of other elements such as Molybdenum, Tungsten, Copper, Silicon, Titanium, Niobium, Nitrogen , enables a wide range of properties to be obtained All stainless steels contain some carbon. Even though it is difficult to get much less than about 0.03 % and sometimes carbon is deliberately added up to 1.00% or more, modern melting processes allow to reduce the content below 0.015 or even 0.010%, providing stainless steels with superior resistance to intergranular corrosion. The more carbon there is, the more chromium must be used, because carbon can take from the alloy about seventeen times its own weight of chromium to form carbides. Chromium carbide is of little use for resisting corrosion. The carbon, of course, is added for the same purpose as in ordinary steels to make the alloy stronger. Nitrogen is often added in modern stainless steels this element provides high mechanical properties, better resistance to pitting initiation and more generally improves the corrosion resistance thanks to a better micro structural stability. From a micro structural point of view, alloying elements may be classified as either Austenite formers or Ferrite formers. Depending upon the ratio between austenite former elements and ferrite former elements, the resulting microstructure may be Ferritic (Body-Centered-Cubic crystal) or Austenitic (Face-Centered- Cubic crystal). The Martensitic structure (Close-Packed Hexagonal crystal) is the result of the transformation of austenite to martensite during cooling or during strong cold working. A large number of stainless steels are available. Their corrosion resistance, mechanical properties, and cost vary over a broad range. For this reason, it is important to specify the exact stainless steel desired for a given application. There are five main types of stainless steel: ferritic, martensitic, austenitic, precipitation hardening and duplex. The ferritic and martensitic grades are so named because of their crystal structures. Both are iron-chromium-based alloys and were the type of stainless steel first developed in the early 1900’s. The ferritic and martensitic stainless steels are fully magnetic; duplex stainless steels are partly magnetic. The martensitic stainless steels can be hardened by a heat treatment similar to that used to harden ordinary steel, namely, heating to a high temperature, quenching, then reheating to an intermediate temperature (tempering) to achieve the desired balance of hardness and ductility. Stainless and heat resisting steels possess unusual resistance to attack by corrosive media at atmospheric and elevated temperatures, and are produced to cover a wide range of mechanical and physical properties for particular applications.

2.1 Problem Identification

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

Molybdenum electrodeposition coating process the problems were identified as. :

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

2.2 Problem Statement

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

2.3 Proposed Solution

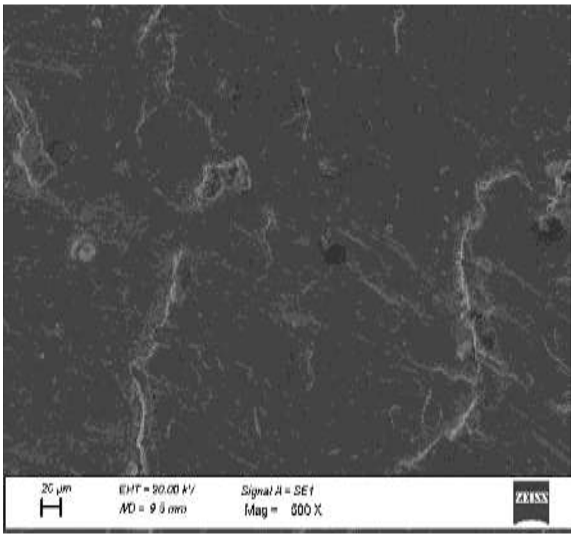
The expected outcome of the proposed work is to increase the corrosion resistance and the wear resistance of the base metal mainly in the saline water that can be used in the underwater pipelines, valves and the marine applications. This also improves the structural and the optical properties of the base material.

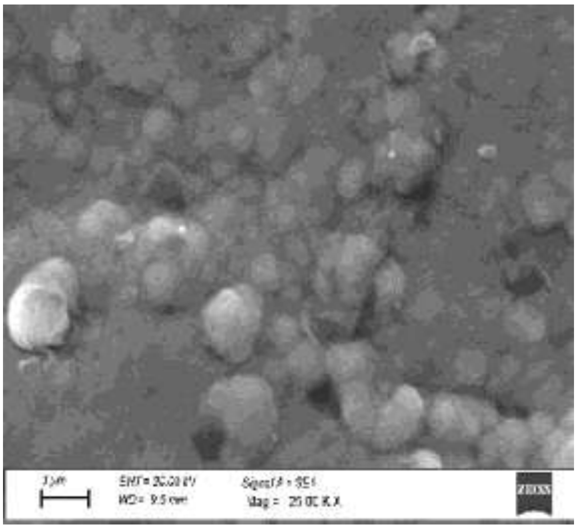
3 Testing and Validation

Originally microscopy was based on the use of the light microscope and could provide specimen resolutions on the order of 0.2 microns. To achieve higher resolutions, an electron source is required instead of light as the illumination source, which allows for resolutions of about 25 Angstroms. 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 Backscattered electrons are a result of an elastic collision and scattering event between incident electrons and specimen nuclei or electrons. Backscattered electrons can be generated further from the surface of the material and help to resolve topographical contrast and atomic number contrast with a resolution of >1 micron. While there are several types of signals that are generated from a specimen under an electron beam the x-ray signal is typically the only other signal that is used for scanning electron microscopy. The x-ray signal is a result of recombination interactions between free electrons and positive electron holes that are generated within the material. The x-ray signal can originate from further down into the surface of the specimen surface and allows for determination of elemental composition through EDS (energy dispersive x-ray spectroscopy) analysis of characteristic x-ray signals.

All of the primary controls are accessed through the computer system using the mouse and keyboard. The user need only be familiar with the GUI or software that controls the instrument rather than control knobs and switches typically found on older style scanning electron microscopes. The image that is produced by the SEM is usually viewed on CRTs located on the electronic console but, instead with FEI the image can be seen on the computer monitor. Images that are captured can be saved in digital format or printed directly.

3.1 Image For Sem Test

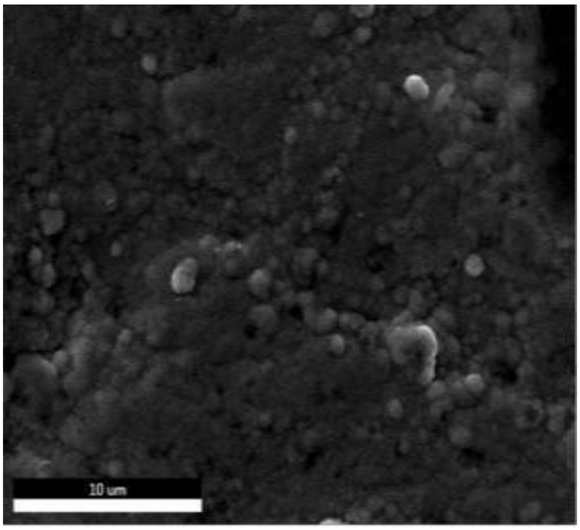


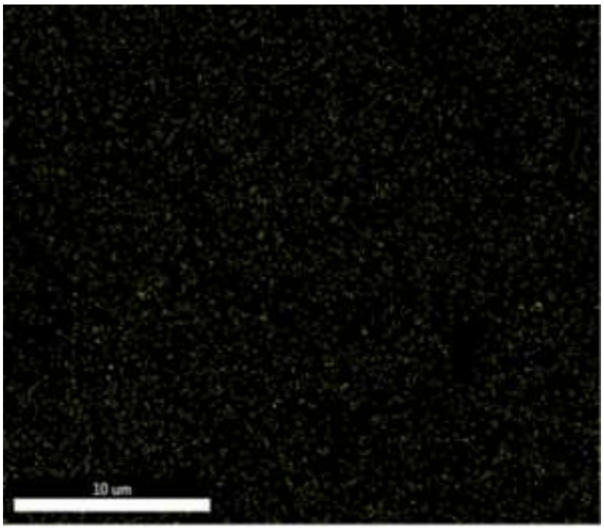


3.2 Energy Dispersive X-Ray Spectrometry (Eds)

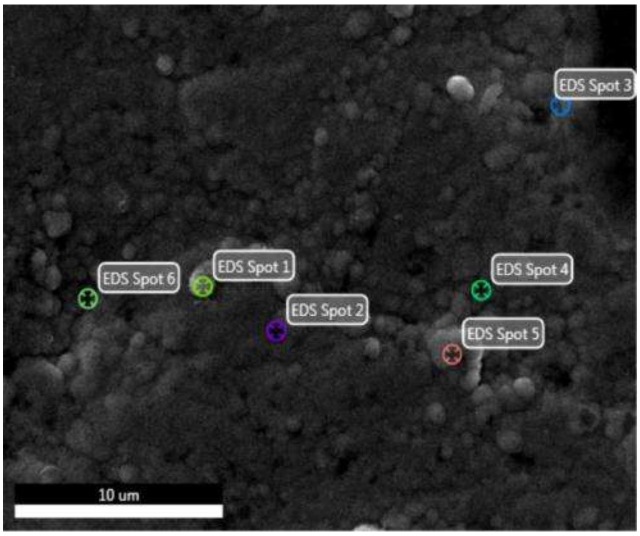
EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with aFocused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of 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. Figure 4 shows the 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 35 it is 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).

3.3 Image For Eds Test





3.4 Pointing Of Molybdenum In Eds



EDS Spot 1

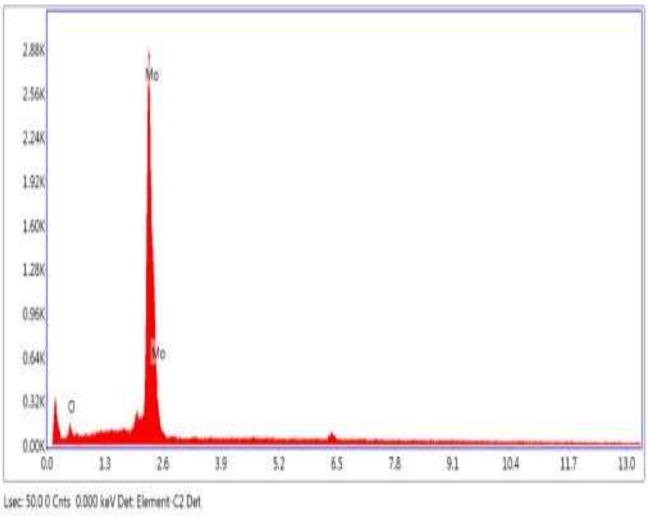


Figure 3.1 Ezaf Smart Quant Results

EDS Spot 2

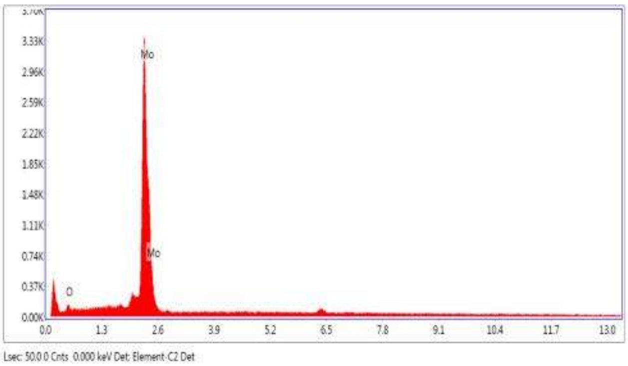


Figure 3.2 Ezaf Smart Quant Results

3.5 XRD characterization

The XRD analysis was taken using Cukα radiation in the range of $2\Theta = 10° - 80°$. XRD analysis was taken for the powder and the coated sample. The XRD diffractometry pattern of the synthesized powder from fig2. Confirms the presence of Yttrium stabilized Zirconia at peak angle formed at 30°,

$32 \leq 2\Theta \leq 37°$, 50° and confirms the tetragonal symmetry at $72° \leq 2\Theta \leq 76°$. From figure. The XRD data of the EPD coated sample confirms the deposition of zirconia coating on steel substrate using the EPD process. The peak for metal substrate is seen at an angle $45° \leq 2\Theta \leq 48°$.

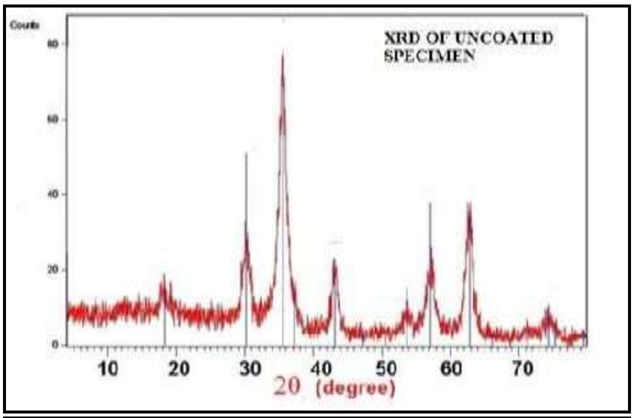


Figure 5.1 Xrd Report Of Uncoated Sample

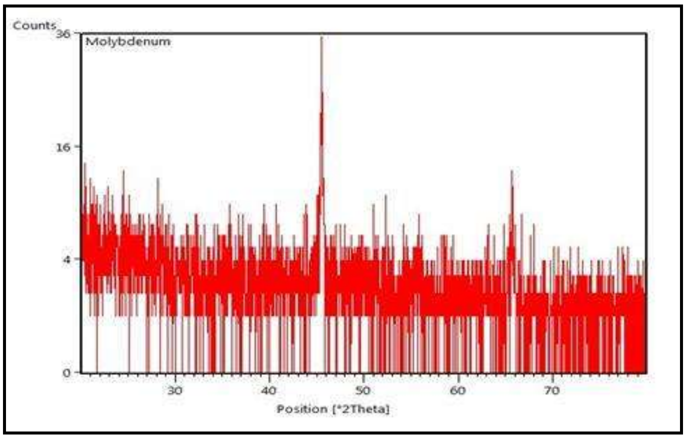


Figure 3.4 Xrd Result Of Coated Specimen

3.6 Result and Findings

- Molybdenate is coated on A216 steel by electrodeposition coating process.
- Ease of fabrication.
- Deposition rate and thickness can be controlled.

4 Conclusion

Details of literature survey conducted in the area of material science engineering in the manufacturing field are presented in this chapter. On the whole, the work enabled the research scholar to study the principles, and role of nanocoating in material science engineering. During the earlier period, hardfacing, plasma spray coating, high energy coating method were viewed as the effective methods for the prevention of corrosion and wear problems, but during the contemporary period nanocoating is recognized by most of the researchers as one of the important strategies for ensuring the prevention of corrosion and wear problems. 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 advocated widening 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 nanocoating 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.

Detailed literature survey indicated that risk assessment of coating techniques used in earlier times such as hard facing, plasma spray coating, high velocity oxy fuel coating. 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 nanocoating in literature hinted that nanocoating could be applied for the reduction of failures in coating due to coating methods of earlier period.The specimen was coated with Molybdenum electrodeposition coating process. From the mentioned process the ceramic materials with metals have been nano-coated.

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