Alternative Method of Processing BIDRI-WARE CRAFTS: An Electrochemical Study

A THESIS

Submitted by

AKSHAYKUMAR VARMA

MM13B006

Under the guidance of

Dr. LAKSHMAN NEELAKANTAN

DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY MADRAS.

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CERTIFICATE

This is to certify that the thesis **Alternative Method of Processing BIDRI-WARE CRAFTS: An Electrochemical Study**, submitted by **Akshaykumar Varma**, to the Department of Metallurgy and Materials Engineering at Indian Institute of Technology Madras, Chennai in partial fulfillment of the requirement for award of the degree of **Bachelor of Technology**, is a bona fide record of the research work done by him under my guidance. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

Dr. Lakshman Neelakantan

Assistant Professor
Department of Metallurgy and Materials Engineering
IIT-Madras
Chennai - 600 036

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Friends and family have been an integral part throughout my stay at IIT Madras. I would like to thank them for their constant support. Finally, I would like to place my sense of gratitude to all those who directly or indirectly contributed to my success and the strong foundation that has been laid for my future.

AKSHAYKUMAR VARMA
MM13B006

ABSTRACT

Striking strokes of silver against a deep, dark black, one that does not fade with time – these defining characteristics of Bidriware from Karnataka in Southern India bear testimony to the fine craftsmanship involved in creating this metal inlay work. Believed to have been brought to Bidar (hence the craft's name) by the Bahamani Sultans who ruled there in the 14th – 15th Century, the craft is said to have originated in Persia with an intermingling of Turkish, Persian and Arabic influences.

The bidar fort sand is used for formation of black patina. The underlying mechanism of patination is still not clearly understood. Also the fort being an heritage center, an alternative to the sand has to be developed. Hence the aim of this project is to find a viable chemical substitute and identifying the process is important

This investigation studies the use of KNO_3 as a source of nitrate (present in sand) to achieve Dark Black patina. For the first time, an attempt has been made to identify the electrochemical parameters like potential and corrosion rate. The corrosion rate in the alternate chemical is studied by weight loss and by accelerated corrosion studies like potentiodynamic polarization.

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ABBREVIATIONS

XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
FE-SEM	Field Emission Scanning Electron Microscope
ICDD	International Centre for Diffraction Data
EDX	Energy-dispersive X-ray spectroscopy
FT IR	Fourier Transform Infrared
GI-XRD	Grazing Incidence X-Ray Diffraction
OCV	Open Circuit Voltage
PD	Potentiodyanamic
EIS	Electrochemical Impedance Spectroscopy
PEIS	Potentiostatic Electrochemical Impedance Spectroscopy
SE	Secondary Electron
BSE	Back Scattered Electrons

CHAPTER 1

INTRODUCTION

In pre-modern India several traditions of art works based on metals, alloys, gems and stones flourished and became internationally famous. Many of these traditions started in ancient India and continue vigorously in modern India.

Bidri ware, the sleek and smooth dark coloured metalwork with intricate eye-catching designs on its glossy surface, is famous all over the world. This metalwork as well as the technique to produce it are found in India alone.

FIGURE 1.1: A Bidri Craft as seen in the Louvre Museum, Paris [15]

Bidri is an alloy which contains 76 to 98% (normally in the neighborhood of 95%) zinc, 2 to 10% copper, upto 8%. lead, 1 to 5% tin and trace of iron Occasionally high percentage of lead and tin have been noted. However mostly it is high zinc low copper alloy. Up to 1% copper in the zinc forms the terminal solid solution h ; above 1% copper the Î phase precipitates at the grain boundaries in this phase field. The usual yellow brass may contain

not more than 40-50% zinc, often less; copper constitutes the remainder or the predominant phase. Thus brass and bidri represent the two opposite ends of the zinc- copper phase diagram.[4]

1.1 ORIGIN

The origin of Bidriware is usually attributed to the Bahamani sultans who ruled Bidar in the 14th–15th centuries. Bidriware originated in ancient Persia. It was brought to India by the followers of Khwaja Moinuddin Chisti. The art form developed in the kingdom was a mix of Turkey, Persia and Arabic countries which were intermingled with the local styles and thus a unique style of its own was born. Abdullah bin Kaiser, a craftsman from Iran was invited by the Sultan Ahmed Shah Bahmani to work on decorating the royal palaces and courts. Along with local artisans, the art ware spread far and wide and was handed over to generations as time passed. Fortunately, the art did not die with the kings, it was later on patronized by subsequent kingdoms and today, we can enjoy its exclusivity. It is a family business and in some artisans' families, even women take part in the making of the metal ware. Since then, the craft has been handed down succeeding generations mostly among the local Muslim and Lingayat sects.

1.2 MANUFACTURING PROCESS

The materials used to make bidri ware are consistent in all the accounts. It is a cast zinc copper alloy, inlaid with silver and sometimes brass or gold, and its main characteristic is its black patina, which contrasts with the bright polished inlays. Zinc is well known for its malleability and resistance to corrosion. It forms a pale grey/white protective layer, usually of zinc oxide and hydroxide, which reduces the rate of any further corrosion of the surface. The black patina on bidri ware also seems to protect it from unattractive corrosion growths under a range of normal atmospheric conditions. Bidriware is manufactured from an alloy of copper and zinc (in the ratio 1:16) by casting. The zinc content gives the alloy a deep black color.

The first stage is sand casting. The sand casting ‘flask’ is a two-part metal frame that forms the sides of the mould. The two halves of the frame are laid onto boards and rammed full of a mixture of sand and a binder. The surface is scraped flat and dusted with a release agent. A model, also coated with a powder release agent is embedded between the two halves then removed, leaving a hollow impression of the shape required. The two halves are then put back together and the frame is tightly bound together to prevent it slipping during the casting process. The frame is tilted at an angle to allow the molten zinc alloy to be poured into the in gate seen on the front face of the frame, while allowing gases to escape.

The as-cast surface is cleaned by scraping and filing, then it is polished. This finishing process is important to the final result: the as-cast surface of the metal does not take on the decorative patina if the surface casting skin is not removed.

The prepared surface is temporarily coloured by immersion in a copper sulphate[3] solution to obtain a temporary black coating over which designs are etched freehand with the help of a metal stylus. This is then secured in a vise and the craftsman uses small chisels to engrave the design over the freehand etching. Fine wire or flattened strips of pure silver or gold or brass are then carefully hammered into these grooves.

The final stage after the inlay has been burnished, is to blacken the surface of the piece so that the inlay stands out. This is done by applying a paste of ammonium chloride, potassium nitrate, sodium chloride, copper sulphate and mud which darkens the body by producing a characteristic black patina while having no effect on the inlay. The paste is later washed off and finally oil is rubbed into the piece to deepen the blackness of the patina. The result is a lustrous dense black body to contrast with the shining lining white (silver) or yellow (brass or gold). As a finishing touch, oil is applied to the finished product to deepen the matt coating. The finished product appears black with brilliant inlay.

FIGURE 1.2: Steps of Manufacturing of Bidriware craft (1-Melting, 2-Moulding, 3-Pouring, 4-Machining, 5-Pattern Etching, 6-Engraving, 7-Patination, 8-Final product [16]

1.3 BIDRI ALLOY COMPOSITION

They are usually high zinc alloys with between 2 and 10% copper, with the majority between 2 and 5% copper. Lead, tin and iron are sometimes mentioned in the literature, but do not appear consistently and are probably accidental ingredients.

An examination of the copper-zinc equilibrium diagram (figure 1.3) is relevant to the understanding of the bidri alloy. The small amount of copper added to the molten zinc will enter into solid solution to a maximum of about 2.7%, the remainder of the copper forming intermetallic compounds with the zinc.

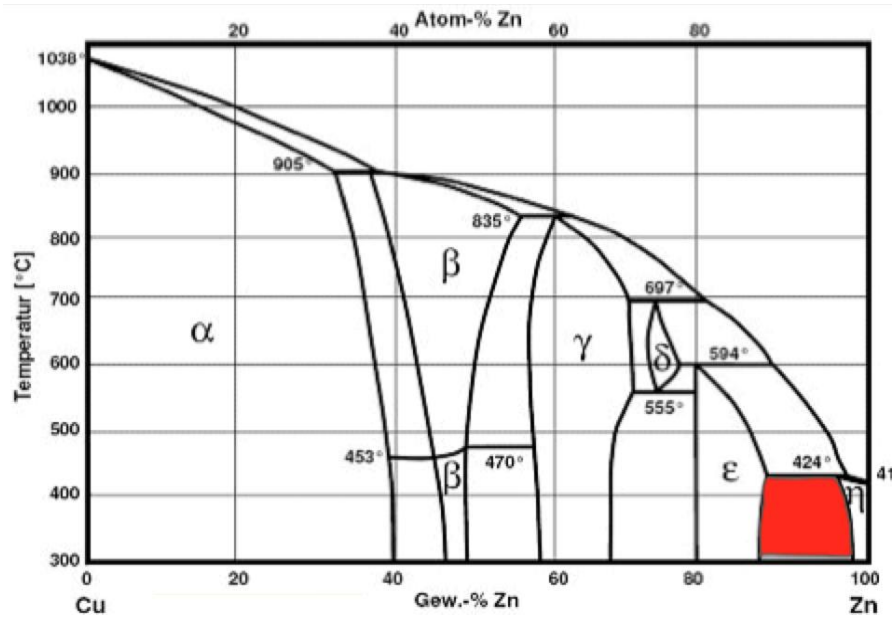


FIGURE 1.3: Zinc Copper Phase Diagram [17]

1.4 ANALYSIS OF POURBAIX DIAGRAM

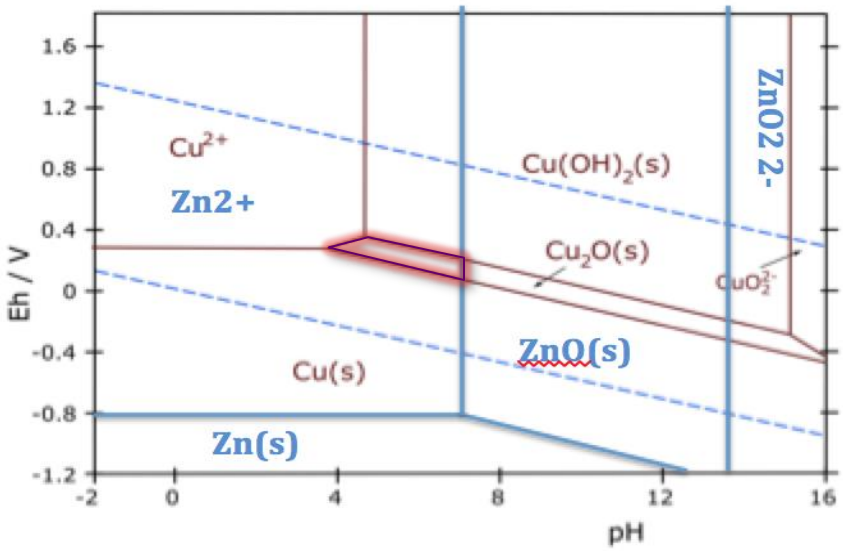


FIGURE 1.4: Pourbaix diagram of copper and zinc [18]

The pourbaix diagram shows that the pH should be between 4-7 as zinc is dissolving and copper is oxidizing. Hence the shaded region is our point of interest for this study.

CHAPTER 2

LITERARY SURVEY

2.1 EXPERIMENTAL REPLICATION

The traditional patination process uses the soil from beneath the mud-brick walls of the fort of Bidar city which is said to have special oxidizing properties. The soil is boiled with ammonium chloride and the products are dipped into the. Almost instantaneously the zinc alloy turns black but the brass inlay is unaffected, even though brass is also an alloy of zinc and copper, but containing more copper than zinc.

The main significance of the soil around the fort used in the traditional recipes is that it is saturated with salts because the walls are commonly used as a latrine. An adequate chemical substitute for the soil is to make a solution of potassium nitrate (1 part), ammonium chloride (4 parts). The temperature of the solution is said to have a marked effect on the rate at which zinc and zinc alloys react and perhaps more importantly for the production of a decorative patina, the form and adherence of the corrosion layer.

In the replication experiment a clean pure zinc sheet was immersed in the above solution, when a pale grey patina of zinc oxide and chloride was produced. When the experiment was repeated with the addition of copper sulphate, a reasonably good but superficial black patina formed almost instantaneously. Again only zinc oxide and chloride were the main crystalline products. XRD analysis identified $Zn_5(OH)_8$ Cl_2, ZnO and Cu_2O (cuprite) as the crystalline phases. None of these explains the blackness of the patina which was amorphous and contained copper.

Similar experiments were performed with a specially prepared alloy of zinc containing 4% copper. When this alloy was dipped in a warm solution of potassium nitrate and ammonium chloride, it turned as deep black instantly and the patina was even and adhered well to the metal surface.

2.2 ANALYSIS

La niece and Martin have postulated that ammonium chloride preferentially dissolves the zinc from bidri and the resulting copper-enriched surface or the copper-rich phase precipitate gets oxidised by potassium nitrate producing the black colour. The use of clay does not seem to be crucially important. It could merely serve as a source of alkali nitrate and as a poultice to absorb the unwanted zinc chloride formed during the process.

The two main methods of examination and analysis used in this study were Debye Scherrer Powder X-ray diffraction (XRD) using the standard ICDD database for crystallographic pattern matching, and Field Emission Scanning Electron Microscope (FE-SEM) operated at 20 kV to provide high resolution images of the patina structure.

XRD analysis of samples of the black patina taken from these experimental pieces and from historic bidri items identified the three main crystalline components of all the object and experimental patinas analysed:-

Simonkolleite, zinc hydroxychloride ($Zn_5(OH)_8\ Cl_2$)

Zincite, zinc oxide (ZnO)

Cuprite, copper I oxide (Cu_2O)

The two zinc compounds identified are white in colour and cuprite appears reddish, so these results do not directly explain the black colouration of the patina. The copper II oxide *tenorite* (CuO) does appear black, and had been expected to be present, but it was only rarely found in the patina, along with other occasional finds of silver chloride and lead compounds.

To provide more information, the experimental patina was examined using FE SEM-EDX.

The depth of the patina was measured in cross- section using the SEM and found to be only of the order of three to ten micrometres thick. The areas of the patina analysed by

EDX. The alloy composition of the unpatinated surface is approximately 4% copper and 96% zinc. In the patinated area the dendrites were found to contain 12-30% copper and the interdendritic phase 2-5% copper.

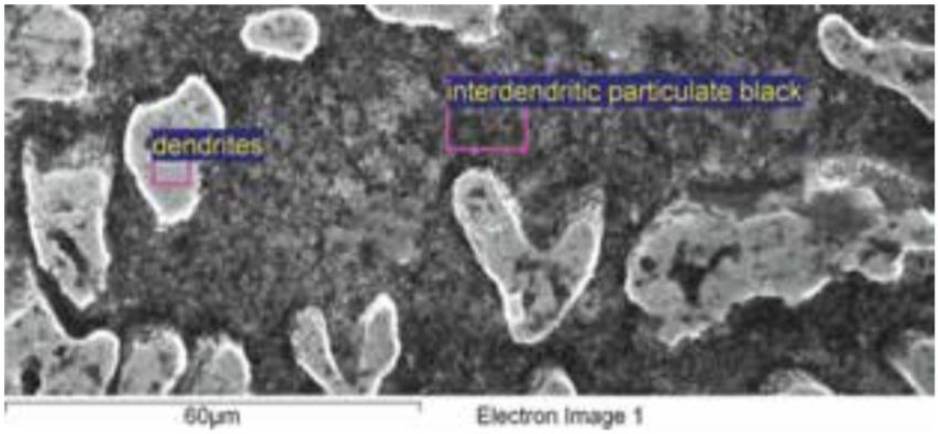


FIGURE 2.1:- SEM secondary electron image showing the dendrites and interdendritic zone in the patinated surface. the areas analysed and reported in table 1.1 are marked. [2]

TABLE 1.1:- Bidri Semi-quantitative Analysis

Area analysed	**Cu wt%**	**Zn wt%**	**Cl wt%**
Unpatinated metal	4	96	trace
Patina in interdendritic zone	5	80	15
Patina on dendrite	28	71	1

FIGURE 2.2:- SEM secondary electron image of a part-patinated piece of experimental bidri alloy. [3]

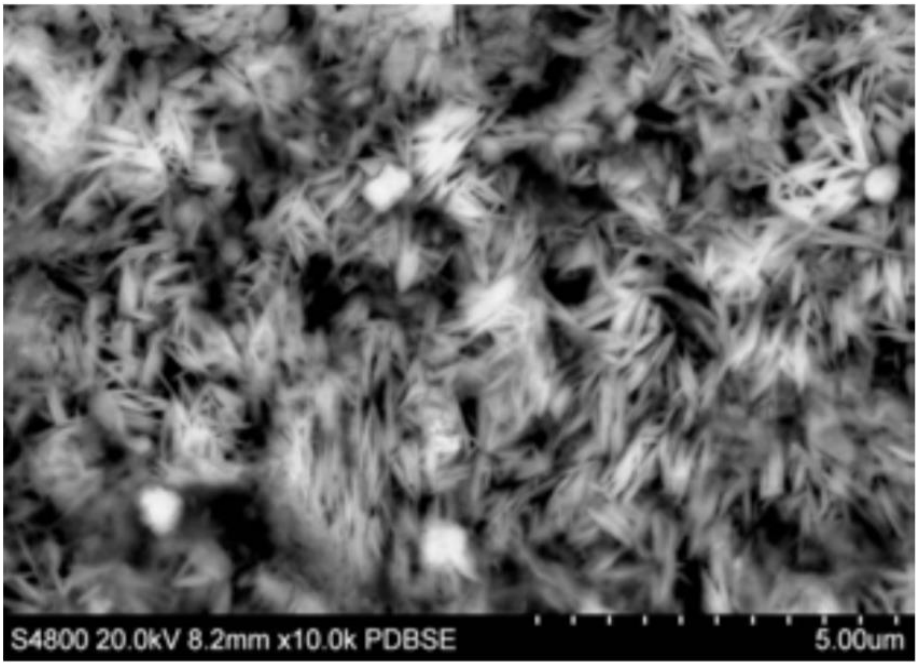


FIGURE 2.3: SEM back scattered electron image of the patina particles in the interdendritric area, taken at 10,000 times magnification showing their fine loosely packed, acicular structure. [3]

CHAPTER 3

OBJECTIVES AND METHODOLOGY

3.1 OBJECTIVES

The bidar fort sand is used for formation of black patina. But artisans now do not have access to the sand which poses a challenge to follow the tradition. Hence the objectives of the present work are as follow.

i. To find a viable chemical substitute.
ii. To understand the process in detail.
iii. Surface morphological comparison of conventional Bidri works and the one using alternate method.

3.2 METHODOLOGY

For the first part all the available literature was looked up following which the experiments mentioned in the literature were repeated. Certain parameters were also tweaked to find the best alternative.

The second part was performing electrochemical characterization of the alloy in a synthetic solution making use of a modified setup. Each characterization was performed twice for the sake of repeatability. The corrosion rate in the alternate chemical is studied by weight loss.

Finally the results of the alternative method are compared with the actual bidri sample by using various surface and morhological characterization techniques such as SEM, FTIR.

CHAPTER 4

EXPERIMENTAL DETAILS

The Chapter describes the experimental procedure carried out and also outlines the procedure for surface, structural, and electrochemical characterization techniques used in the present work.

4.1 SAMPLE PREPERATION

4.1.1 Casting

Castings of the specimens were carried out in the foundry workshop by taking Zinc 95% and copper 5%. The mixture was heated in a furnace to 1200^{o}C (Melting pint of copper is 1083^{o}C, Zinc is 420^{o}C) and then poured into a cylindrical mould and were allowed to cool. Upon cooling, the as cast material is cut into discs 5mm diameter. The as casted sample rod is sliced with about 3mm thickness using Electrical discharge machining (EDM) cutting.

4.1.2 Surface Preparation

The surfaces were polished using emory paper of varying grit sizes followed by diamond polishing, the following table provides the stages of the polishing as carried out in the Physical Metallurgical Laboratory (PML). Wet polishing was not suitable as it oxidizes the metal surface and forms grey oxide which hinders the patination process

TABLE 4.1: Sample polishing details

Stage	Abrasive	Lubricant
Fine Grinding	120, 400, 600, 800, 1000.	Nil
Final Polishing	6 to 0.5 micron diamond paste	Aerosol spray

4.2 SOLUTION PREPARATION

In normal practice the artisans use a sand and ammonium chloride mixture. This is heated to approximately 80^{o}C following which the sample is dipped in it. The sand is rich in nitrate due to there being a latrine nearby. As an alternative potassium nitrate was used with ammonium chloride instead of Bidri Sand, As per literature the nitrate content is believed to promote the patination process.

4.3 REPLICATION EXPERIMENTS

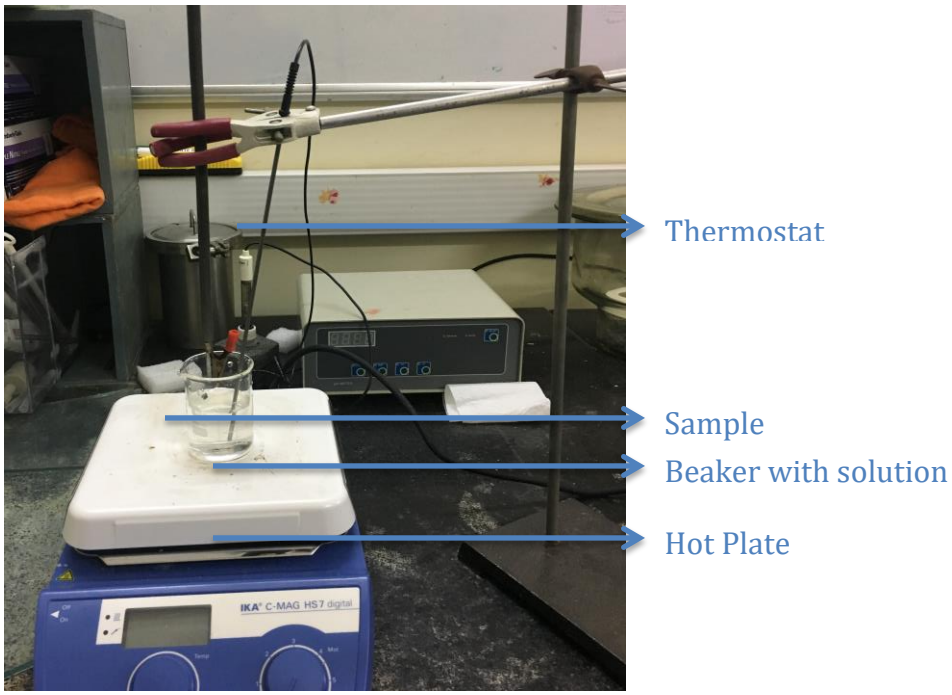


FIGURE 4.1:- Experimental Setup for the Patination Process

4.3.1 Sample dipped in Bidri sand solution.

The cast specimen was tested using the Bidri sand and Ammonium Chloride and replicated the process just same as that of the Bridri artefact in the laboratory for reference purposes and other surface characterization studies like SEM and XRD.

4.3.2 Alternative Process-1

The replication experiment includes the following chemicals and process.

i. Potassium nitrate (KNO_3) – 5g.
ii. Ammonium chloride (NH_4Cl) – 20g.
iii. De-ionised water (H_2O) – 100mL.
iv. Heating the chemical mixture above 80°C and dipping it for 2 minutes at least
v. Apply oil (coconut oil was used) after the removal and allow it to dry for minimum 24 hours.

4.3.3 Alternative Process-2

This includes the use of sand (SiO_2) to mimic the role played by sand in conventional techniques.

i. Potassium nitrate (KNO_3) – 5g.
ii. Ammonium chloride (NH_4Cl) – 20g.
iii. De-ionised water (H_2O) – 100mL.
iv. Silicon oxide (SiO_2) – 15g.
v. Rotate the mixture for 500 rpm with sand (silica) particle size of 0.1 to 0.3 mm.
vi. Heating the chemical mixture above 70°C and dipping it for 2 minutes at least
vii. Apply oil (coconut oil was used) after the removal and allow it to dry for minimum 24 hours.

4.3.4 Alternative Process-3

This process involves copper deposition prio to exposure in identified solution.

i. Potassium nitrate (KNO_3) – 5g.
ii. Ammonium chloride (NH_4Cl) – 20g.
iii. De-ionised water (H_2O) – 100mL.
iv. Dip in the cupric sulphate solution ($CuSO_4$) for 2 minutes before dipping prescribed chemicals.
v. Heating the chemical mixture above 70°C and dipping it for 2 minutes at least

vi. Apply oil (coconut oil was used) after the removal and allow it to dry for minimum 24 hours.

4.3.5 Alternative Process-4

This process was to identify the optimal time of delay to attain smooth surface.

i. Potassium nitrate (KNO_3) – 5g.
ii. Ammonium chloride (NH_4Cl) – 20g.
iii. De-ionised water (H_2O) – 100mL.
iv. Heating the chemical mixture above 80°C and dipping it for 24 seconds(This time is inferred by trial and error).
v. Apply oil (coconut oil was used) after the removal and allow it to dry for minimum 24 hours.

4.3.6 Nitrate Content Effect

A solution with 100mL water and 20g Ammonium chloride was made and kept at 80^oC. 0.5g Potassium Nitrate was added step by step and the patination was done at each step.

4.4 SURFACE CHARACTERIZATION

4.4.1 X-ray Diffraction

The atomic plane of the crystal cause an incident beam of x-rays to interfere with each other as they leave the crystal. The phenomenon is called x-ray diffraction which is essentially a scattering phenomenon

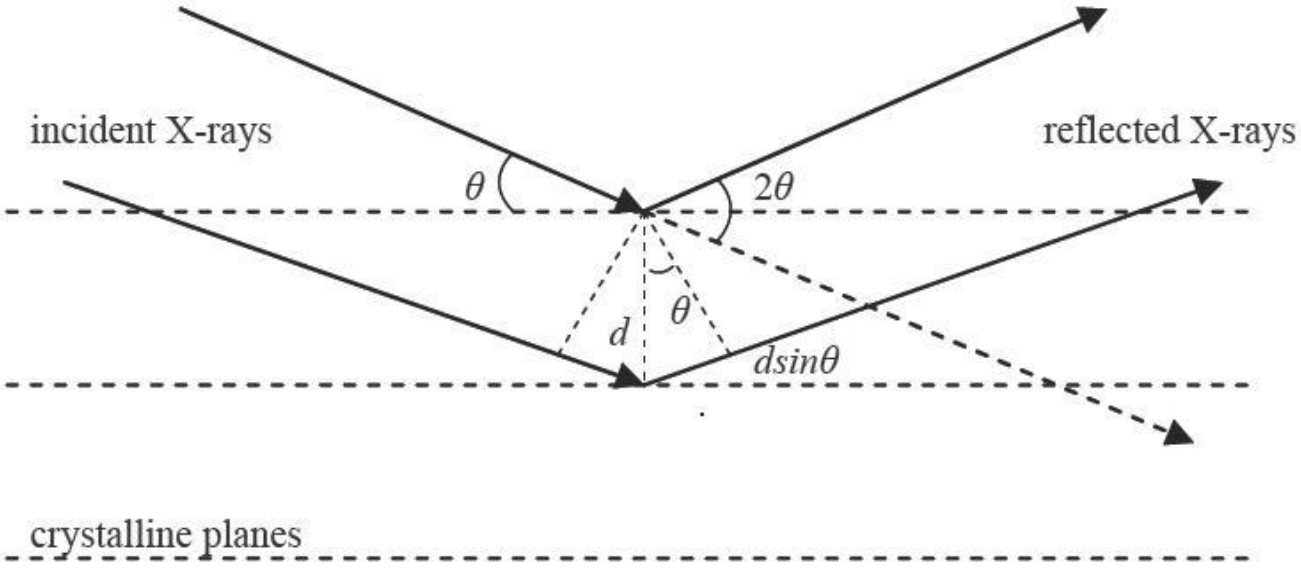


FIGURE 4.2:- Braggs Law – Diffraction if X-ray in single crystals. [19]

Figure above shows diffraction of x-rays by a crystal where there is a path difference between ray 1 and ray 2 = 2d'sinθ. Bragg's law states the condition at which diffraction is to occur

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

where, n is the order of reflection, d' is the spacing of the planes, θ is the angle between the incident beam and particular crystal planes under consideration and λ is the wavelength of monochromatic x-rays. Since sinθ cannont be greater than 1,

$$\frac{n\lambda}{2d'} = sin\theta < 1$$

which can also be written as

$$\lambda = \frac{2d'}{n} sin\theta$$

As the coefficient of λ is now unity, a reflection of any order can be considered as first order reflections spaced at a distance of $1/n$, which helps in using $d = d'/n$, and hence the below formula can be used

$$n\lambda = 2dsin\theta$$

In this study, XRD measurements were carried out using the patinated samples. XRD (X'Pert PRO, PANalytical) was carried out using an Cu K_α radiation (λ=1.54 Å), TUBE VOLTAGE OF 30KV, IN THE 2θ range of 5^o/min. Analysis of X-ray diffractogram was carried out by using PANalytical X'pert HighScore Plus software.

4.4.2 Scanning Electron Microscope

SEM produces an image by using an electron beam which scans the surface of a specimen inside a vacuum chamber. The SEM uses electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by heating of the filament. The electron beam follows a vertical path through the column of the microscope. It passes through electromagnetic lenses which focus and direct the beam down towards the sample. The incident electron beam is scattered in the sample, both elastically and inelastically which gives rise to various signals that can be detected.

Once the beam hits the sample, the back scattered or secondary electrons eject from the sample. Detectors collect these electrons and convert them to a signal that is sent to a viewing screen which is a cathode ray tube monitor, producing an image

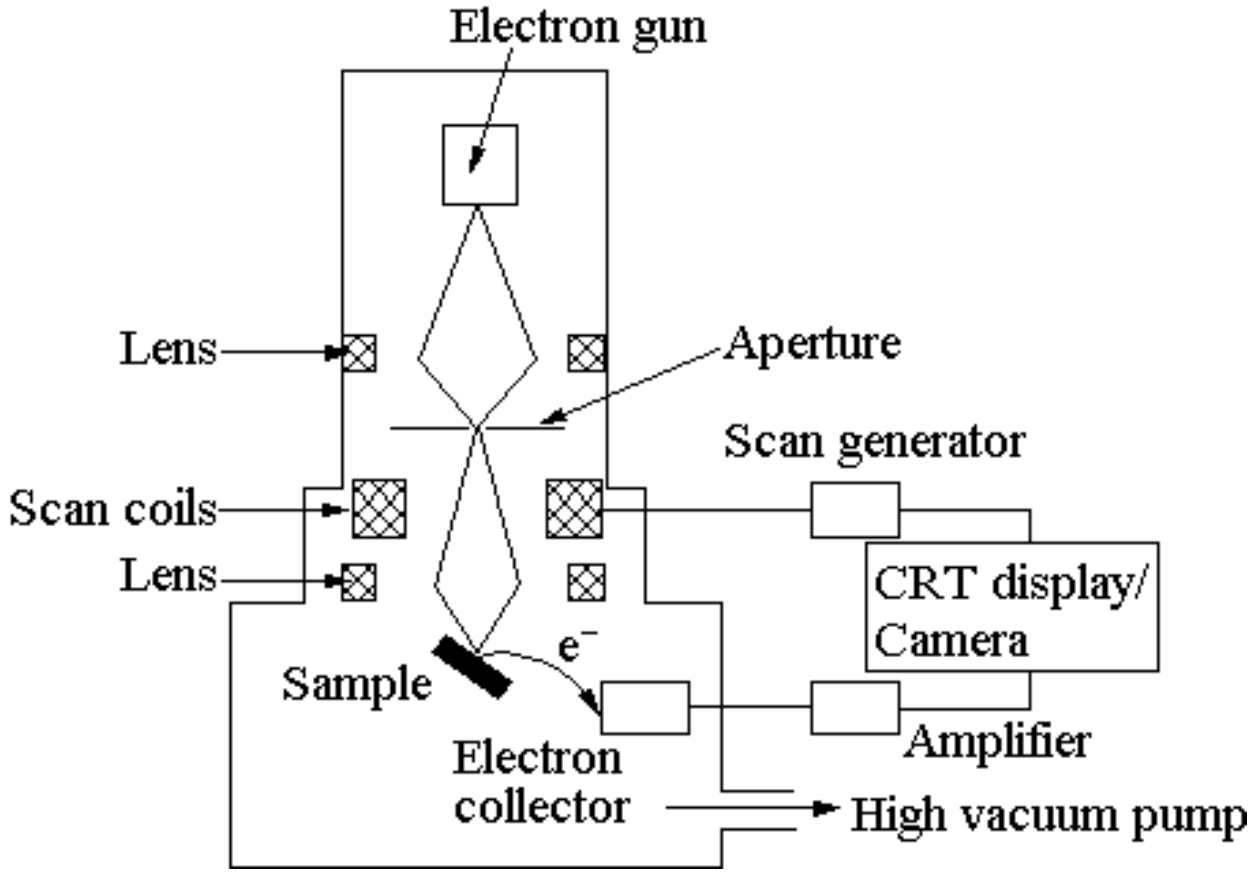


FIGURE 4.3:- Schematic of SEM [20]

Interaction volume increases with increasing acceleration voltage and decreases with increasing atomic number. Backscattered electrons gives the contrast due to difference in the atomic number of materials in the specimen and the secondary electron (SE) detector gives the contrast due to topography of the specimen. Secondary electrons are generated from the collision between the incoming electrons and the loosely bonded outer electrons. They are low electrons (10-50 eV) and the secondary electrons are generated from the close to surface of the specimen giving the details about the surface topography.

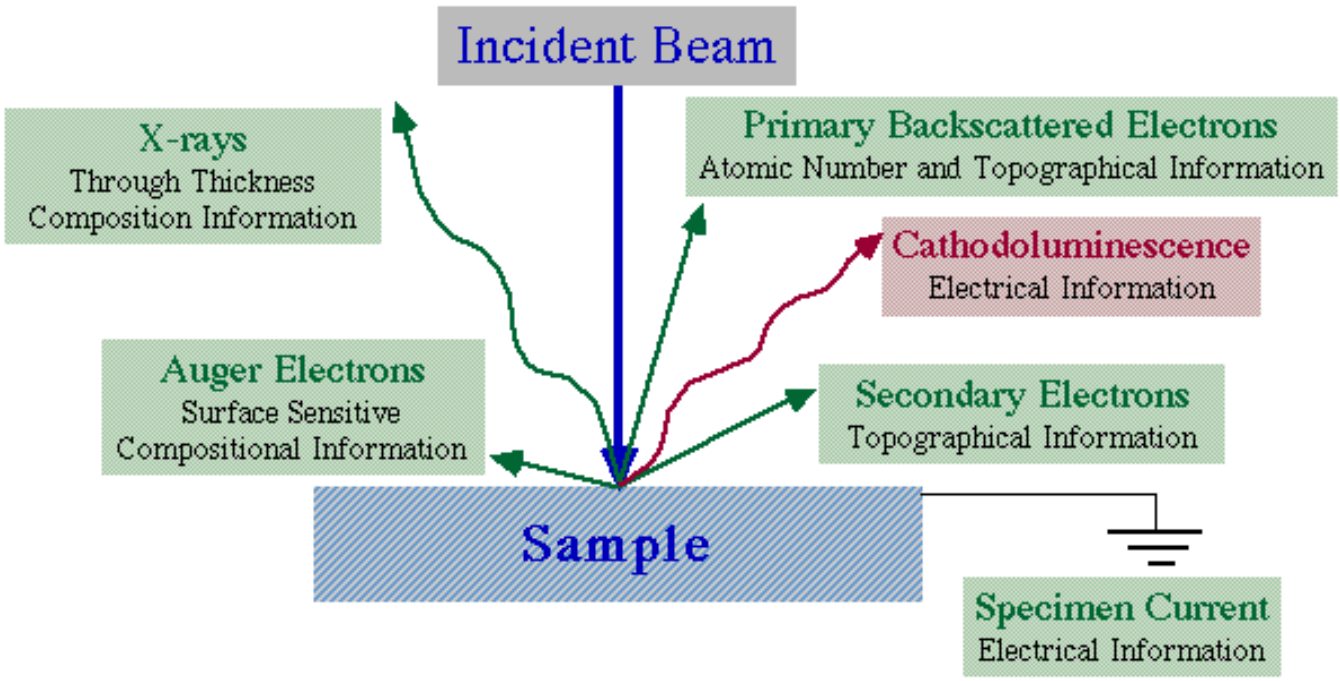


FIGURE 4.4:- Different emission from sample surface using SEM [20]

Backscattered electrons possess more energy than secondary electrons, and have a definite direction, As such, they cannot be collected bt a SE detector unless the detector is directly is their path of travel. All emission above 50 eV are considered to be backscattered electrons.

Energy dispersive X-ray Spectroscopy (EDAX) analysis is useful in identifying materials, as well as estimating their relative concentrations on the surface of the specimen. Based on the energy values, the element can be identified is a given sample. The intensity of the signal provides an idea about the elemental composition.

In this study, the microstructure of the patinated samples were examined using SEM (Inspect F). EDAX fitted to SEM was used to analyze the elemental composition of the as cast specimen. All the samples were examined with an accelerating voltage of 30 kV and a working distance of 10mm.

4.4.3 Fourier Transform Infrared Spectroscopy

When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum representing a molecular 'fingerprint' of the sample. The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints.

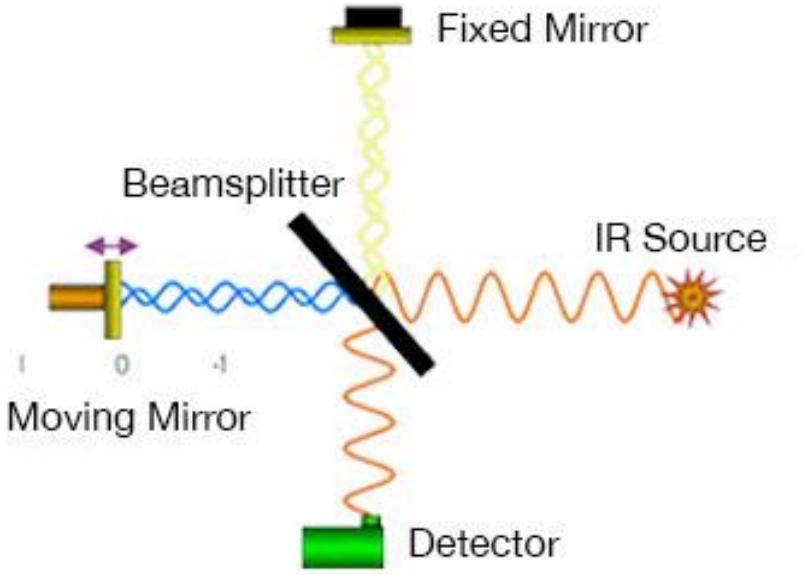


FIGURE 4.5:- Schematic of FTIR [21]

The FTIR uses interferometry to record information about a material placed in the IR beam. The Fourier Transform results in spectra that analysts can use to identify or quantify the material.

FTIR can be a single purpose tool or a highly flexible research instrument. With the FTIR configured to use a specific sampling device – transmission or ATR for instance – the spectrometer can provide a wide range of information:

- Most commonly, the identification of an unknown
- Quantitative information, such as additives or contaminants
- Kinetic information through the growth or decay of infrared absorptions
- Or more complex information when coupled with other devices such as TGA, GC or Rheometry.

4.5 WEIGHT LOSS EXPERIMENT

4 samples were metallographically prepared and placed in a solution containing aq. KNO_3 and NH_4Cl (1:4) kept at 80^oC for 5, 10, 15 and 20 minutes respectively. The initial and final weights were recorded. The change of weight was calculated as a function of exposure time and plotted on a graph.The slope of this graph gives the rate of weight loss from which we can calculate rate of reaction.

$$W = \frac{Eq.Wt \times i \times t}{96500}$$

where W is rate of weight loss per unit area, i is rate of reaction in Amperes, t is time in seconds.

This rate of reaction calculated by the weight loss method was compared with the one deduced using the potentiodynamic polarization method.

4.6 ELECTROCHEMICAL CHARACTERIZATION

There is literally no information on the electrochemical parameters during the patination process. Apart from identifying alternate chemicals for patination, the aim of this work is to understand the electrochemical processes by measuring the potential changes and the corrosion rate of the system.

4.5.1 Setup Modifications

In order to measure the potential, a reference electrode has to be used. This becomes an issue as the solution is at 80^oC and we cannot normally use a reference electrode as it will get damaged at such high temperatures. In order to overcome this, a simple system was established. A salt bridge using filter paper was created so that the reference electrode need not be inserted into the hot electrode. The figure6.6 shows the paragraph of such an arrangement.

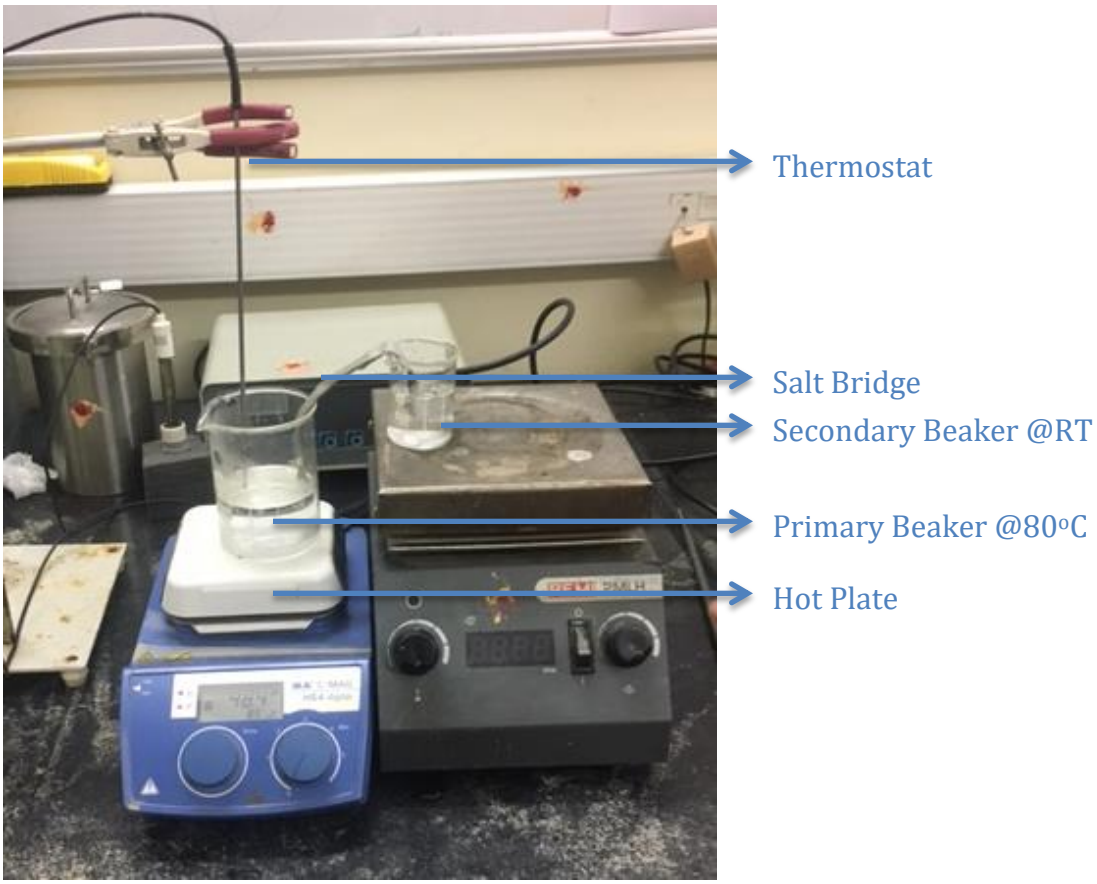


FIGURE 4.6:- Modified Setup for Electrochemical Parameter Measurement

4.5.2 Open Circuit Potential (OCP) Transient

OCP transient ere recorded by dipping the specimen into the electrolyte of aq. KNO_3 and NH_4Cl (1:4) kept at 80^oC. The potential was recorded using a Bio-Logic potentiostat in DC mode for a till a constant potential is achieved.

4.5.3 Potentiodynamic Polarization

The Potentiodyanamic polarization tests were carried out in a 3 electrode cell by sweeping the potential from -0.9 V to 0.2 V at a scan rate of 1 mVs^{-1}.

4.7 LIST OF CHEMICALS USED

TABLE 4.1:- List of chemicals used and their Manufacturer's details

Chemicals	**Formula**	**Company**
Ammonium Chloride	NH_4Cl	Rankem
Potassium Nitrate	KNO_3	HiMedia
Artificial Sand	SiO_2	-
Ferric oxide	Fe_2O_3	HiMedia
Calcium carbonate	$CaCO_3$	Rankem
Cupric Sulp8hate	$CuSO_4$	Rankem
Sodium hydroxide	NaOH	Rankem

CHAPTER 5

RESULTS AND DISCUSSION

5.1 REPLICATION EXPERIMENT AND ALTERNATE PROCESSES

The aim of the experiment was to find an alternative to Bidri sand. The first step was to replicate the process using bidri sand and the parameters used by Bidri craftman following which surface and morphological charecterizations were carried out. These result were compared with the results achieved using alternate parameters to find a suitable alternative.

5.1.1 Sample dipped in Bidri sand solution.

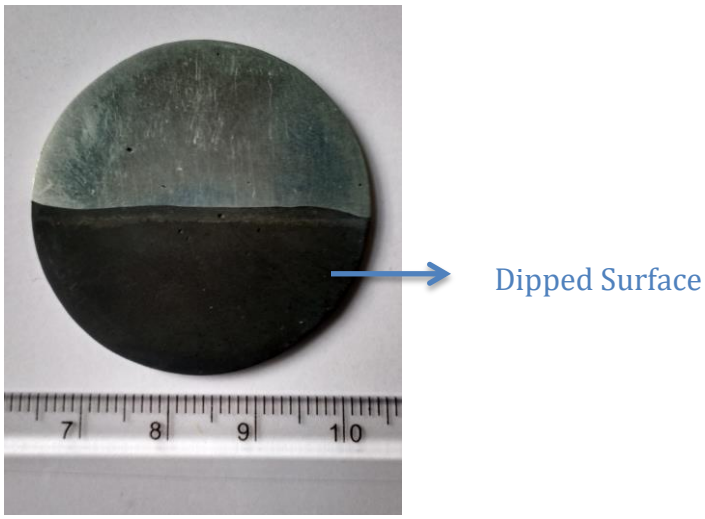


FIGURE 5.1:- Specimen subjected to Bidri sand and ammonium chloride solution.

The as cast specimen was treated by diping it using the Bidri sand and Ammonium Chloride. This was done for reference purposes, so the modified replications can be compared. The resulting morphology and phases can be compared.

The ammonium chloride which is added helps in dissolving Zinc as zinc is more reactive then hydrogen.

$$Zn = Zn^{2+} + 2e^{-1}$$

Zinc is getting depleated and copper is getting enriched on the surface. The sand is rich in nitrates which oxidizes copper to CuO and Cu_2O as seen in the equations below. This gives the black patination to the surface.

$$Cu + 2e^- = Cu^{2+}$$

$$Cu + e^- = Cu^{1+}$$

Various surface characterization techniques were used which form a basis for comparison. The XRD below shows the peaks of all the phases present

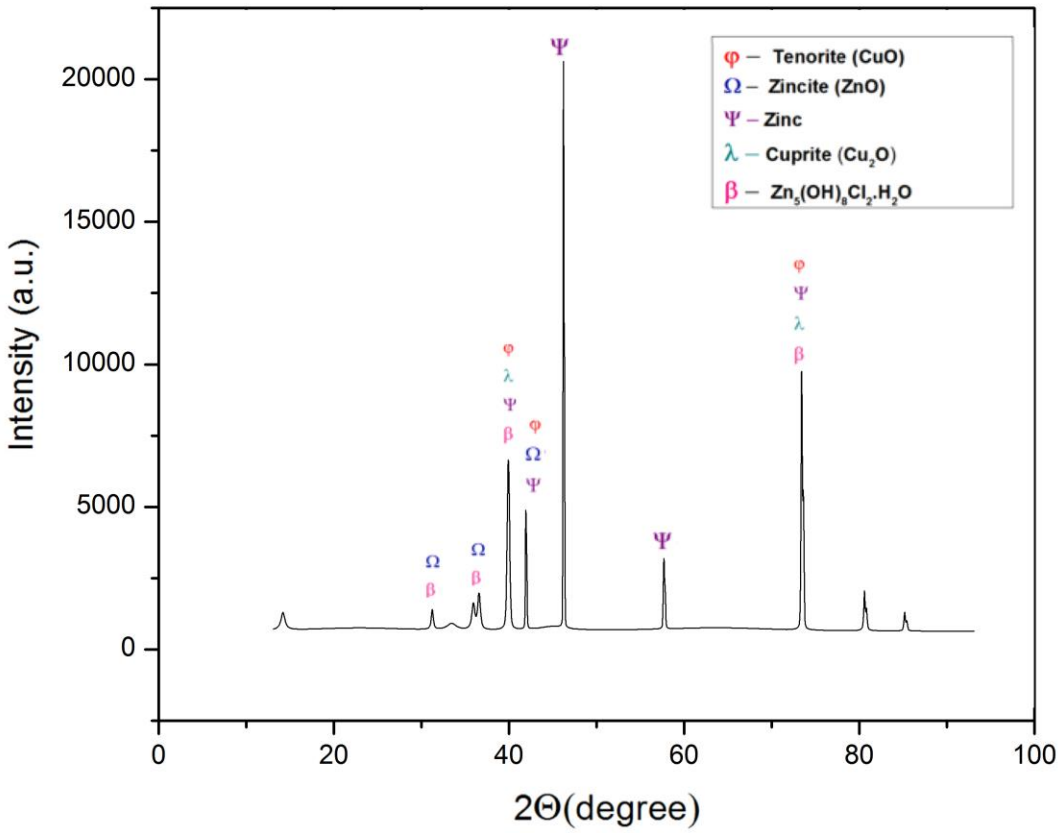


FIGURE 5.2: XRD of surface treated with Bidri Sand

The EDAX spectroscopy was also performed on the base metal and patinated region. As seen from the results below it is confirmed that the copper content is increaing and zinc content is reducing. The EBS imaging was also done using INSPECT F.

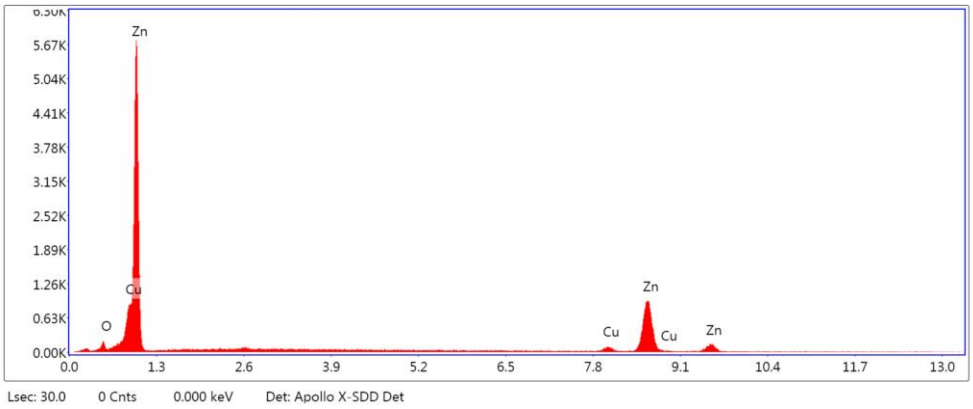


FIGURE 5.3: EDAX of surface of base metal.

TABLE 5.1

Element	Wt %
O K	3.54
CuK	4.94
ZnK	91.52

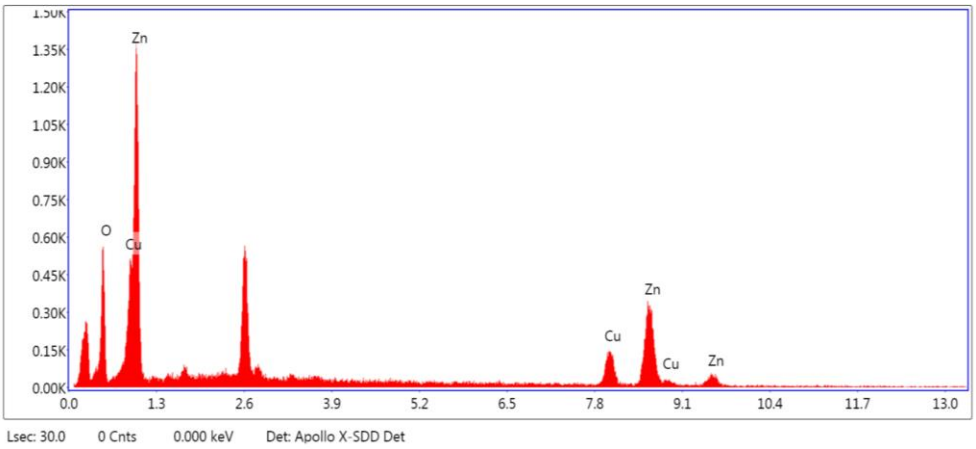
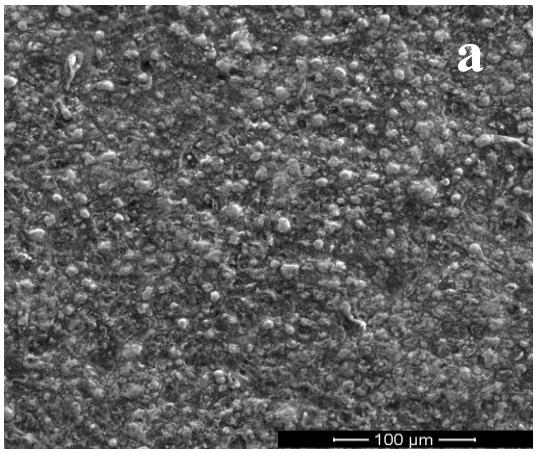
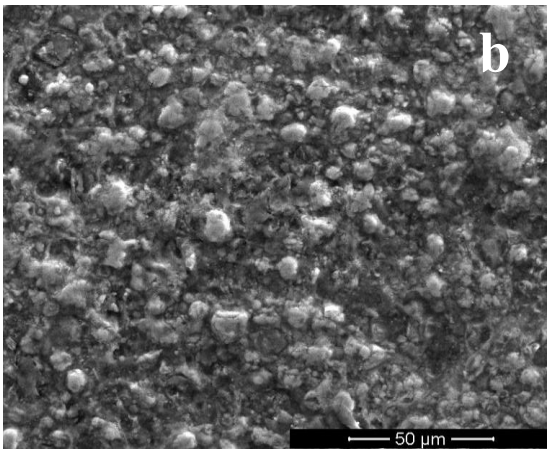


FIGURE 5.4: EDAX of surface treated with Bidri Sand

TABLE 5.2

Element	Wt %
O K	21.86
CuK	17.28
ZnK	60.86





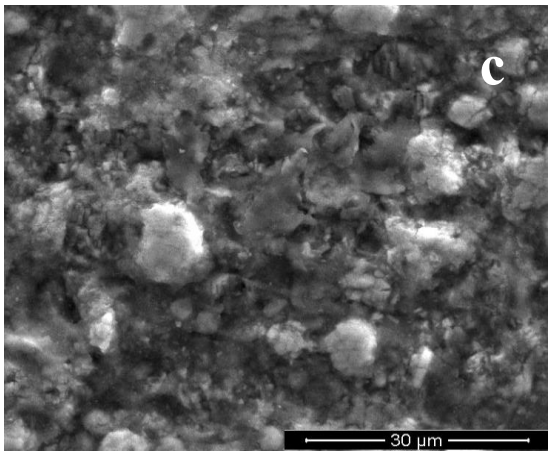


FIGURE 5.5: SEM of surface treated with Bidri Sand
a. 100 µm, b. 50 µm, c. 30 µm

We then try various alternate parameters to find best suitable technique

5.1.2. Alternate process-1

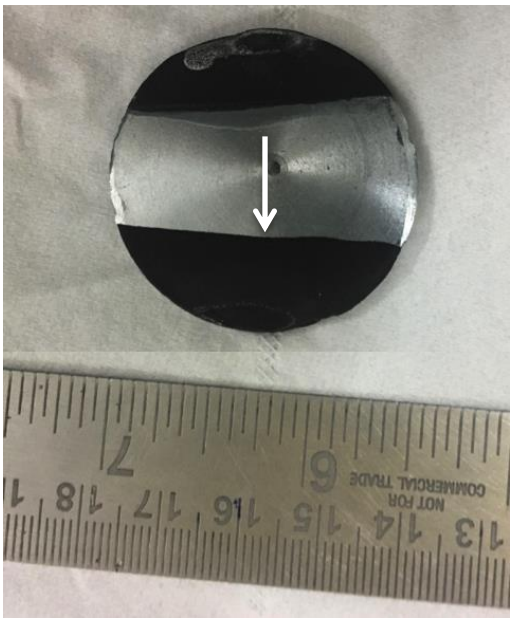


FIGURE 5.6:- Specimen subjected to alternative process-1 solution that contains 1:4 weight ratio of KNO_3 and NH_4Cl in De-ionised water.

The first option was to replicate the experiment given in literature. 5g of potassium nitrate (KNO_3), 20g of ammonium chloride (NH_4Cl) was dissolved in 100 ml of de-ionised water (H_2O). The mixture was heated to 80°C and the specimen was dipped for 2 minutes in the solution, further oil was applied oil and allowed to dry for minimum 24 hours.

This process gave the patination as shown in the figure, the amount of potassium nitrate caused the patination on the copper to get oxidized, and the zinc was dissolved preferentially due to the presence of ammonium chloride. The patination obtained was rough. The reason for this is the Zinc which is dissolving from the surface causes a lot of porosity and hence we obtain a rough surface which is unwanted.

The SEM micrograph was done using INSPECT F and are shown below.

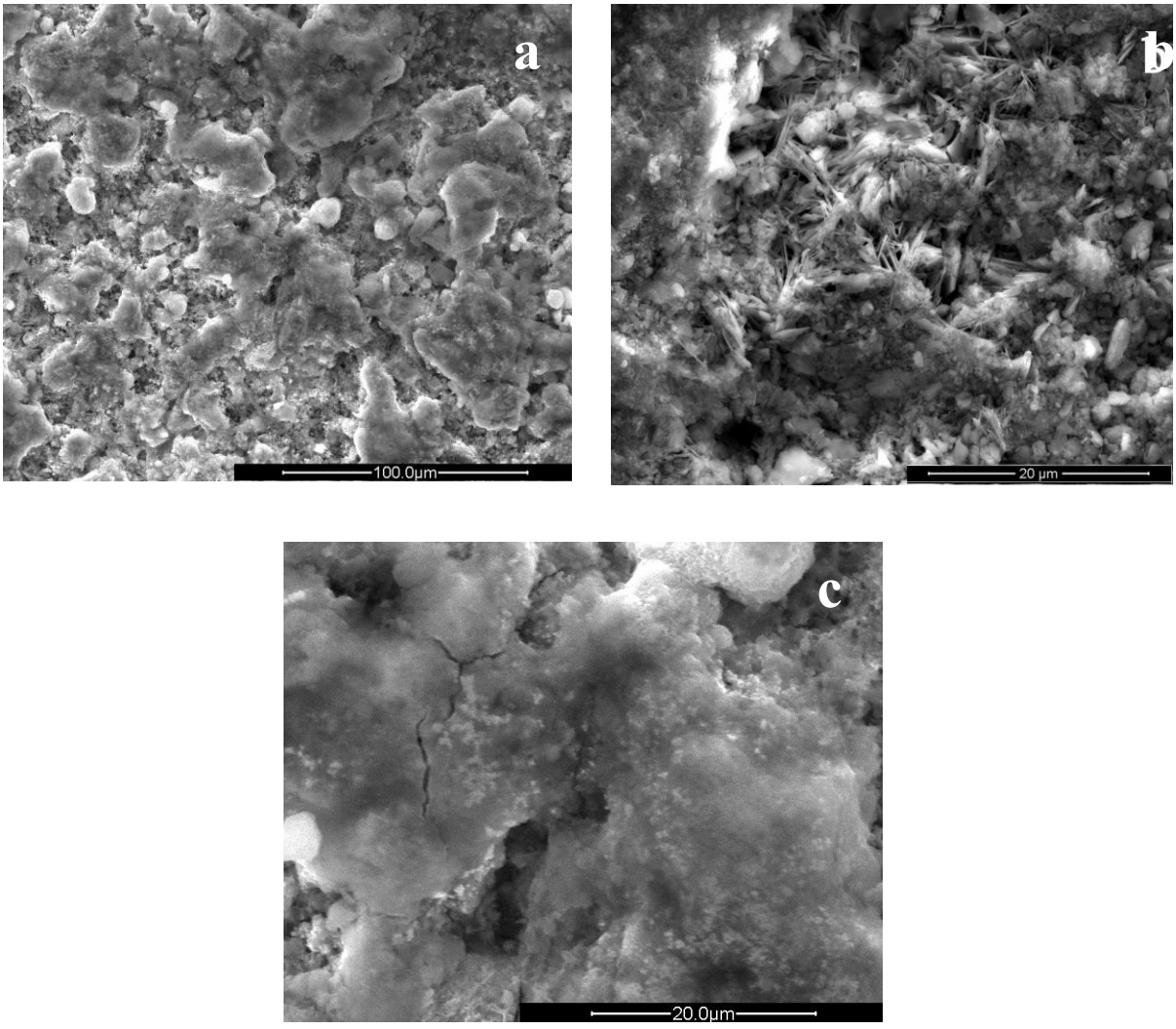


FIGURE 5.7: SEM of surface treated with Alternate Process-1
a. 100 µm, b. 30 µm, c. 20 µm

5.1.3 Alternate process-2

To mimic the effect of sand which was used in the process we add silica and stir it @ 500 RPM. The replication experiment included the following chemicals and process and modified in laboratory – 5g of potassium nitrate (KNO_3), 20g of ammonium chloride (NH_4Cl), 100 ml of de-ionised water (H_2O) 15g of silicon oxide (silica) particle size of 0.1 to 0.3 mm. The chemical mixture was heated to 80°C and specimen was dipped in it for 2 minutes, further oil was after removing it from the solution and allowed to dry for minimum 24 hours. The final product was as seen below. A very rough surface with pits were obtained which does not satisfy our requirement.

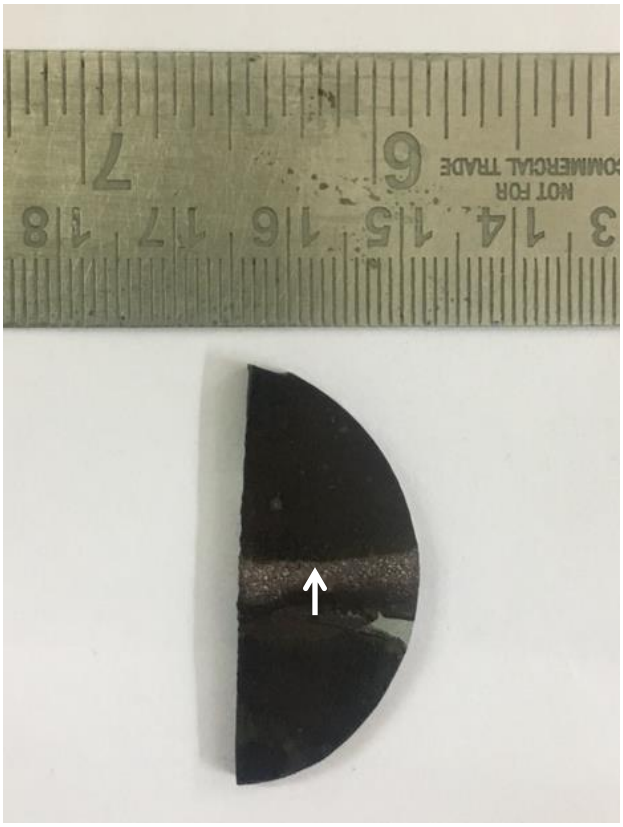


FIGURE 5.8: Specimen subjected to alternative process-2 solution that contains 1:4 weight ratio of KNO_3 and NH_4Cl, in De-ionised water (stirred with silica SiO_2).

5.1.4 Alternate process-3

Bidri craft artisans dip the surface in $CuSO_4$ before etching the design on the sample. Dipping the sample in the solution causes the enrichment of the surface with copper and also provides a dark surface which makes it easier to etch the design. This process was replicated.

The replication experiment included the following chemicals and process in laboratory – 5g of potassium nitrate (KNO_3), 20g of ammonium chloride (NH_4Cl), 100 ml of de-ionised water (H_2O), dip in the cupric sulphate ($CuSO_4$) solution which is mixed with 15.9g in 100 ml de-ionised water, for 2 minutes before dipping. The chemical mixture was heated to 80°C and specimen was dipped in it for 2 minutes, further oil was after the removing it and allowed to dry for minimum 24 hours.

The pre-treatment with cupric sulphate solution ($CuSO_4$) made the surface black in colour, but it was only temporary, the specimen was subjected to the solution to attain the stable patina. The black colour patination was uneven on the surfaces of the specimens. Hence this process is also not feasible.

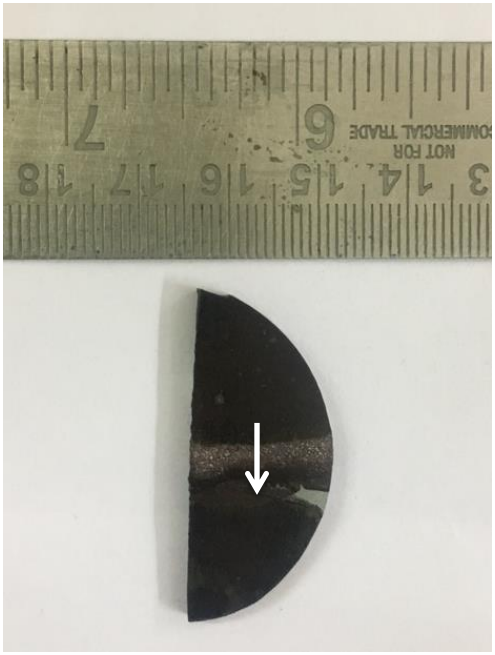


FIGURE 5.9: Specimen subjected to alternative process-3 solution that contains 1:4 weight ratio of KNO_3 and NH_4Cl in de-ionised water and also it is pre-dipped in CuSO4 solution.

5.1.5 Alternate process-4

The best results we had achieved was by using alternate process 1. The colour was pretty much similar though it was much more rougher as compared to the actual Bidri Sample. The roughness is mainly due the excess dissolution of zinc. To prevent this the sample was dipped for a much lesser time. The replication experiment included the following chemicals and process – 5g of potassium nitrate (KNO_3), 20g of ammonium chloride (NH_4Cl), 100 ml of de-ionized water (H_2O). The chemical mixture was heated to 80°C and within no time the specimen was dipped for 24 seconds in the solution, further was applied after removing it from the solution and allowed to dry for minimum 24 hours.
This process gives the patination as shown in the figure, the amount of potassium nitrate causes the patination on the copper to get oxidized, and the zinc is dissolved preferentially due to the presence of ammonium chloride.

This gives an outcome which is similar to that of Bidri sand both in terms of colour and roughness.

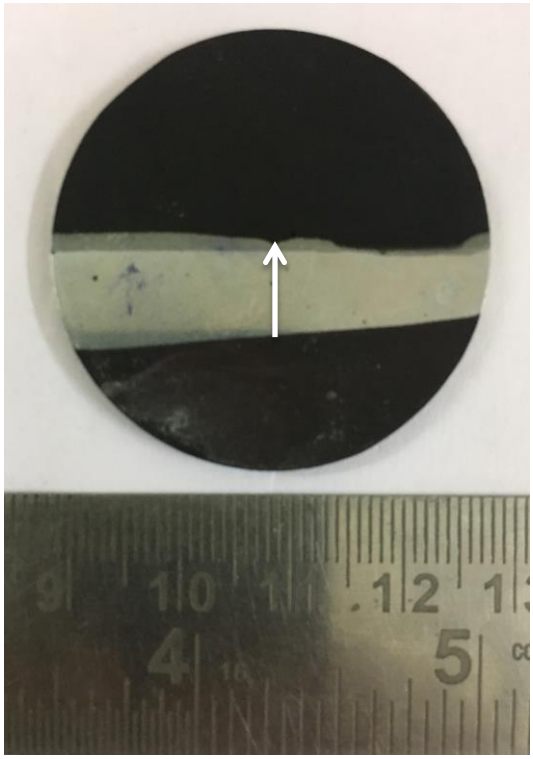


FIGURE 5.10: Specimen subjected to alternative process-4 solution that contains 1:4 weight ratio of KNO_3 and NH_4Cl in De-ionized water for 24 seconds

The XRD below shows the phases present in the patinated region. As the peaks are almost in the same postion and of the same intensity as compared to that of the sample trated with Bidri sand, it could be concluded that the phases are similar in both cases.

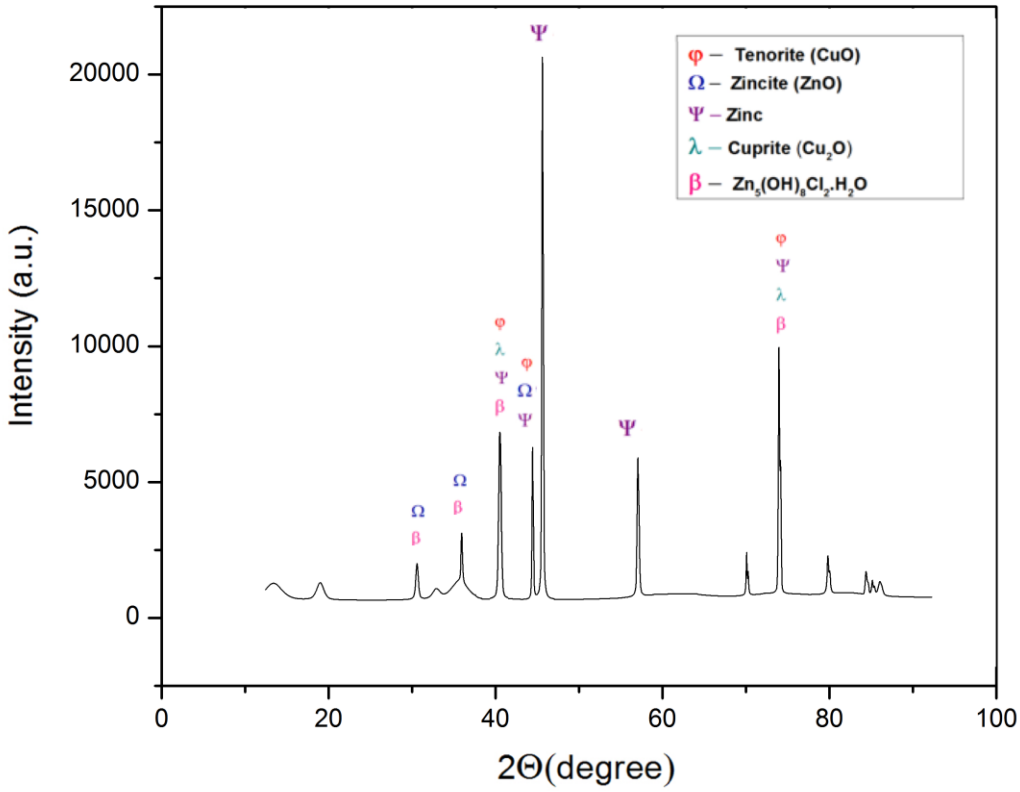


FIGURE 5.11: XRD of surface treated with Alternate Process-4

The EDAX and SEM imaging were also performed. The EDAX results below show that the elemental composition is similar to that of the Bidri sand treated sample.

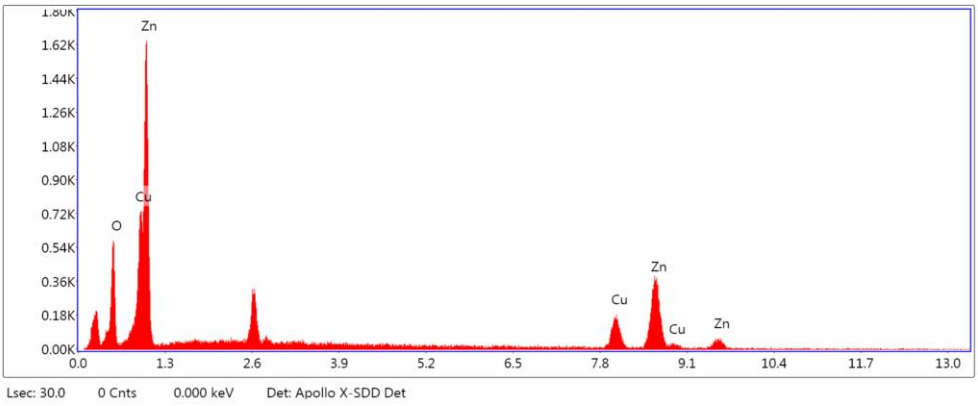


FIGURE 5.12: EDAX of surface treated with Alternate Process-4

TABLE 5.3

Element	Wt %
O K	20.52
CuK	18.91
ZnK	60.57

The SEM images shown below are also very similar to that of the Bidri sand treated sample. We can hence conclude that Alternate process 4 provides us with the best alternative.

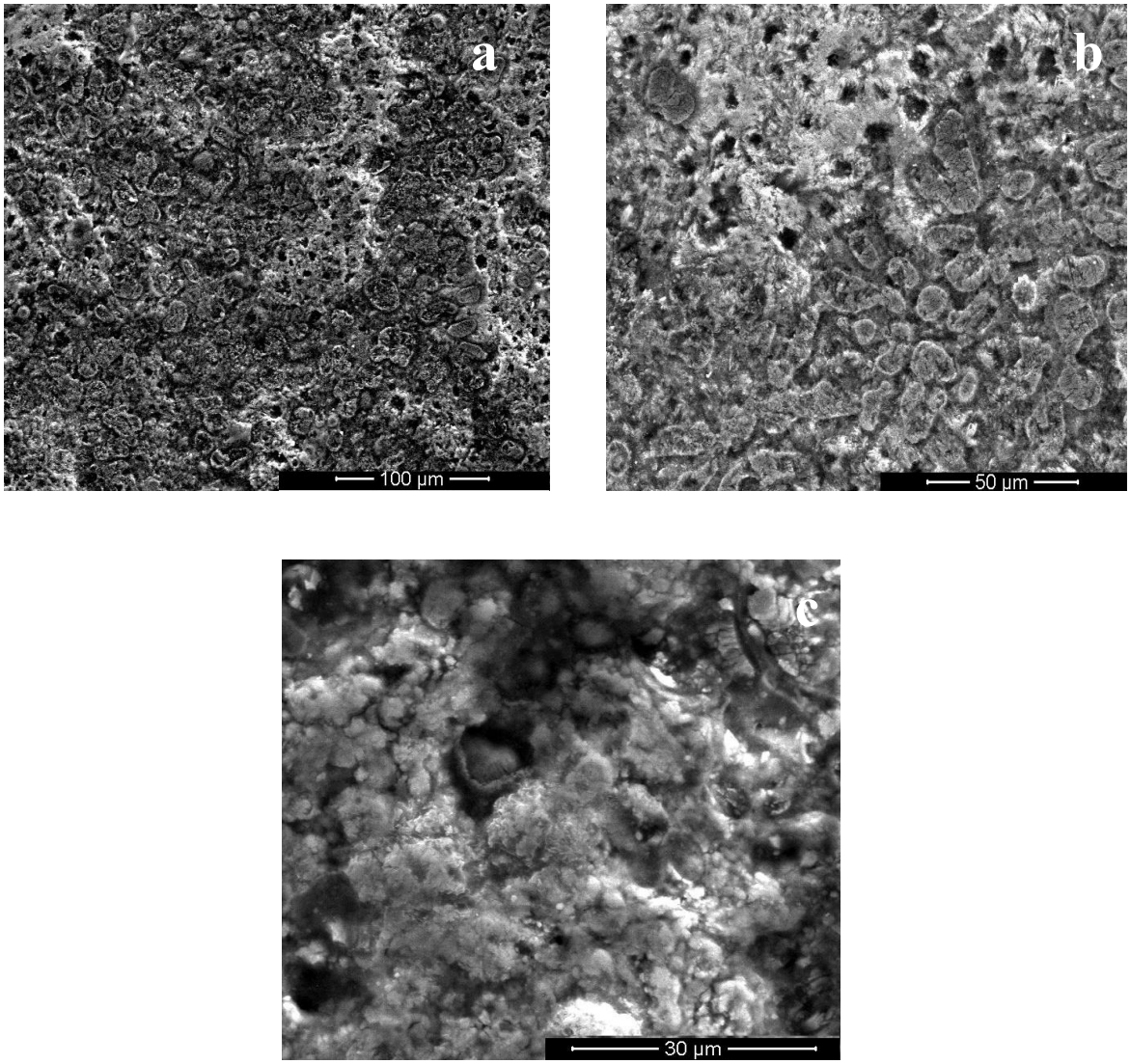


FIGURE 5.13: SEM of surface treated with Alternate Process-4
a. 100 µm, b. 50 µm, c. 30 µm

To further compare both the surfaces in terms of colour we perform FTIR in absorption mode. Comparing both the plots below we can conclude that as both samples have peaks at almost same wavenumbers and Absorbance levels, their structural composition, bond flexibility and hence colour is almost same.

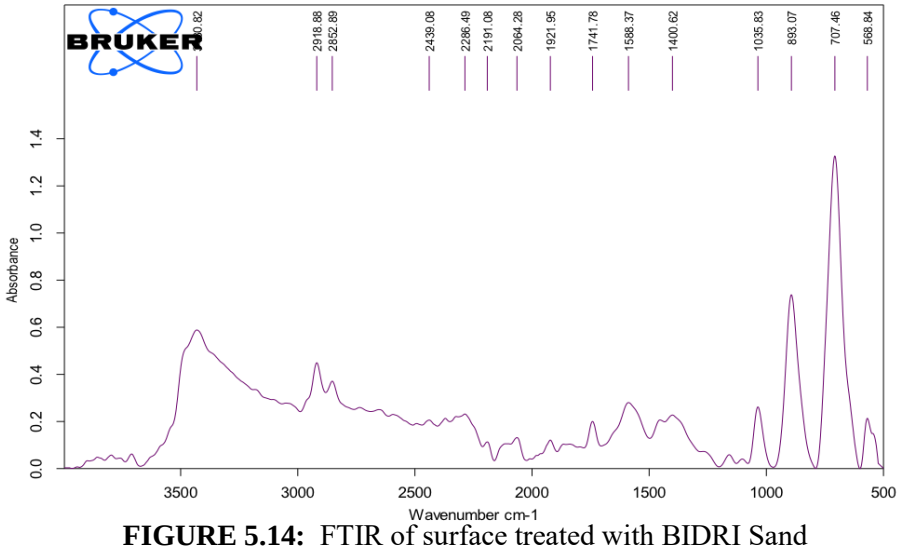


FIGURE 5.14: FTIR of surface treated with BIDRI Sand

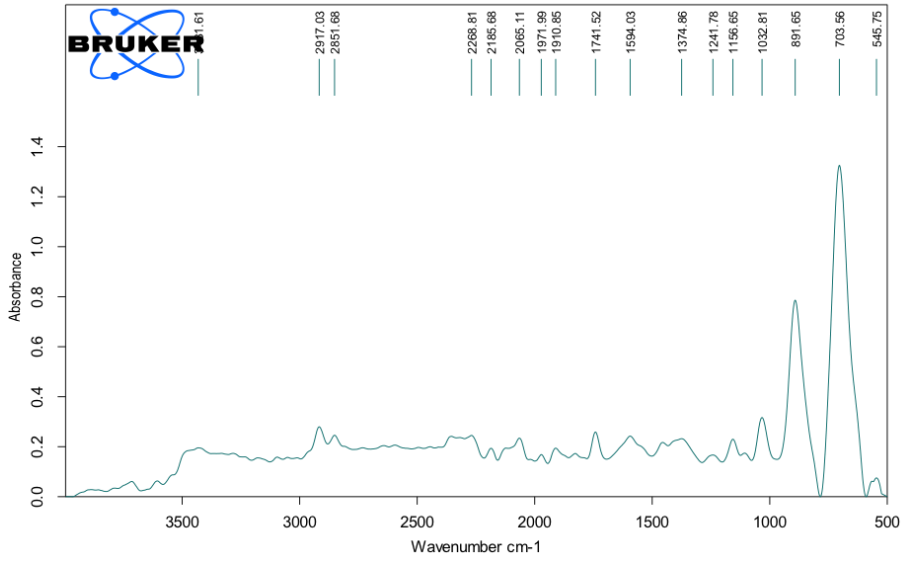


FIGURE 5.15: FTIR of surface treated with Alternate Process-4

5.2 NITRATE EFFECT

The Nitrate present in the sand is the reason for the patination to occur. The nitrate oxidizes copper to its oxides which give its black colour. To prove this the nitrate content is varied and the patination process is carried out. The results were then recorded.

i. With 0.5g KNO_3 – No significant Effect

ii. With 1g KNO_3- Pattination starts to appear

FIGURE 5.16: Specimen subjected to alternative process-4 solution that contains 1:20 weight ratio of KNO_3 and NH_4Cl in De-ionised water for 24 seconds

iii. With >1.5g KNO_3- Pattination becomes darker

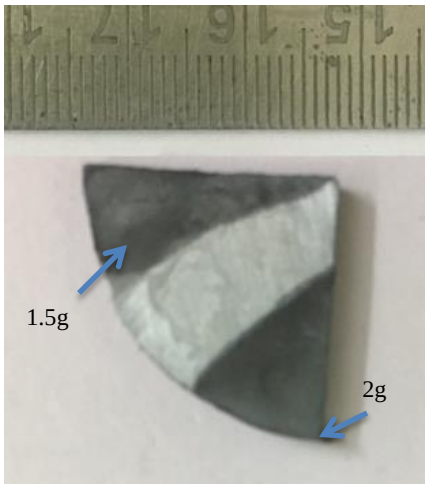


FIGURE 5.17: Specimen subjected to alternative process-4 solution that contains 1:15 and 1:10 weight ratio of KNO_3 and NH_4Cl in De-ionised water for 24 seconds

5.3 WEIGHT LOSS METHOD

A suitable process was identified. To note the effect of time, weight loss experiment was carried out. 4 samples were taken and kept in the solution at $80^{o}C$ for 5, 10, 15 and 20 minutes respectively. The initial and final weights were recorded.

PARAMETER	SAMPLE 1	SAMPLE 2	SAMPLE 3	SAMPLE 4
Reaction Time - t (s)	300	600	900	1200
Initial Weight (g)	5.557	5.5	5.581	5.64
Final Weight (g)	5.38	5.14	5.07	4.82
dm (g)	0.177	0.36	0.511	0.82
dm/dt (g/s)	0.031851719	0.065454545	0.091560652	0.145390071

TABLE 5.18: Initial and Final weight of sample treated for 5, 10, 15, 20 mins

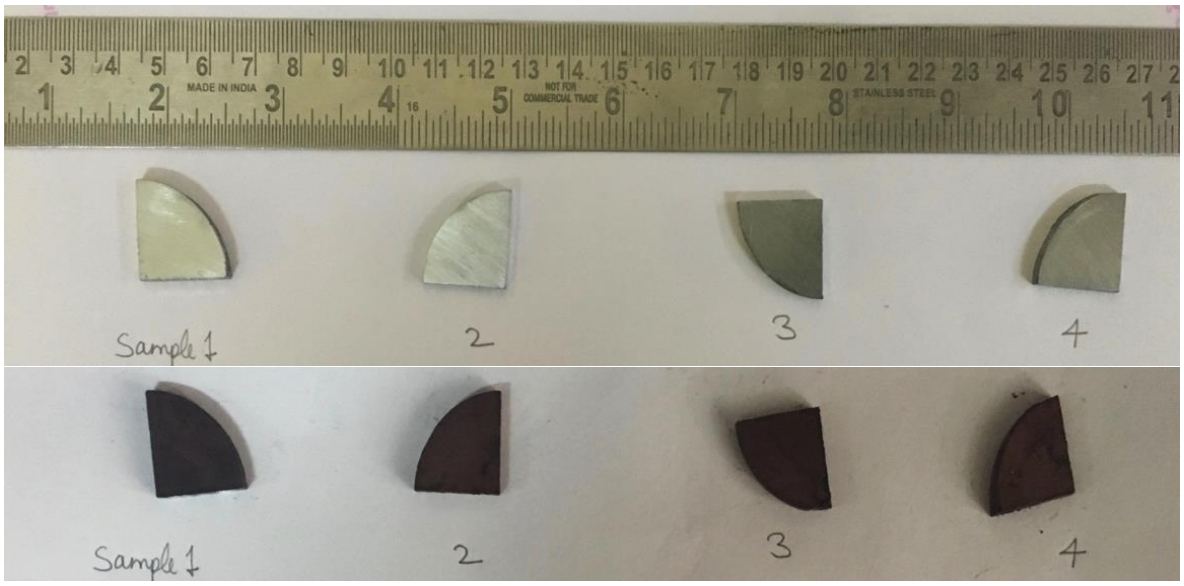


FIGURE 5.18: Samples before and after Weight Loss Experiment

Figure 5.20 shows that as time increases the surface turns brown. The change in mass vs time was plotted and the slope gave us the rate of weight loss which was 6.7×10^{-4} gs^{-1}. Using the faradays equation of electrolysis.

$$Weight\ Loss = \frac{Eq.Wt \times i \times t}{96500}$$

100% zinc was assumed for calculating Equivalent rate. The rate of weight loss when converted to rate of reaction gave us i=0.27 Acm^{-2}.

This rate of reaction is very close to the value calculated from the potentiodynamic polarization method as seen in the next section.

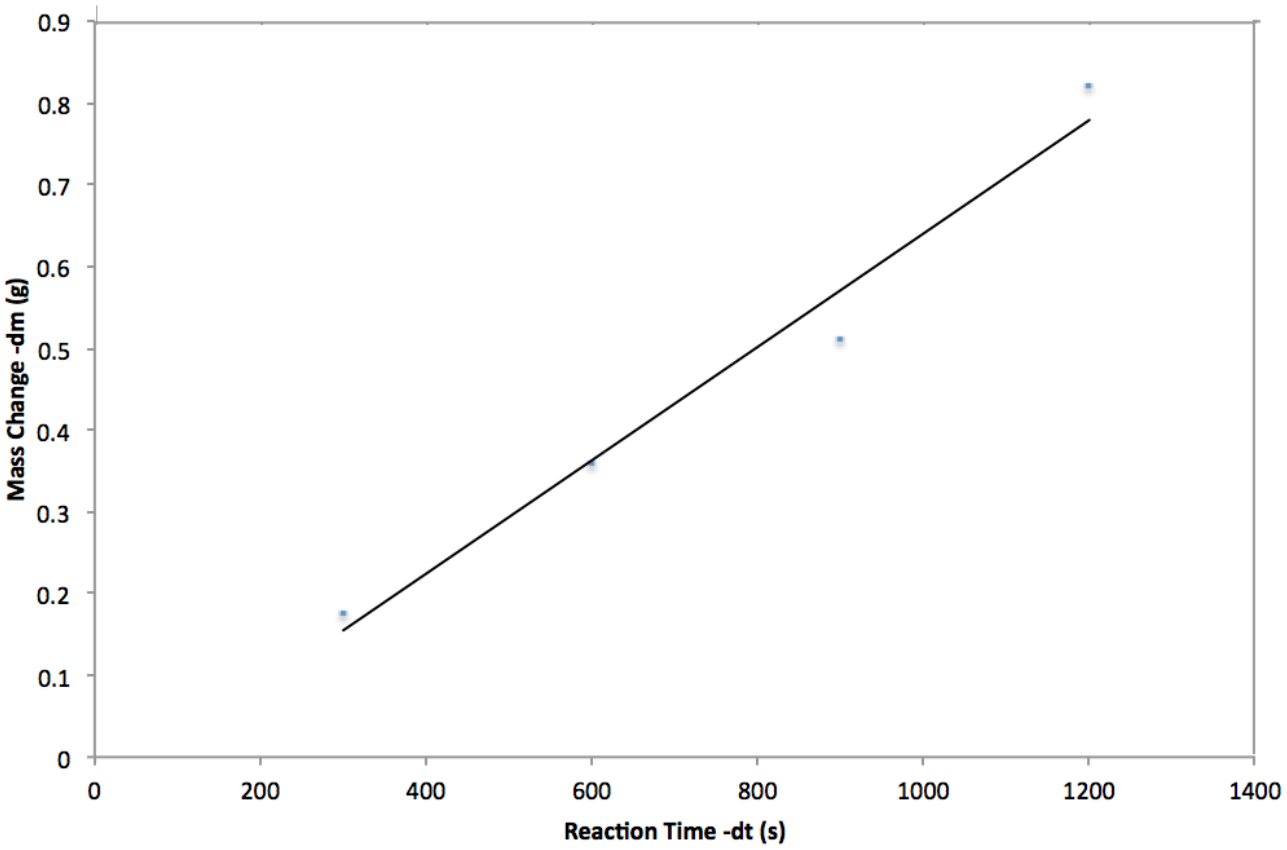


FIGURE 5.19: Plot of mass change vs time for weight loss experiment.

5.4 ELECTROCHEMICAL CHARACTERIZATION

The final step is to get a thorough understanding of the processes thaking place during the patination.

5.4.1 Open Circuit Potential Transients

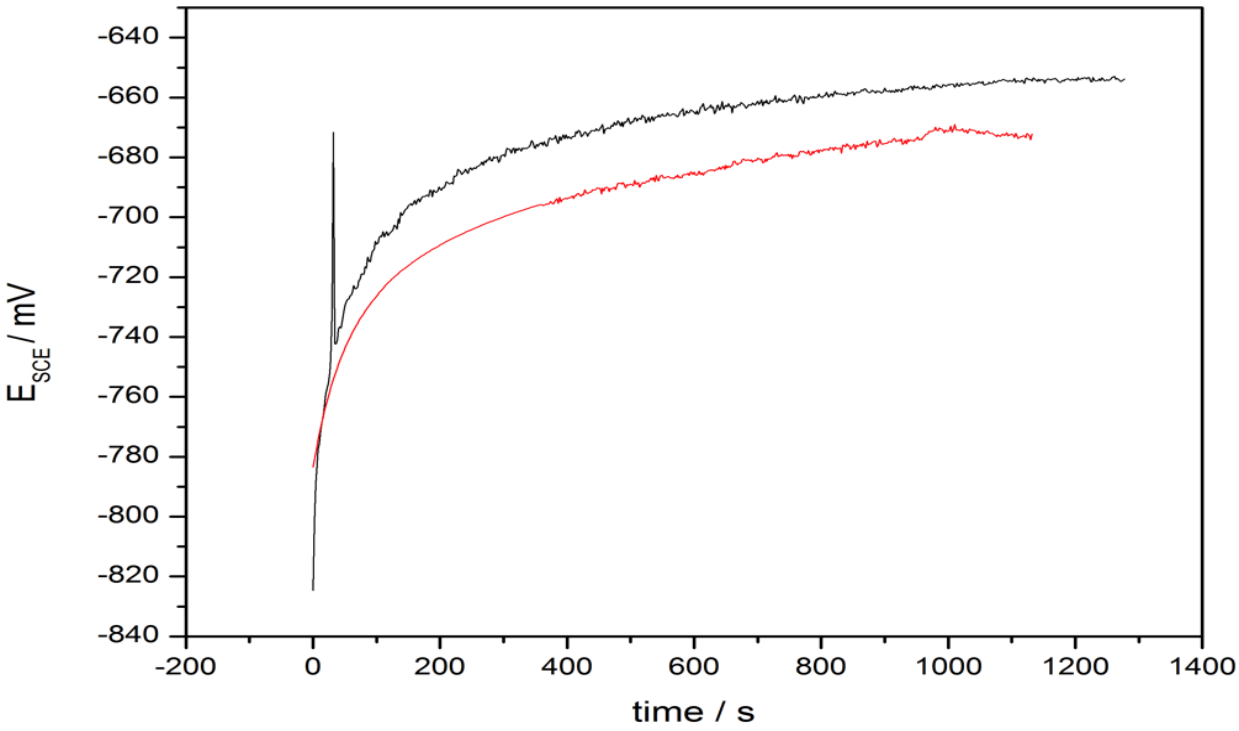


FIGURE 5.20: OCP Curve of sample dipped in solution of Ammonium Chloride and Potassium Nitrate (4:1) (2 curves for repeatability)

The surface is almost pure zinc (95%) so in the beginning the measured potential is close to that of zinc (Standard Reduction Potential of zinc is -0.76V). As the reaction continues zinc keeps on dissolving and ennoblement of the surface takes place due to Cu enrichment. The voltage keep moving toward copper (Standard Reduction Potential of copper is 0.34V). Near -650 to -680mV the reaction is stable and voltage is constant.

5.4.2 Potentiodynmic Polarization

After measuring OCP, the PD polarization curve is extracted using the Bio-logic Potentiostat. The P.D is plotted from -0.9A to -0.2 A. As seen in Figure 5.19 the E_{corr} ≈ 650-670 mV. Using tafels extrapolation the rate of reaction is found i, to be 0.1A cm^{-2}. This rate of reaction is very close to the value calculated from the weight loss experiment in the last section.

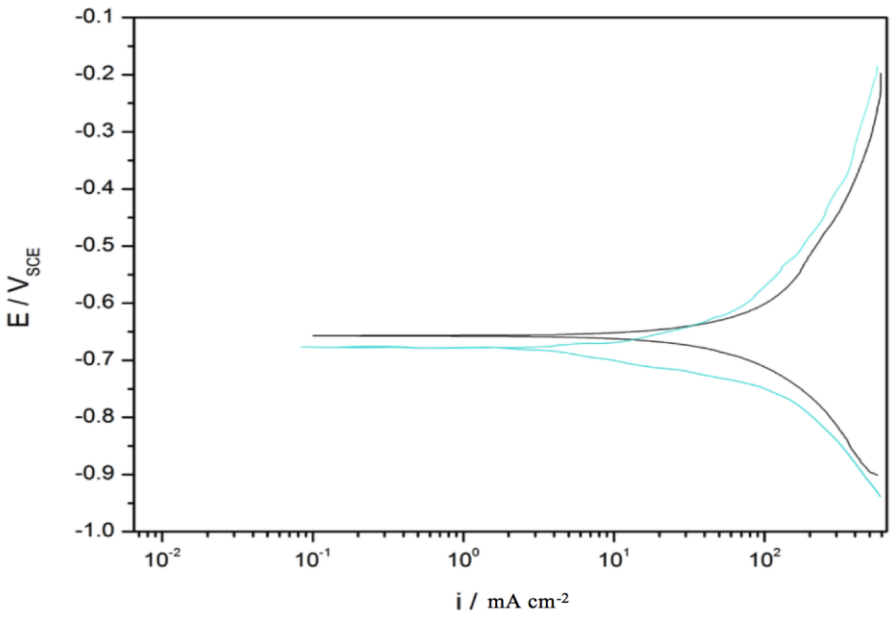


FIGURE 5.21: PD Curve of sample dipped in solution of Ammonium chloride and Potassium Nitrate (4:1) (2 curves for repeatability)

CHAPTER 6

CONCLUSION AND FUTURE WORK

From the current investigation, the following can be inferred

1. An alternative to Bidri sand has been identified. A mixture of NH_4Cl and KNO_3 (20g:5g) in 100mL of de-ionized water renders black patina on the surface similar to one seen with Bidri sand.
2. Time, temperature and electrolyte components play a role in obtaining the desired patina.
3. In such a solution zinc dissolves preferentially leading to copper enriched surface, which in nitrate containing solution converts to CuO and Cu_2O. These oxides render the black appearance.
4. XRD analysis of samples mimicking Bidri in alternate solution reveals peaks in same position with similar intensity thus showing the phases are similar.
5. SEM micrograph reveals loosely packed acicular structure which is close to that observed in Bidri samples.
6. An attempt was made to identify the electrochemical parameters to get a thorough understanding of the process taking place.
7. OCP Transient measurement reveals that the voltage stabilizes at about -650 mV
8. The rate of reaction obtained from the PD polarization curve is about 0.1 Acm-2 and the one obtained from the weight loss experiment is 0.27 Acm-2. Both these are in close range and hence we can conclude the rate of reaction is somewhere in this range.

The scope of furture work is as follows

1. The surface finish obtained is very similar to that of bidri but a closer alternative can still be found. For this a viscous organic solution can be used

instead of water. This would reduce the dissolution of zinc and hence provide a smoother finish

2. 2. The impedance curve is very unusual showing inductor behavior. Furthur analysis should be carried out on this study.

APENDIX A

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

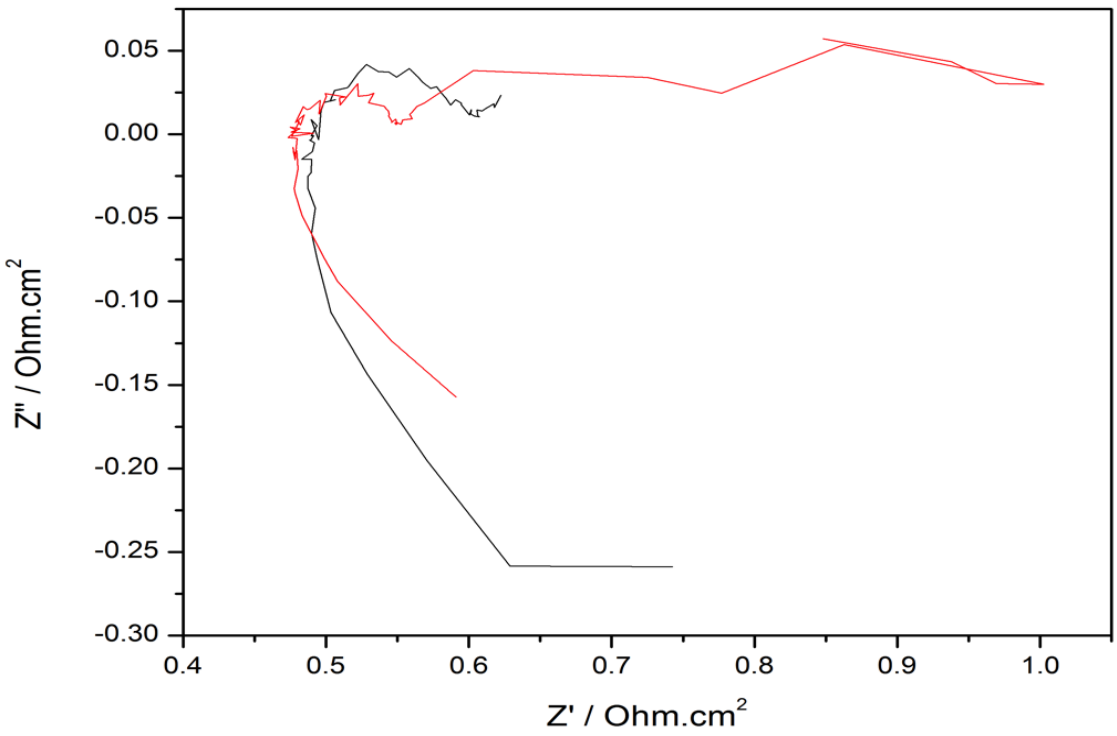


FIGURE A.1: Nyquist Impedance Curve of sample dipped in solution of Ammonium chloride and Potassium Nitrate (4:1)

(2 curves for repeatability)

The PEIS on the patinated phase was performed by sweeping the frequency(high to low and vice versa) to check for stability. The frequency varied from 100 kHz and 10mHz with AC pertubations of 10 mV, and the data was recorded with 10 point per decade.

This mainly shows that at high frequency current passes through the system and is inductive in nature. At low frequencies the curve follows a capacitative loop i.e. no current passes through it. The reason for that is not known and this can be a scope of future work.

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