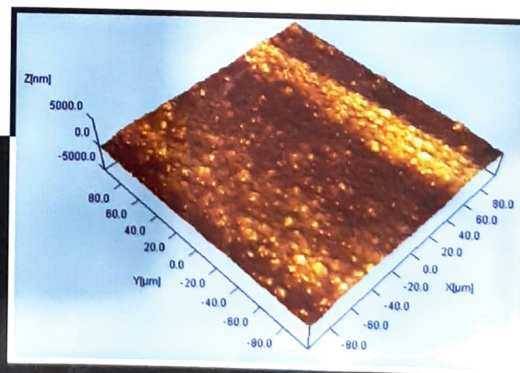
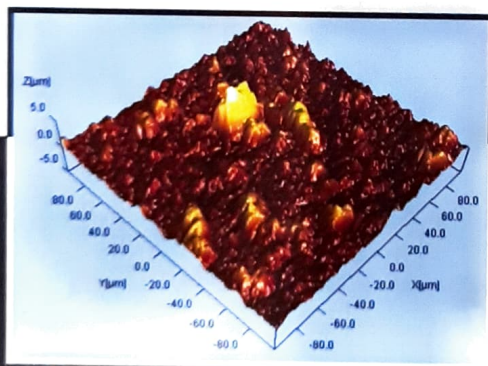


Journal of

**METALLURGY AND
MATERIALS SCIENCE**
Special Issue on Specialised and Smart Coatings



(J. Met. Mater. Sc.)

Vol. 62, No. 1-2, January-June 2020

Journal of Metallurgy and Materials Science

ISSN : 0972-4257 (Print version)

ISSN : 0974-1267 (Electronic version)

www.indianjournals.com

Editor in Chief

Indranil Chattoraj

Editorial Advisory Board

Arvind Sinha	Kaushik Chatterjee
Ashok Saxena	SK Mishra
Kantesh Balani	S Tarafder
K. Bhanu Sankara Rao	Thomas Webster

Principal Editor

Mita Tarafder

Co-Principal Editor

S. Sivaprasad

Editorial Board

J Pal	Ferrous Metallurgy
Jay Chakrabarty	Physical Metallurgy
Manish K Jha	Waste Valorization
R.K Sahu	Functional Materials
Sanchita Chakravarty	Analytical Science
Sobhana Dey	Mineral Processing
Vikas K Srivastava	Materials Processing

Technical Support

A K Sahu

Scope of the Journal

Journal of Metallurgy and Materials Science (JMMS) publishes original articles, review reports and short communications in the areas of minerals, metals and materials tracing the overall life cycle of structural as well as functional materials. The journal lays special emphasis on fundamental sciences related to metallic materials and their applications.

The scope of JMMS may be enumerated as: Mineral processing; Extractive metallurgy: ferrous and non ferrous; Processing of metals; Advanced joining of metals; Mechanical behaviour of materials; Materials failure mechanisms including Fatigue, Fracture and Corrosion; Valorization of materials; Nanotechnology; Technique of functional materials;

Computational materials engineering; Metallurgical waste recycling and utilization of metallurgical and electronic wastes.

Copyright

- On acceptance of manuscript for publication, the copyright is automatically transferred to publisher by authors.
- Only unpublished work and the paper not submitted for publication elsewhere will be published. Papers presented in conference where full papers not submitted, work published in reports, reviews, or thesis may be considered.
- Consent from all co-authors is mandatory prior to submission of the manuscript. On receiving the manuscript, it is presumed

that the corresponding author has taken consent from co-authors.

Plagiarism policy

- Authors are requested to submit unique manuscript free from plagiarism.
- Follow the guideline of UGC for handling plagiarism as per rule published here: https://www.ugc.ac.in/pdfnews/7771545_academic-integrity-Regulation2018.pdf
- Manuscripts within 10% similarity will be accepted for review.
- Authors will be asked to resubmit manuscript if the similarity is above 10 to 40%.
- For more than 40% similarity, the manuscript will be rejected.

Publisher: Director, CSIR-National Metallurgical Laboratory, Jamshedpur-831007, India

www.nmlindia.org

Editorial Note

I am extremely delighted to publish a special issue of the Journal of Metallurgy and Materials Science on "Specialized and Smart Coatings" to commemorate the completion of 70 years of CSIR-National Metallurgical Laboratory (NML).

The Journal of Metallurgy and Materials Science (JMMS), is one of the oldest journals among Indian Metallurgical Journals, first published in 1959. Dr. Balraj Nijhawan, the first Indian Director of the laboratory, conceived the idea of publishing a scholarly journal in the fields of metallurgy and materials science. This Journal was earlier known as the NML Technical Journal and in 2000, it was renamed as the Journal of Metallurgy & Materials Science. JMMS aims to provide a forum for communication among metallurgists and materials scientists. All the important indexing and abstracting services of the world devoted to materials science take cognizance of this journal.

I am thankful to Dr. Suman Kumari Mishra, Chief Scientist, CSIR-NML, for her co-ordination as the Guest Editor, in bringing out this special issue on "Specialized and Smart Coatings", in which the state-of-the-art R&D knowledge by eminent researchers working in this field are documented. I acknowledge with gratitude all the authors featured in this issue, for contributing their research experiences and knowledge.

I sincerely acknowledge the contribution of the editorial advisory board members and the editorial team for their editorial services for improving the technical content and overall presentation of this journal.

Indranil Chatteraj
Editor-in-Chief

Foreword

I am happy to put forward as Guest Editor of the special theme issue **Specialised and Smart Coatings** of "Journal of Metallurgy and Materials Science (JMMS), CSIR-NML on the **70 years of CSIR- National Metallurgical Laboratory**. The coatings are very much required in many industrial processes as well as general civil life for enhancing the performances of components, get different functional properties etc.

This special issue discusses different important coatings as well review on important topics such as corrosion-resistant, self healing, hydrophobic coatings, coatings for turbines, advanced steel coatings, different engineering coatings by PVD process, techniques of understanding interfaces in water splitting and other processes, vacuum furnace designing for industrial applications. I am sure these will enrich the knowledge and help the researchers for deciding many applications and their plans for the developments of advanced coatings.

I am grateful to all the contributors, who accepted the invitation for this special issue, which helped this issue to be published.



Suman Kumari Mishra
Chief Scientist CSIR-NML
Guest Editor of this issue

Journal of Metallurgy and Materials Science
(Formerly NML Tech. Journal)

Vol. 62, No. 1-2, January-June 2020

CONTENTS

	Pages
✓ 1 A brief review on the development of self-healing, hydrophobic and antifouling epoxy coating S S ANANTHAPADMANABHAN, GEETANJALI MISHRA and SMRUTIRANJAN PARIDA	1 - 11
✓ 2 High performance specialized coatings for applications in corrosive environments SC VANITHAKUMARI, RP GEORGE and U KAMACHI MUDALI,	13 - 27
3 Formation and growth of iron-zinc intermetallics during annealing treatment of galvanized steel GK MANDAL, M DUTTA, TIPU KUMAR, AVIK MONDAL, MG WALUNJ, S K MISHRA, S K DAS, R PAIS and LC PATHAK	29 - 47
✓ 4 Metallic gold thin film micropattern on polydimethylsiloxane film for flexible electronic sensors and circuits A KAKATI and S DAS	49 - 55
✓ 5 Vacuum based coatings for engineering applications V VASUDEVA RAO and V RAVINDRA	57 - 61
✓ 6 Multifunctional properties of electrodeposited nickel composite coating containing nanosized monoclinic zirconia particles ST ARUNA, S LATHA and RV LAKSHMI	63 - 74
7 Techniques for investigation: Semiconductor/electrolyte interface processes in photoelectrochemical cell for solar water splitting DIIPIKA SHARMA, SAKSHI GUPTA and B R MEHTA	75 - 84
8 Effect of annealing on structure and properties of pulse electroplated Ni-W alloy coating CHINMAYA KUMAR SARANGI, BIBHU PRASAD SAHU, BARADA KANTA MISHRA and RAHUL MITRA	85 - 96
✓ 9 Vacuum furnaces for metallurgical processing V VASUDEVA RAO and V RAVINDRA	97 - 101

A brief review on the development of self-healing, hydrophobic and antifouling epoxy coating

S. S. ANANTHAPADMANABHAN, GEETANJALI MISHRA and SMRUTIRANJAN PARIDA*

Department of Metallurgical Engineering and Materials Science,
Indian Institute of Technology Bombay, Mumbai, India.

Abstract : Epoxy coatings are the most used industrial coating system. While corrosion resistance through the barrier performance of the coating is well tested, the addition of multifunctionality is the new research objective. The responsiveness of the epoxy coating to the mechanical damage will not only add to its barrier performance but also delay the corrosion of the underlying metal. Such responsiveness of the coating is desired to manage the maintenance schedule. Various methods tested to add the “self-healing” attribute to the epoxy coatings are discussed. Surface modification to add hydrophobic character to the epoxy coating is also another functionality for value addition and is useful in many applications. For marine applications, fouling resistance is very important. Attempts made to develop anti-fouling epoxy coating are also reviewed. The brief review, giving a broad overview of the research trend, is intended to give a way forward in the development of the epoxy coating.

Keywords : Epoxy coatings, self-healing, anti fouling coatings.

INTRODUCTION

To prevent corrosion damages of the metals exposed to various environments, the surface coatings are used as a passive barrier between the metal and the atmosphere. However, the prevention power of such coatings diminishes with time. In addition to this, the metal substrate can get exposed to the unfavorable atmosphere due to the crack formation and damage of the coating surface. The corrosion damage of the metal substrate can continue unnoticed under the cracks, as early detection of the latter in time can be difficult. So, there is always a requirement of timely detection and maintenance of coating damages. Here comes the necessity of smart coatings with self-healing phenomenon, which can help in “healing” the initial micro-cracks in the coatings, till the maintenance is carried out, and thus, prolonging the life of the structure.

The self-healing is a property of a material to reform the structural integrity after undergoing the surface damages, akin to the biological species which heal the damages like wounds on their own. In surface coatings, the self-healing capability is achieved by intrinsic and extrinsic healing (Fig.1)^[1]. The intrinsic healing can be attained by the physical or chemical interaction of the coating itself (Fig.1A). By blending the coating formulation with another polymer which can form reversible bonds like hydrogen bond with the base material it is possible to achieve the physical interaction. The chemical interaction involves the strong covalent or non-covalent bond formation which results in healing. The intrinsic healing does not require any additional catalyst system but requires external influences like the change in pH or change in temperature to trigger the healing process^[1-3]. The extrinsic healing mechanism involves the use of an “external” agent for the healing process (Fig.1B). The “external” agents include the corrosion inhibitor encapsulated in a microcapsule or other types of nanoscopic anchors^[4-7]. The main requirement for the extrinsic healing is that the “external agent” should be able to cover the damaged area within an appropriate time. In the extrinsic healing crack repairing mechanism is not recyclable.

Recently research works to develop self-healing coatings are based on these mechanisms by using microcapsules, hollow fibers, by blending with polymers, or by using the network structures. The major challenge is to develop a self-healing coating without deteriorating the other coating properties.

* Corresponding Author Email : paridasn@iitb.ac.in

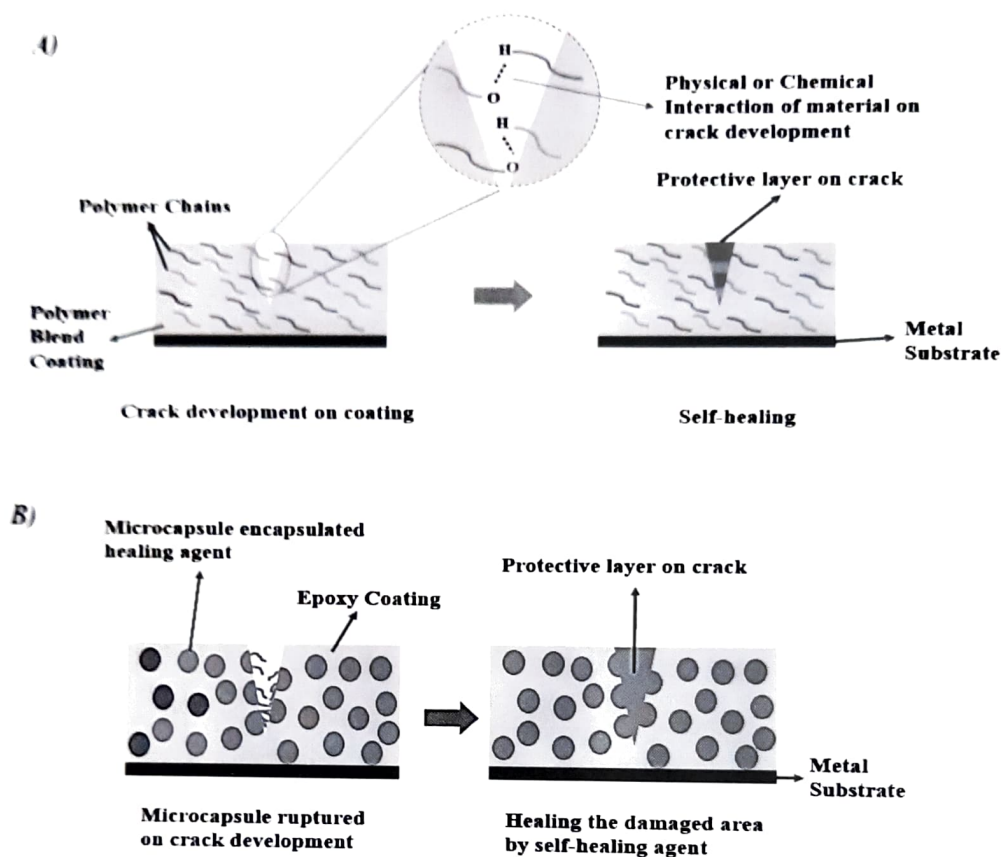


Fig. 1: Mechanism of the A) intrinsic and B) extrinsic self-healing in organic coatings

The superhydrophobic coatings surfaces are resistant to wetting with a water contact angle beyond 150° and a sliding angle below 10° . Such surfaces and coatings have undergone a century of development due to its potential applications^[8-10]. The micro- and nano hierarchical roughness and low surface energy cause the superhydrophobicity.^{[11][12]} The superhydrophobicity also adds properties like self-cleaning, anti-fogging, anti-icing, antibacterial, corrosion resistance, etc.^[13-17]. Therefore these surfaces have vast applications in the field of engineering, defense, and medical science. In the past decades, several routes have been adopted to impart superhydrophobicity to surfaces such as electrodeposition, chemical vapor deposition (CVD), electrospinning, plasma treatment, lithography, etc.^[18-21] The real-life applications of these coatings are challenged by their inadequate mechanical strength^{[12][22-27]}.

Marine biofouling is a well-known problem in the sea-water environment, which is responsible for increased hydrodynamic drag, bio-corrosion, increased fuel demand, etc., posing danger in marine water operations^[28]. Marine biofouling occurs due to the settlement and growth of various algae, microorganisms, etc., undesirably, on the underwater structures. For a long time, eco-friendly antifouling materials and methods are being researched to stop and control the biofouling without affecting the marine ecosystem.

A brief overview of the research works on the development of the aforesaid types coatings based on epoxy resin for application on metals is presented.

SELF-HEALING EPOXY COATING

The self-healing property is achieved by the use of inhibitor and the polymeric healing agents. The healing by the polymeric healing agents to protect the surface use thermoplastic or thermosetting polymers. Since inhibitors

protect the metal surface from corrosion, most of the research focuses on incorporating an inhibitor in a smart encapsulant, where the healing agent slowly releases at the damage. By the encapsulation method, microcracks formed in the polymer film surface can be mended by the formation of a layer of healing agents, preventing further damage.

Inhibitor Based Healing Method

The most researched approach for the development of self-healing epoxy coating is based on the microcapsules loaded with the corrosion inhibitors. The nano or micro containers are used to entrap the inhibitor in the core of a shell and release at the damaged site in a controlled manner in response to the mechanical damage, the pH, and temperature change. The uniform dispersion of the microcapsules and its controlled release are necessary to achieve the proper healing. Both organic and inorganic nanocontainers are used for the purpose. The organic containers for self-healing coatings include polystyrene (PS), polyurea formaldehyde (PUF), Polymelamine formaldehyde (PMF) microcapsules, and cellulose nanofibers (CNF) [4][29][30]. The inorganic containers include halloysite nanotubes (HNT), and mesoporous silica [5][31-33].

The research on the development of the encapsulated inhibitor-based epoxy self-healing coatings is discussed in the following. One of the recent studies used graphene sheets containing porous polyhedral oligomeric silsesquioxane (POSS) loaded with benzotriazole (BTA) in the epoxy composite coatings^[34]. The spontaneous release of BTA from graphene-based nanocontainers is the basis of the self-healing function, which works by the formation of the adsorption layer of BTA on metal by its controlled release from the nanocontainer. In another approach Suwadee et al., tried using organosilane modified nanosilica along with the microcapsule with self-healing functionality for improved corrosion resistance of the epoxy coating^[35]. Perfluorooctyl triethoxysilane (POT), ethanolamine (ETA), and diethanolamine (DEA) encapsulated in PUF shell are used as the inhibitors in self-healing coating. Also added to the coating are nanosilica surface-modified with (3-glycidoxypentyl) trimethoxysilane and (3-aminopentyl) trimethoxysilane for the proper dispersion in the epoxy resin. The observation was that by the addition of modified silica and POT, better self-healing is achieved due to the formation of silane base film by the self-hydrolyzed reaction of POT in the aqueous environment and due to decreased permeability of the coating.

Odarczenko et al. made an inhibitor-based approach to develop the self-healing coating^[6]. They encapsulated the inhibitor lawsone (2-hydroxy-1,4-naphthoquinone) in the polyurethane (PU) shell to form the microcapsules and are incorporated into the epoxy coating system. In this system, the mechanical damage results in the breakage of microcapsules incorporated into the coating, thereby triggering the release of the inhibitor into the damaged area. A solid protective barrier is formed due to the diffusion and evaporation of carrier solvent and the formed layer passivates and protects the underlying steel substrate and the self-healing property to the epoxy coating. By using this coating system, a 70% corrosion inhibition efficiency is reported. Kim et al. developed a pH-responsive nanocapsule by encapsulating triethanolamine (TEA) inhibitor into the shell produced by the free radical microemulsion polymerization of methyl methacrylate (MMA), methacrylic acid (MAA), and butyl acrylate (BA) monomers^[7]. By EIS study it was found that when the change in pH occurs, the encapsulated TEA was gets released into the damaged area and prevents the corrosion by forming a protective layer at the damaged site. By incorporation of TEA inhibiting agents, corrosion inhibiting efficiency of about 85% is reported.

Nawaz M and his co-workers used dodecylamine (DOC) inhibitor and polyethyleneimine (PEI) as a healing/inhibiting agent encapsulated in the cellulose microfibrils (CMFs)^[29]. By the synergic effect of DOC and PEI, the self-healing effect in the epoxy coatings was achieved. The self-release of PEI can be triggered by mechanical damage and localized pH change. Sneha et al. has developed the inhibitor encapsulated nanocontainers by the Pickering emulsion technique and used in the epoxy coating formulation to achieve the self-healing property. The work used the 8-hydroxyquinoline (8-HQ) encapsulated graphene oxide- stabilized polystyrene (GO/PS)

nanocontainers. By the use of these nanocontainers, the work showed a 20% increase in the polarization resistance at the scratched coating, demonstrating the self-healing property^[30]. Zhou C and his co-workers utilized zeolitic imidazole framework-8 (ZIF-8) as the core material for inhibitor loading^[31]. The ZIF-8 is a pH-responsive material and can be triggered in both acidic and alkaline conditions. The corrosion inhibitor, benzotriazole (BTA) are encapsulated in the cavity and mesopores of hollow mesoporous silica nanoparticle (HMSN). The HMSN is encapsulated by using ZIF-8 (HMSN-BTA@ZIF-8). The HMSN-BTA@ZIF-8 has compatibility with epoxy resin due to covalent interaction and helps in the uniform dispersion of nanocontainers in the coatings. The BTA forms the protective film in the scratched area, in addition to the hydrophobic nature of the filler, where improved corrosion resistance and self-healing capability of coatings was observed.

Demian et al. used the halloysite clay nanotubes (HNTs) loaded with inhibiting agents, benzotriazole (BTA), and 2-mercaptobenzothiazole (MBT) and glutaraldehyde (CTS) polymer film encapsulation are given^[36]. The BTA MBT inhibitors and HNTs inhibitor enhanced the corrosion resistance by healing the crack developed on the surface by release and adsorption of these agents. Huang et al. proposed a shape memory polymers and dual-function microspheres based self-healing protective coating system^[5]. The dual-function microspheres consisted of polycaprolactone (PCL) and the corrosion inhibitor 8-hydroxyquinoline (8HQ). They used both inhibitor and polymer healing methods to achieve the self-healing function. In this is a triple-action coating, first, the release of inhibitor 8HQ suppress the corrosion at the cracked area, secondly, the crack closure by the shape memory polymer matrix, and third is the crack sealing by the melted PCL microsphere. They found that upon heat treatment, self-healing property can be activated and improved corrosion resistance can be obtained.

Polymer Healing Method

In the polymer healing method, the crosslinking reaction between the monomer and the curing agent takes place at the damaged site, and this cross-linked product retains the original coating property. Both thermosetting and thermoplastic polymers can be used in this method. Thermosetting type polymers function by the crosslinking reaction at the damaged location. In the case of thermoplastic polymer, a secondary phase or as a miscible phase is formed at the damaged site, and their healing process is activated by heat.

Several approaches have been made to develop a self-healing coating based on the polymer healing method. Yuan D and his co-workers have conducted the study by using the thermoplastic polyurethane (TPU) and self-healing is visualized by the help of SEM^[37]. They found that by using the TPU, the initial crack of 50 mm was completely healed upon heating of system at 80 °C for about 10 minutes. The healing was due to the diffusion of molten TPU into the damaged area to heal the crack. Yi. H et al. used the polyurea microcapsules embedded with epoxy and tetraethylenepentamine (TEPA). The self-healing function of the microcapsules was demonstrated by incorporating microcapsules into the epoxy coating and carrying out an accelerated corrosion test by immersion into the salt solution^[38]. The study observed that in response to the crack, the core materials (epoxy and amine) outflow from the microcapsules, forms a protective film by the crosslinking reaction. Yanxuan Ma et al. prepared polyurea microcapsules with ethylenediamine (EDA) as the core material and incorporated them into the coating system. By incorporation these microcapsules, it was found that the coating system has greatly repaired the crack and exhibited excellent anti-corrosion performance. This was attributed to the release of the reactive isocyanates and EDA at the crack due to the breakage of the encapsulating microcapsules. Then, the crosslinking reaction between the released materials leads to the formation of the polyurea at the crack, which acts as a protective film against the harsh medium^[2].

Self-healing coating based on the epoxy ester from tall oil fatty acid and poly urea-formaldehyde microcapsules were also proposed by several workers. The healing is achieved by the formation of a protective layer in the damaged area by the auto-oxidation and epoxy ester crosslinking reaction through a hydrogen bonding^[39]. Safaei et al. also conducted a similar study by using microcapsules of polyureaformaldehyde (PUF) and epoxy resin as

the core substance^[40]. The self-healing ability of the coatings was due to the release of the epoxy resin from the broken microcapsules and the crosslinking reaction with the matrix's hardener. Haddadi et al. reported the self-heal ability of carbon hollow spheres (CHSs) encapsulating epoxy and polyamine incorporated into the epoxy coating system. The CHS loaded with the film-forming agents healed by the formation of protective film at the damaged site, released upon the breakage of microcapsules. The film formation takes place by the nucleophilic substitution ring-opening reaction between the amino hydrogens (NH) and epoxide groups of the epoxy chains^[41]. O. Tezel et al. used polyurea-formaldehyde epoxy resin (PUF-epoxy) microcapsules to get the self-healing ability to the coating formulation. The epoxy matrix used in the coating consists of the thiol end groups. The self-healing is achieved by the formation of a protective film on crack as a result of the reaction between epoxy released from the broken microcapsule and the thiol group in the epoxy matrix^[42].

A.M. Atta, et al. have proposed a self-healing coating using amino-functionalized smart silica composites and nanoparticles from microgels prepared from N-isopropylacrylamide-co- vinyltrimethoxysilane (NIPAM-VTS), tetraethoxysilane (TEOS), and 3-aminopropyl triethoxysilane (APTS) by a hydrolyzing process^[43]. For amino-functionalized NIPAM-VTS-polysiloxane, the self-healing capability was due to the formation of the film with a hydrophobic network by the crosslinking reaction between amino-functionalized silica functional groups and the amide groups of NIPAM. This film is observed to have hydrophobic and anticorrosive characteristics. T. Chen, et al. has proposed the polyurea-urethane/epoxy polymer blends for the self-healing coating. The coating properties are improved by the reaction between maleimide groups in the furan group terminated thermoplastic polyurea-urethanes (FTPU) and furan groups in epoxy oligomers. In addition to these reactions, the reversible disulfide bonds in FTPU also assists the healing process. By this system, about 80% of healing efficiency was reported^[44]. Yuan D et al. also proposed a similar type of polymer blend approach for the self-healing coating development^[3]. They blended the diglycidyl ether of diphenolate esters (DGEDP) based epoxy with thermoplastic polyurethane (TPU) prepolymers to prepare the self-healing coating. By using the lower molecular weight TPU, a miscible blend was obtained, which formed a flexible epoxy network. This network helps in the easier flow of TPU into the cracks and cause healing. But the decrease in the mechanical property due to the lower crosslink density is also reported.

Hia and his co-workers developed a self-healing coating with a multicore microcapsule of alginate biopolymer encapsulated with diglycidyl ether of bisphenol A based epoxy and mercaptan/tertiary amine-based hardener^[45]. Both the microcapsules are loaded into the epoxy matrix. They found that by using this dual-capsule self-healing system it is possible to get up to four healing cycles with about 68-85% healing efficiency. Fang et al. proposed a different approach to the development of self-healing coating. They used the four epoxy coatings with dense irreversible Network I, dense reversible Network II, loose irreversible Network III, and partially irreversible-partially reversible Network IV to study the effect of the network structure^[46]. Using the dense reversible Network II, a quick crack healing in 40 seconds and complete crack disappearance in 80 seconds was reported. Due to the higher crosslink density improved mechanical property was also obtained. The mesoporous silica (MS) and TiO₂ nanotubes (TNTs) were also used as nanocontainers^[32]. Epoxy-encapsulated TiO₂ nanotubes and amine-immobilized mesoporous silica were incorporated into the epoxy matrix to develop the self-healing coating. The corrosion protection and self-heal ability were due to the crosslinking reaction of healing agents to form the protective film at the crack.

Guo et al. has developed epoxy-based UV-triggered self-healing coating containing a single microcapsule as a healing agent. The epoxy and cationic photo-initiator were encapsulated into the SiO₂ microcapsule via combined interfacial / in situ polymerization and these microcapsules are loaded into the epoxy coating system to develop the self-healing coating. Upon the crack development, the microcapsule break and UV irradiation trigger the photocuring process^[33]. Li and his co-workers proposed a Diels-Alder (DA) network-based coating system from amino-functionalized multiwall carbon nanotubes and the epoxy resin for the self-healing coating application^[47].

This work is based on the photothermal conversion ability of the amino-functionalized MWCNTs to initiate the crosslinking reaction (dynamic covalent DA network). Upon exposure of the cracked area to the heat treatment or the near-infrared (NIR) irradiation, the amino-functionalized MWCNT initiate the crosslinking reaction and form the DA network structure at the cracks and reconstructs the protective coating at the damaged site. They reported that NIR irradiation is better than direct heating because the latter initiates the reaction at the undamaged area which affects the overall coating performance.

SUPERHYDROPHOBIC EPOXY COATING

Epoxy (EP) resins are commonly used coating systems for industrial applications because of their stable physical, chemical, mechanical properties and excellent adhesion to a metallic substrate, besides giving options for self-healing. But, epoxy resins are hydrophilic, for which the preparation of hydrophobic epoxy coatings with low surface energy is crucial for widespread applications (Fig.2).



Fig. 2: Schematic representation of the synthesis procedure of epoxy superhydrophobic coating on various substrate

In this context, polytetrafluoroethylene (PTFE) surface coatings give effective nonwetting surfaces owing to its lowest surface tension ($19 \text{ mJ} \cdot \text{m}^{-2}$)^[22]. Superhydrophobic epoxy coatings have been synthesized by fluorination of epoxy resin followed by the physical addition of PTFE particles^[48]. The above coating is reported to withstand aqua regia up to 1 h. of immersing. However, weak interfacial bonding between epoxy and PTFE and poor abrasion resistance was also observed in this work. So, by the enhancement of the epoxy-PTFE interfacial bonding and simultaneously providing a multilayer of micro/nanostructure on the surface of the coating, the design of superhydrophobic coating with good mechanical properties will be feasible. To enhance the interfacial bond of EP-PTFE, melt extrusion was used for the uniform dispersion of PTFE on the epoxy^[22]. Then dopamine was added to increase active hydroxyl groups on the surface of graphene and finally, nanosilica particles have been grown on the modified graphene surface through in situ process to get three-dimensional graphene-polydopamine - SiO_2 (i.e. GP- SiO_2) particles. After that, modification of GP- SiO_2 surface with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS) was carried out to fabricate epoxy-PTFE/GP- SiO_2 -POTS coating, which is superhydrophobic. Moreover, the lamellar structure of graphene induces the dispersion of the SiO_2 particles. This coating with a multi-layered structure revealed excellent wear resistance, self-cleaning and antifouling properties. The hydrophobicity of epoxy-PTFE coating was higher as compared to pristine epoxy coatings with a water contact angle of 104.2° versus an initial value of 84.3° . To optimize the wettability, contents of GP- SiO_2 -POTS particles (from 0.2 to 1.4 wt%) added to the epoxy-PTFE coating were also controlled. The coating surface showed superhydrophobicity with a contact angle of $156.3 \pm 1.5^\circ$ and a sliding angle of $3.5 \pm 0.5^\circ$ after the addition of 1 wt% of GP- SiO_2 -POTS and after that, there is no increase in contact angle by the increasing amount of GP- SiO_2 -POTS. The prepared coating also demonstrated high repellency against other liquids such as milk, juice, coffee, and tea.

Superhydrophobic coatings having only waterproof capacity also cannot fulfill the requirements in every aspect. Multifunctional coatings with superhydrophobic nature have become the demand for the current period. The $\text{Mg}(\text{OH})_2$ (MH) is one of the green and cost-effective functional material which has various day-to-day applications in the fields of food, medicine, flame retardance, adsorption of heavy metals, etc. but its superhydrophobic studies are scarce as MH is super hydrophilic^{[49][50]}. The nanosheets of superhydrophilic MH have been modified by

stearic acid (STA) to turned it into superhydrophobic STA-MH^[51] following a scheme generalized in Fig. 2. The epoxy@STA-MH superhydrophobic coatings showed efficient waterproof ability (WCA is of 160° and SA nearly 5°) and have several additional beneficial properties such as antifouling, anti-corrosion, anti-icing, and flame retardancy, which are required in day-to-day applications. The possibility of synthesis in large-scale and long-term storage ability is the main advantage of this material. However, at the same time, the surface properties of the original substrates altered which is the limitation of the material towards wide-scale applicability.

Similarly, epoxy-polydimethylsiloxane-graphene oxide (EPG) nanocomposite coatings have been synthesized by the addition of various wt% of graphene oxide (GO) nanosheets to epoxy-hydroxy-terminated polydimethylsiloxane (EP-hPD) matrix through an in situ process^[52]. The addition of graphene nanosheets (GNs) enhances the modulus of elasticity and showed an antifouling mechanism by the generation of oxidative stress on marine-based microbes causing anti-adhesion. Water contact angle (WCA) also increased after 1 wt% loading of GN to the matrix.

Anti-wetting coatings with small sliding angles (SA) are of abundant importance for real-world applications. Nevertheless, several types of destruction of the coatings can occur during practical applications resulting in the loss of the anti-wetting effect. A slippery and transparent coating has been reported by Yang et al. with very low water SA, which was synthesized by embedding polydimethylsiloxane (PDMS) brushes covalently in a cross-linked framework of epoxy resin^[53]. The as-obtained coating revealed a slippery action for aqueous liquids (10 μ L), SA < 3°, and simultaneously sliding speed of 1.16 mm/s because of the extremely small surface energy and high movement capacity of PDMS. It has been tested that a 10 μ L water droplet at 80°C can slide off the coating at an extremely low sliding angle (i.e. <5°) and there is no change in the angle after increasing the temperature up to 120°C. Moreover, due to its corrosion resistance and antifouling capacity, it was proposed to be applied to various substrates for the development of slippery coatings.

In another study, the robust superhydrophobic coating has been developed by taking commercial epoxy resin as the core framework and embedding SiO₂ nanoparticles followed by texturing micropores on those coatings^[12]. This particular coating represented high mechanical stability (due to the presence of micropores, the surface can bear mechanical pressure) and superhydrophobic nature. The superhydrophobicity is reportedly maintained even after various mechanical abrasions. The durability of the adhesive coating has been tested for liquid penetration by immersing in various media for a long time. The spherical droplets have been sustained on the surface of adhesive coating even in immersion solutions such as milk, coffee, solutions of different pH, and different temperatures.

ANTI-FOULING FUNCTIONALITY

The antifouling coatings are based on two mechanisms such as biocide-release-based and non-biocide-release-based, as presented in the schematics in Fig. 3. However, due to environmental regulations, the latter method is the focus of the current research. In the following, a brief review of the development of the non-biocide-release epoxy-based coatings is presented.

Among all, promising results for marine antifouling applications have been observed in the case of the polysiloxane-based (PDMS) coatings. The PDMS coatings with there low surface energy ($\sim 22 \text{ mN m}^{-1}$) and low modulus^{[54][55]}, decrease the adhesion strength between the coating and fouling agents resulting in easy removal of the marine deposits and accumulations. However, PDMS coatings have low adhesion strength with the metal substrate and coatings peel-off is observed. To enhance the mechanical strength and adhesion properties of PDMS-based materials, chemical modification by the introduction of epoxy resin into the matrix has been employed^[56]. The epoxy modified PDMS materials have high mechanical strength as well as adhesion capacity. The combination of epoxy to the PDMS describes effective crosslinking, which improved its mechanical strength. The marine application test of epoxy modified polysiloxane resins demonstrated that very good antifouling property.

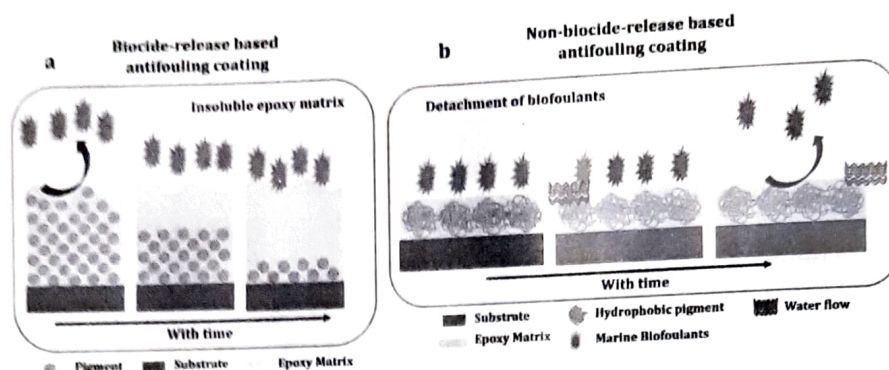


Fig. 3: Schematic representation of the mechanisms of antifouling coating

Similarly, Rath et al. have reported modification of aliphatic epoxy resin. In this case, pristine PDMS polymer capped by isocyanate group used with aliphatic epoxy resin, and the coating prepared by reacting with polyether diamine^[57]. The availability of silicone groups on the surface of the modified resins leads to a decrease in surface energy as well as roughness. The effectiveness of the modified resin towards the detachment of biofouling was tested by immersing the coating in seawater. The biofouling found formed on the coated surface after 60 days of immersion (slime and settlement of barnacles, oysters, polychaetes, and ascidians) got detached easily as compared to the unmodified resin. When the number of days of immersion increased from 60 to 90 days, some of the biofouling found remain attached after washing with running-hose water. This decrease in the antifouling property of the coating after 90 days was attributed to the water penetration into the layer of PDMS resulting in a change in the surface energy which promoted adhesion of the bio-organisms. Consequently, from the results of antifouling efficiency studied against the various category of microorganisms the coating can be considered better in comparison to commercial silicone formulations^[58].

CONCLUSIONS

Several encouraging developments in the quest for self-healing epoxy coatings are not devoid of limitations. Quantifying the “self-healing” property is required to compare the effectiveness of various mechanisms. Though standard electrochemical impedance spectroscopy is efficient for laboratory evaluation, evaluation under the aggressive salt-spray and other accelerated conditions are essential. Development of self-healing and the other functionality must consider the wide variability of the “trigger” – pH, ion concentration, damage force, and temperature. The major drawback with the hydrophobic surface is salinity, pH and temperature realized in application condition. The robustness of the hydrophobic modification must be tested considering these parameters. Though the research on anti-fouling epoxy-based coating is limited, more workable strategies are required for its development. Besides, the mechanism of the additive functionality must be scalable for larger adoption and cost-effective. Nevertheless, the development of the multifunctional epoxy coating will increase the scope of its application and will be a useful value addition to an already popular coating system.

REFERENCES

- [1] Pulikkalparambil H, Siengchin S, Parameswaranpillai J: Corrosion protective self-healing epoxy resin coatings based on inhibitor and polymeric healing agents encapsulated in organic and inorganic micro and nanocontainers, *Nano-Structures & Nano-Objects* 16, 381–395, 2018 doi:10.1016/j.nanoso.2018.09.010
- [2] Ma Y, Zhang Y, Liu J, Sun Y, Ge Y, Yan X and Wu J: Preparation and Characterization of Ethylenediamine-Polyurea Microcapsule Epoxy Self-Healing Coating, *Materials* 13: 326, 2020. doi:10.3390/ma13020326
- [3] Yuan D, Bonab VS, Patel A, Yilmaz T, Gross RA and Manas-Zloczower I: Design Strategy for Self-Healing Epoxy Coatings, *Coatings* 10: 50, 2020. doi:10.3390/coatings10010050
- [4] Daradmare S, Pradhan M, Raja VS, Parida S: Parametric studies of formation and morphology of sub-micron sized GO stabilized PS/GO containers encapsulating 8-HQ, *Polymer* 118: 116-126, 2017. doi:10.1016/j.polymer.2017.04.072

- [5] Huang Y, Deng L, Ju P, Huang L, Qian H, Zhang D, Li X, Terryn HA, and Mol JMC : Triple-Action Self-Healing Protective Coatings Based on Shape Memory Polymers Containing Dual-Function Microspheres, *ACS Appl. Mater. Interfaces* 10:23369-23379, 2018. doi:10.1021/acsami.8b06985
- [6] Odarczenko M, Thakare D, Li W, Yang K, Tang S, Venkateswaran SP, Sottos NR, and White SR, Self-Protecting Epoxy Coatings with Anticorrosion Microcapsules, *ACS Omega* 3:14157-14164, 2018. doi:10.1021/acsomega.8b01950
- [7] Kim C, Karayan AI, Milla J, Hassan M, and Castaneda H : Smart Coating Embedded with pH-Responsive Nanocapsules Containing a Corrosion Inhibiting Agent, *ACS Appl. Mater. Interfaces* 12:6451-6459, 2020. doi: 10.1021/acsami.9b20238
- [8] Su B, Tian Y, Jiang L Bio-inspired Interfaces with Super-Wettability: From Materials to Chemistry. *J. Am. Chem. Soc.* 138: 1727–1748, 2016. doi:10.1021/jacs.5b12728
- [9] Liu K, Cao M, Fujishima A, Jiang L: Bio-Inspired Titanium Dioxide Materials with Special Wettability and Their Applications. *Chem. Rev.* 114: 10044-10094, 2014. doi:10.1021/cr4006796
- [10] Darmanin T, Guittard F: Recent Advances in the Potential Applications of Bioinspired Superhydrophobic Materials. *J. Mater. Chem. A* 2: 16319–16359, 2014. doi:10.1039/C4TA02071E
- [11] Wang B, Zhang, Y, Shi, L, Li, J, Guo, Z : Advances in the Theory of Superhydrophobic Surfaces, *J. Mater. Chem.* 22: 20112-20127, 2012. doi:10.1039/C2JM32780E
- [12] Jia S, Deng S, Luo L, Qing Y, Yan N, Wu Y :Texturing commercial epoxy with hierarchical and porous structure for robust superhydrophobic coatings, *Applied Surface Science* 466: 84-91, 2019. doi:10.1016/j.apsusc.2018.10.017
- [13] Zhang XS, Zhu FY, Han MD, Sun XM, Peng XH, Zhang HX: Self-Cleaning Poly(dimethylsiloxane) Film with Functional Micro/ Nano Hierarchical Structures. *Langmuir* 29:10769-10775, 2019. doi:10.1021/la4023745
- [14] Ren TT, He JH : Substrate-versatile approach to robust antireflective and superhydrophobic coatings with excellent self-cleaning property in varied environments, *ACS Appl. Mater. Interfaces* 9: 34367–34376, 2019. doi:10.1021/acsami.7b11116
- [15] Ma XB, Shen L, Zhang YF, Liu WT, Zhai WT, Zheng : Porous superhydrophobic polymer/carbon composites for lightweight and self-cleaning EMI shielding application, *Compos. Sci. Technol.* 158: 86–93, 2018. doi:10.1016/j.compscitech.2018.02.006
- [16] Xing YJ, Xue YP, Song JL, Sun TK, Huang L, Liu X, Sun J: Superhydrophobic coatings on wood substrate for self-cleaning and EMI shielding, *Appl. Surf. Sci.* 436: 865–872, 2018. doi:10.1016/j.apsusc.2017.12.083
- [17] Yin K, Du HF, Dong XR, Wang C, Duan JA, He J: A simple way to achieve bioinspired hybrid wettability surface with micro/ nanopatterns for efficient fog collection, *Nanoscale* 9: 14620–14626, 2017. doi:10.1039/C7NR05683D
- [18] Nuraje N, Khan WS, Lei Y, Ceylan, M, Asmatulu R: Superhydrophobic Electrospun Nanofibers. *J. Mater. Chem. A* 1: 1929–1946, 2013. doi: 10.1039/C2TA00189F
- [19] Pakdel A, Bando Y, Golberg D: Morphology-driven Nonwettability of Nanostructured BN Surfaces. *Langmuir* 29: 7529–7533, 2013. doi:10.1021/la4004356
- [20] Zhang M, Pang JY, Bao WH, Zhang WB, Gao H, Wang CY, Shi JY, Li J: Antimicrobial cotton textiles with robust superhydrophobicity via plasma for oily water separation, *Appl. Surf. Sci.* 419: 16-23, 2017. doi:10.1016/j.apsusc.2017.05.008
- [21] Huang S, Song JL, Lu Y, Chen F, Zheng HX, Yang XL, Liu X, Sun J, Carmalt CJ, Parkin IP, Xu WJ : Underwater spontaneous pumpless transportation of nonpolar organic liquids on extreme wettability patterns, *ACS Appl. Mater. Interfaces* 8: 2942–2949, 2016. doi:10.1021/acsami.5b08596
- [22] Zhang X, Liu Z, Li Y, Wang C, Zhu Y, Wang H, Wang J :Robust superhydrophobic epoxy composite coating prepared by dual interfacial enhancement, *Chemical Engineering Journal* 371: 276–285, 2019. doi:10.1016/j.cej.2019.04.040
- [23] Chang KC, Lu HI, Peng CW, Lai M, Hsu S, Hsu M, Tsai Y, Chang C, Hung W, Wei Y, Yeh J : Nanocasting Technique to Prepare Lotus-leaf-like Superhydrophobic Electroactive Polyimide as Advanced Anticorrosive Coatings. *ACS Appl. Mater. Interfaces* 5: 1460–1467, 2013. doi:10.1021/am3029377
- [24] Guo J, Yang F, Guo Z: Fabrication of Stable and Durable Superhydrophobic Surface on Copper Substrates for Oil–water Separation and Ice-over Delay. *J. Colloid Interface Sci.* 466: 36–43, 2016. doi:10.1016/j.jcis.2015.12.015
- [25] Tian XC, Shaw S, Lind KR, Cademartiri L: Thermal processing of silicones for green, scalable, and healable superhydrophobic coatings, *Adv. Mater.* 28: 3677–3682, 2016. doi:10.1002/adma.20150644

- [26] Chen L, Sun XY, Hang JZ, Jin LJ, Shang D, Shi LY: Large-scale fabrication of robust superhydrophobic coatings with high rigidity and good flexibility, *Adv. Mater. Interfaces* 3: 1500718, 2016. doi:10.1002/admi.201500718
- [27] Song JL, Zhao DY, Han ZJ, Xu W, Lu Y, Liu B, Carmalt CJ, Deng X : Parkin IP, Super-robust superhydrophobic concrete, *J. Mater. Chem. A* 5: 14542–14550, 2017. doi:10.1039/c7ta03526h
- [28] Banerjee I, Pangule RC, Kane RS: Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms, *Adv. Mater.* 23: 690–718, 2011. doi:10.1002/adma.201001215
- [29] Nawaz M, Habib S, Khan A, Shakoor RA and Kahraman R: Cellulose microfibers (CMFs) as a smart carrier for autonomous self-healing in epoxy coatings, *New J. Chem.* 44: 5702, 2020. doi:10.1039/c9nj06436b
- [30] Daradmare S, Pradhan M, Raja VS, and Parida S: Encapsulating 8-hydroxyquinoline in graphene oxidestabilized polystyrene containers and its anticorrosion performance, *J Mater Sci* 51: 10262-10277, 2016. doi:10.1007/s10853-016-0254-4.
- [31] Zhou C, Li Z, Li J, Yuan T, Chen B, Ma X, Jiang D, Luo X, Chen D, Liu Y: Epoxy composite coating with excellent anticorrosion and self-healing performances based on multifunctional zeolitic imidazolate framework derived nanocontainers, *Chemical Engineering Journal* 385: 123835, 2020. doi: 10.1016/j.cej.2019.123835
- [32] Vijayan P, & Al-Maadeed MSA : TiO₂ nanotubes and mesoporous silica as containers in self-healing epoxy coatings, *Scientific Repo Rts* 6: 38812, 2016. doi: 10.1038/srep38812
- [33] Guo W, Jia Y, Tian K, Xu Z, Jiao J, Li R, Wu Y, Cao L, Wang H: UV-Triggered Self-Healing of a Single Robust SiO₂ Microcapsule Based on Cationic Polymerization for Potential Application in Aerospace Coatings, *ACS Appl. Mater. Interfaces* 8: 21046-21054, 2016. doi:10.1021/acsami.6b06091
- [34] Ye Y, Chen H, Zou Y, Ye Y, Zhao H : Corrosion protective mechanism of smart graphene-based self-healing coating on carbon steel, *Corrosion Science* 174: 108825, 2020. doi: 10.1016/j.corsci.2020.108825
- [35] Kongparakul S, Kornprasert S, Suriya P, Le D, Samart C, Chantarasiri N, Prasassarakich P, Guan G : Self-healing hybrid nanocomposite anticorrosive coating from epoxy/modified nanosilica/ perfluorooctyl triethoxysilane, *Progress in Organic Coatings* 104, pp 173–179, 2017. doi: 10.1016/j.porgcoat.2016.12.020
- [36] Njoku DI, Cui M, Xiao H, Shang B & Li Y :Understanding the anticorrosive protective mechanisms of modified epoxy coatings with improved barrier, active and selfhealing functionalities: EIS and spectroscopic techniques, *Scientific reports* 7: 15597, 2017. doi:10.1038/s41598-017-15845-0
- [37] Yuan D, Bonab VS, Patel A, Manas-Zloczower I : Self-healing epoxy coatings with enhanced properties and facile processability, *Polymer* 147: 196-201, 2018. doi: 10.1016/j.polymer.2018.06.017
- [38] Yi H, Deng Y, Wang C : Pickering emulsion-based fabrication of epoxy and amine microcapsules for dual core self-healing coating, *Composites Science and Technology* 133: 51-59, 2016. doi: 10.1016/j.compscitech.2016.07.022
- [39] Zhang C, Wang H, Zhou Q : Preparation and characterization of microcapsules based self-healing coatings containing epoxy ester as healing agent, *Progress in Organic Coatings* 125: 403-410, 2018. doi: 10.1016/j.porgcoat.2018.09.028
- [40] Safaei F, Khorasani SN, Rahnama H, Neisiany RE, Koochaki MS : Single microcapsules containing epoxy healing agent used for development in the fabrication of cost efficient self-healing epoxy coating, *Progress in Organic Coatings* 114: 40-46, 2018. doi: 10.1016/j.porgcoat.2017.09.019
- [41] Haddadi SA, Ramazani SAA, Mahdavian M, Taheri P, Mol JMC, Gonzalez- Garcia Y : Self-healing epoxy nanocomposite coatings based on dual-encapsulation of nano-carbon hollow spheres with film-forming resin and curing agent, *Composites Part B* 175: 107087, 2019. doi . 10.1016/j.compositesb.2019.107087
- [42] Tezel O, Çiği ABL, Kahraman MV : Design and development of self-healing coating based on thiol–epoxy reactions, *Reactive and Functional Polymers* 142: 69–76, 2019. doi: 10.1016/j.reactfunctpolym.2019.06.004
- [43] Atta AM, Ezzat AO, El-Saeed AM, Tawfeek AM, Sabeela NI :Self-healing of chemically bonded hybrid silica/epoxy for steel coating, *Progress in Organic Coatings* 141: 105549, 2020. doi 10.1016/j.porgcoat.2020.105549
- [44] Chen T, Fang L, Li X, Gao D, Lu C, Xu Z :Self-healing polymer coatings of polyurea-urethane/epoxy blends with reversible and dynamic bonds, *Progress in Organic Coatings* 147: 105876, 2020. doi: 10.1016/j.porgcoat.2020.105876

- [45] Hia IL, Chan ES, Chai SP and Pasbakhsh P: A novel repeated self-healing epoxy composite with alginate multicore microcapsules, *J. Mater. Chem. A* 6: 8470, 2018. doi: 10.1039/c8ta01783b
- [46] Fang L, Chen J, Zou Y, Xu Z and Lu C : Thermally-Induced Self-Healing Behaviors and Properties of Four Epoxy Coatings with Different Network Architectures, *Polymers* 9: 333, 2017. doi:10.3390/polym9080333
- [47] Li QT, Jiang MJ, Wu G, Chen L, Chen SC, Cao YX and Wang YZ : Photothermal Conversion Triggered Precisely Targeted Healing of Epoxy Resin Based on Thermoreversible Diels–Alder Network and Amino-Functionalized Carbon Nanotubes, *ACS Appl. Mater. Interfaces* 9: 20797–20807, 2017. doi:10.1021/acsami.7b01954
- [48] Peng C, Chen Z, Tiwari MK: All-organic superhydrophobic coatings with mechanochemical robustness and liquid impalement resistance, *Nat. Mater.* 17: 355, 2018. doi: 10.1039/c7ta03526h
- [49] Li C, Zhuang Z, Huang F, Wu Z, Hong Y, Lin Z: Recycling Rare Earth Elements from Industrial Wastewater with Flowerlike Nano-Mg(OH)₂, *ACS Appl. Mater. Interfaces* 5: 9719–9725, 2013. doi: 10.1021/am4027967
- [50] Wang M, Han XW, Liu L, Zeng X, Zou H, Wang J, Chen J: Transparent Aqueous Mg(OH)₂ Nanodispersion for Transparent and Flexible Polymer Film with Enhanced Flameretardant Property. *Ind. Eng. Chem. Res.* 54: 12805–12812, 2015. doi: 10.1021/acs.iecr.5b03172
- [51] Si Y, Guo Z, and Liu W : A Robust Epoxy Resins @ Stearic Acid-Mg(OH)₂ Micronanosheet Superhydrophobic Omnipotent Protective Coating for Real-Life Applications. *ACS Appl. Mater. Interfaces* 8: 16511–16520, 2016. doi: 10.1021/acsami.6b04668
- [52] Verma S, Mohanty S, Nayak SK : Preparation of hydrophobic epoxy–polydimethylsiloxane–graphene oxide nanocomposite coatings for antifouling application, *Soft Matter* 16: 1211–1226, 2020. doi: 10.1039/C9SM01952A
- [53] Yang J, Li J, Jia X, Li Y, and Song H: Fabrication of Robust and Transparent Slippery Coating with Hot Water Repellency, Antifouling Property, and Corrosion Resistance, *ACS Appl. Mater. Interfaces* 12: 28645–28654, 2020. doi: 10.1021/acsami.0c06743
- [54] Song Y, Liu M, Zhang L, Mu C, Hu X: Mechanistic interpretation of the curing kinetics of tetra-functional cyclosiloxanes, *Chem. Eng. J.* 328: 274–279, 2017. doi: 10.1016/j.cej.2017.07.036
- [55] Song Y, Tang X, Liang Y, Lee HY, Liu M, Zhang L, Bi S, Mu X, Hu X: Bioinspired reinforcement of cyclosiloxane hybrid polymer, *Chem. Commun. (Cambridge, England)* 54: 13415–13418, 2018. doi: 10.1039/C8CC06671J
- [56] Sun X, Chen R, Gao X, Liu Q, Liu J, Zhang H, Yu J, Liu P, Takahashi K, Wang J: Fabrication of epoxy modified polysiloxane with enhanced mechanical properties for marine antifouling application. *European Polymer Journal* 117: 77–85, 2019. doi: 10.1016/j.eurpolymj.2019.05.002
- [57] Rath SK, Chavan JG, Sasane S, Srivastava A, Patri M, Samui AB, Chakraborty BC and Sawant SN: Coatings of PDMS-modified epoxy via urethane linkage: Segmental correlation length, phase morphology, thermomechanical and surface behavior, *Prog. Org. Coat.* 65: 366–374, 2009. doi:10.1016/j.porgcoat.2009.02.007
- [58] Nurioglu AG, Esteves ACC, With G: Non-toxic, non-biocide-release antifouling coatings based on molecular structure design for marine applications. *J. Mater. Chem. B* 3: 6547–6570, 2015. doi: 10.1039/C5TB00232J

High performance specialized coatings for applications in corrosive environments

S.C. VANITHAKUMARI¹, R.P. GEORGE¹ and U. KAMACHI MUDALI^{2,*}

¹Corrosion Science and Technology Division, Metallurgy and Materials Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India.

²Heavy Water Board, Mumbai.

Abstract : In this paper a short review of various coatings developed based on facile as well as industrially scalable methods and the challenges encountered in enhancing the durability of the coatings in simulated service conditions are presented. These coatings include (i) development of noble metal (Pt/Pd) nanoparticle coated titanium electrodes for electrochemical processes employed in spent nuclear fuel reprocessing, and (ii) development of superhydrophobic (SHP) coatings on titanium, stainless steels, low-chromium steels and copper alloys to address corrosion and biofouling issues in chloride environments of condenser materials in nuclear power plants. Nanostructured noble metal (Pt, Pd) coatings on Titanium and titania nanotube for electrode applications were developed using a novel seed mediated coating technology involving electrodeposition assisted hydrothermal method. Studies demonstrated that by engineering the particle size of Pt, and nano-tubular self assembled arrays of TiO₂ (TiNT), the electrocatalytic activity for methanol oxidation could be enhanced ten times compared to polycrystalline Pt. By employing electrochemical cerium oxidation studies, excellent durability of this Pt nanoparticles coated TiNT electrode surpassing 1000 h in 11.5M nitric acid was also demonstrated. In the second part of the manuscript development of SHP coatings to address corrosion and biofouling issues in chloride medium of condenser materials such as titanium, stainless steels, low chromium steels and copper alloys is detailed. Inspired by the lotus effect two step techniques were adopted for creating a micro-nano roughness pattern, and reducing surface energy by coating with low surface energy material. Micro-nano texturing of different materials was achieved by various methods like polishing, pickling, anodization, sand blasting etc. Attempted different organic fatty acids and silica nanoparticles mixed silane, to enhance durability. Finally durable and stable SHP coatings were demonstrated with high water contact angle and corrosion resistance and reduced microbial attachment indicating superior bio corrosion resistance of the materials studied. Facile techniques were adopted for both coatings in order to support scaling up for real time applications in future.

Keywords: superhydrophobic, coating, biofouling, corrosion, electrode, titanium, nanotubes, nanoparticles, platinum, silanes, anodization

INTRODUCTION

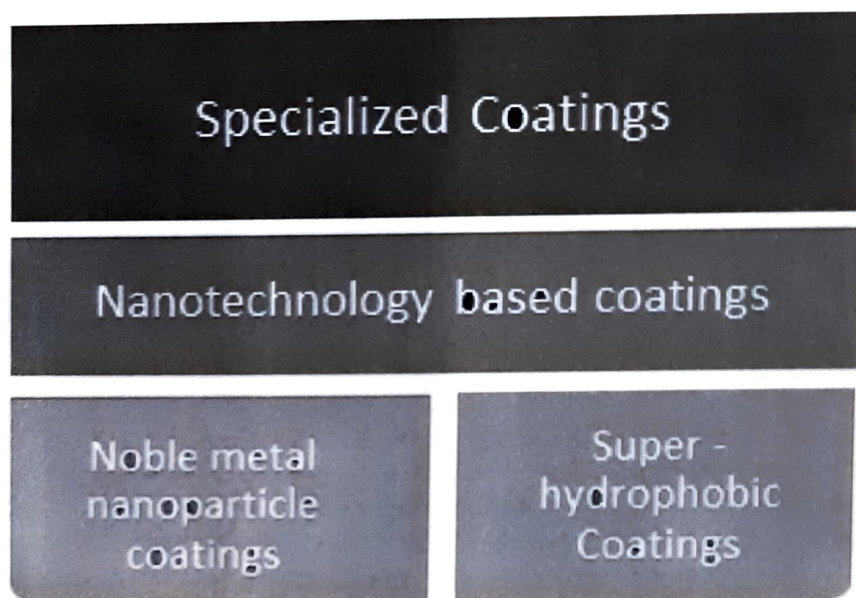
Coatings are known to mankind for a long time and they are employed for protective or decorative purposes or for both. The coatings may consist of organic or inorganic components depending on the application. Over the years, multifunctional coatings are preferred as they offer aesthetic appeal as well as protect the structure from corrosion which is one of the major degradation mechanisms. Electrocatalytic coatings, superhydrophobic (SHP) coatings, self healing coatings, antifouling coatings, oleophobic coatings, thermochromic coatings and so on are the new class of coatings developed for high performance. Depending upon a specific requirement or on identifying a gap area, a suitable coating or surface modification technology can be adapted and improvised to suit the application. In this review two different coatings (Scheme 1) developed for specific applications such as nano Pt/Pd coated electrodes for electro-oxidation of spent nuclear fuels and SHP coatings for corrosion and biofouling resistances are discussed.

Nano Pt/Pd coated electrodes for electrocatalytic applications

In India, a closed fuel cycle policy is followed to ensure long term energy security. Therefore, reprocessing of spent nuclear fuel is of paramount importance in Indian context. Various chemical and electrochemical methods have been employed for the reprocessing of spent nuclear fuel. The electrolyte used for these electrochemical methods is usually high concentrated nitric acid under boiling conditions. Normal electrode materials cannot

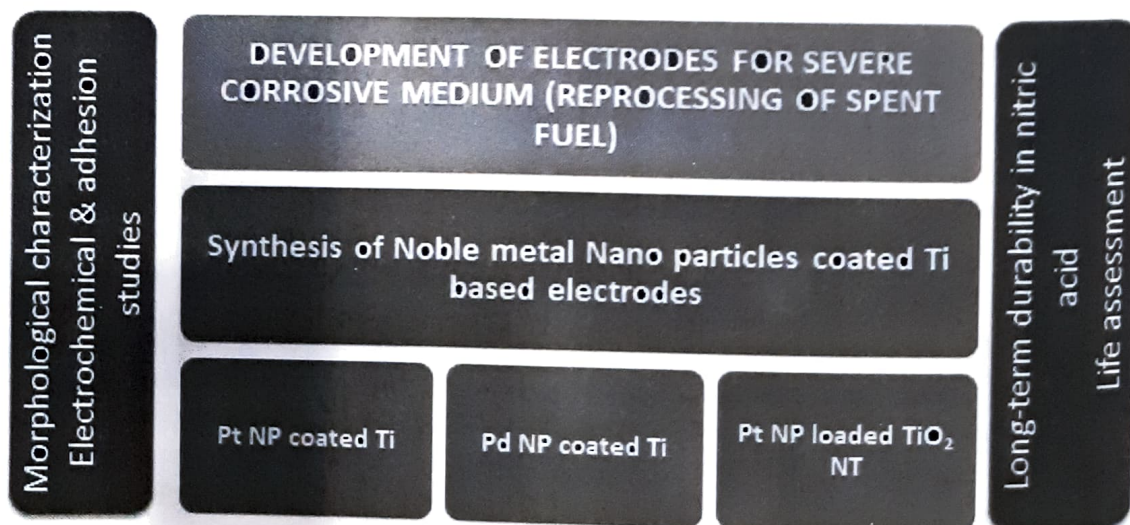
*Corresponding Author. Email : ukmudali1@gmail.com (U. Kamachi Mudali)

Scheme - 1



with stand this severe condition. Platinum is considered for electrode application as it exhibits good corrosion resistance, conductivity and electrocatalytic activity. But economic feasibility and severity of the corrosive environment titanium coated Pt electrodes are preferred when compared to bulk platinum as electrode. Due to the potential for new application and improving the established activities, intense research is going on to design novel platinum and platinum based nanomaterials with unique properties. Platinum being a precious metal, efforts are being made to synthesize Pt-based catalysts with increased catalytic efficiency and low platinum utilization by tailoring the size and shape of nano materials. Recent studies show that reduction in size to nanoscale improved the electrocatalytic activity of Pt. Hence it was decided to synthesize, characterize and study the electrochemical activity of nano Pt coated Ti for electrode application (Scheme 2). The present work deals with the development of Pt and Pd nano particle coated Ti electrode using electrodeposition assisted hydrothermal method. Attempts were also made to enhance the surface area of Ti by anodization leading to the formation of TiO_2 nanotube and coat nano Pt particle on this TiO_2 layer by similar method.

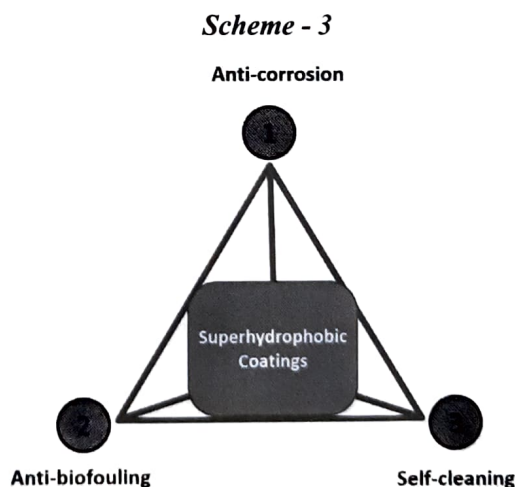
Scheme - 2



SHP coatings for corrosion and biofouling resistances

The cooling water systems in power plants are susceptible to fouling and corrosion which pose a big threat to achieve and maintain the highest possible electrical energy output. The microbes present in the natural sources of cooling water such as rivers, seawater etc., form a complex biofilm on the material surface which hamper the heat transfer property of the condensers. Biofilms also accelerate microbiologically influenced corrosion (MIC) beneath these deposits. The adhesion of microbes on the condenser pipe surface is the first step in biofilm formation leading to biofouling and corrosion. Hence it is beneficial to prevent bacterial attachment and biofilm formation. Environmental concerns drive antifouling technology towards more nonbiocidal or non-toxic approaches based on controlling the surface chemistry, topography and catalytic activity that have significant impacts on the interactions between microorganisms and the surface. Low-surface-energy materials, surface hydrophobicity, photocatalytic activity of certain materials such as titanium and micro-nano topography resist/reduce the attachment of biofouling organisms.

Materials with superhydrophobic properties inspired by leaves, flowers, plants and insects are highly desirable for many potential applications. Thin film silane coating has been introduced as a chromium free multi metal surface pretreatment for corrosion protection, adhesion promotion and surface passivation of metals such as aluminium, steel, zinc, magnesium and others. Controlling the surface energy and the roughness is hence fundamental to achieve the superhydrophobicity. The fabrication methods that are simple, economical and scalable are preferred for preparing self-cleaning superhydrophobic coatings on various substrates such as glass, metal and composites. In this review, the superhydrophobic coatings developed on various materials for antibacterial as well as anticorrosion applications (Scheme 3) were discussed in the context of marine and sea water applications.

**NOBLE METAL NANO PARTICLE BASED COATINGS FOR ELECTRODE APPLICATIONS*****Nano platinum particle based coatings***

Nanotechnology is considered as one of the key technologies of the 21st century, which has a huge impact on the society particularly in areas such as energy, environment, electronics and healthcare. The current focus in nanotechnology is to develop smart coatings with self cleaning and self healing ability, flexible electronics, targeted drug delivery, water purification and green energy. Thus the field of nanoscience and nanotechnology is ever expanding and there is broad scope to develop new materials and technologies that find real time applications.

Reprocessing of spent nuclear fuel forms the back end of the fuel cycle in nuclear industry. There are several industrial processes involved in the reprocessing of nuclear fuel. Electro-oxidative dissolution is one of the advanced techniques preferred for faster and complete dissolution of Pu-rich oxide/carbide fuels of fast

breeder reactors (FBR) over conventional method of refluxing in concentrated nitric acid. The efficiency of the electrochemical processes in the reprocessing plant highly depends on the endurance of the anode in radio-toxic environment. Noble metals especially metallic Pt/Pd based electrodes are considered as outstanding candidates for the electro oxidative dissolution technique. Accordingly, dimensionally stable anodes (DSA) such as mixed oxide coated titanium anodes (MOCTA)^[1] and mixed oxide coated titanium anodes-glazed (MOCTAG)^[2, 3] were developed in early 90s for employing them as anodes in the dissolution and purification processes of the spent (U, Pu) C fuel of fast breeder test reactor (FBTR) in India.

In order to overcome the limitations due to cost, uniformity and adherence of the coating on the base titanium substrate, nanotechnology based seed mediated hydrothermal method was employed to develop Pt and Pd nanoparticle coated titanium electrodes^[4,5] for nitric acid applications. Initially Pt nanoparticle coated titanium substrate was fabricated and the performance was analyzed in severe corrosive environments. There are two steps^[6] involved in the fabrication of nano platinum coated Ti electrodes (NPCT): (i) electrodeposition of Pt nuclei on titanium substrate and (ii) hydrothermal reduction to ensure uniform and complete coverage of the base substrate. The optimized experimental conditions for electrodeposition of Pt nanoparticle on titanium were 1 mM chloroplatinic acid with 0.5 M sulphuric acid as supporting electrolyte for a duration of 60 s at a voltage of -0.08 V^[7]. Field Emission Scanning Electron microscope (FESEM) images showed the deposition of Pt seeds of average size 130 nm on the titanium surface, the higher magnification images revealed the flower shaped morphology of Pt seeds. Further Pt seed deposited Ti substrate was subjected to hydrothermal reduction in a teflon lined stainless steel (SS) autoclave containing chloroplatinic acid, formaldehyde and hydrochloric acid at 100°C for 10 h. The electrodeposited Pt nuclei acted as seed and enhanced further growth and coverage during hydrothermal reduction. The thickness of the Pt nanoparticle coating on titanium substrate was estimated to be around 10 µm. NPCT electrode was subjected to cross hatch tape test to evaluate the adhesion of the Pt coating on the titanium substrate. The electrodes showed a perfect 5B as per ASTM D 3359^[8]. X-ray Photoelectron Spectroscopy (XPS) and X-ray diffraction (XRD) analysis confirmed the presence of metallic Pt in the coating. The complete coverage of the electrode surface and the adherent coating are essential for industrial applications and the NPCT electrode was found to satisfy both these requirements.

The electrocatalytic activity of the NPCT electrode was evaluated by calculating the electrochemically active surface area by conducting hydrogen adsorption - desorption studies in 1 M H₂SO₄ at the scan rate of 100 mVs⁻¹ and the charge associated is calculated from the cyclic voltammogram. The active surface area for NPCT substrate was found to be 108 times higher than that for polycrystalline platinum. It is worthy to note here that the geometrical area is the same for both the electrodes. Similarly, NPCT electrodes performed better than the polycrystalline Pt in oxygen reduction reactions which further confirmed the electrocatalytic activity of the NPCT electrode. The electrocatalytic activity of the NPCT electrode was further validated for methanol oxidation^[8] and the relative intensity ratio of the forward and reverse anodic peak currents, I_f / I_b was found to be 1.55 which was comparable to Pt based catalysts reported in literature and commercially available Pt/Carbon^[9-11].

Ce (III) / Ce (IV) is chosen as the mediated redox catalyst for the electro oxidative dissolution of Pu-rich spent mixed carbide fuel discharged from the Fast Breeder Test Reactor (FBTR) at Kalpakkam. Therefore the efficiency of the synthesized NPCT electrode was evaluated by employing it as anode in the electro oxidation of cerous ions in 11.5 M nitric acid at 0.1 A constant current supplied to the cell^[8]. Since the active surface area of NPCT was 108 times higher than the polycrystalline platinum electrode, complete cerium oxidation was accomplished within 55 % of the time required for the oxidation with polycrystalline Pt electrode. Scanning Electron Microscopy (SEM) analysis revealed that there was no significant damage to the Pt coating on the titanium surface after this experiment. To further evaluate the long term performance of NPCT electrode, the electrode was tested in 11.5 M nitric acid at 9 mA/cm² current density for about 1000 h. The conversion percentage of Ce(III) in 11.5 M nitric acid was found to be better compared to that of polycrystalline Pt. No delamination was observed even after 1000 h

of operation in severe corrosive nitric acid condition at high current density. Stability of the NPCT electrode was evaluated using an advanced characterization technique such as in situ electrochemical atomic force microscopy (ECAFM) in 1 M nitric acid. The morphology and rms roughness of the coating were continuously monitored with applied voltage. The electrode surface was found to be intact upto 4 V applied voltage while in continuous immersion in nitric acid.

Though the NPCT electrode was robust upto 1000 h in extreme conditions, it was felt that the performance could be further enhanced by anodizing the titanium substrate thereby facilitating the formation of titania nanotubes. These nanotubes offer many advantages such as high specific area, corrosion resistance, thermal stability and non-toxicity to name a few. Moreover, vertically aligned TiO_2 nanotubes ensure more dispersion of platinum nanoparticles and serve as better electrode material [12-15]. Anodization was chosen for the fabrication of vertically aligned titania nanotubes on titanium [16,17]. Commercially pure titanium foil was anodized in ammonium fluoride and ethylene glycol at a voltage of 30 for 1 h. Then the anodized titanium substrate was annealed at 450 °C for 3 h to retain crystallinity of the titania nanotubes. FESEM studies showed that the inner diameter of the nanotubes was 85 ± 5 nm and the vertical length was approx. 1 μm [18]. Similar to NPCT electrode, anodized titania nanotubes were subjected to electrodeposition and then hydrothermal reduction for the deposition of Pt nanoparticles (Figure 1). Cross section FESEM and transmission electron microscopy (TEM) analysis confirmed the loading of Pt nanoparticles of size 46 to 200 nm both inside and outside the titania nanotubes. The electrochemically active surface area (ECSA) of Pt nanoparticle coated Ti was found to be more than Pt nanoparticle loaded TiNT because more number of Pt nanoparticles are present on the titanium surface than Pt nanoparticle loaded TiNT. XPS results showed that there is an interaction between the TiNT surface and the Pt nanoparticles whereas similar interaction was absent in the case of NPCT electrode. This interaction is assumed to be responsible for the enhanced electrocatalytic activity of the Pt nanoparticle loaded TiNT electrode for methanol electro oxidation and oxygen reduction reaction. The electrocatalytic activity of Pt deposited on TiO_2 nanotube was found to be ten times more than that of NPCT. In the earlier reports also similar results [19] were discussed highlighting the better contact area between the TiNT support and the Pt nanoparticles resulting in better catalytic activity and stability.

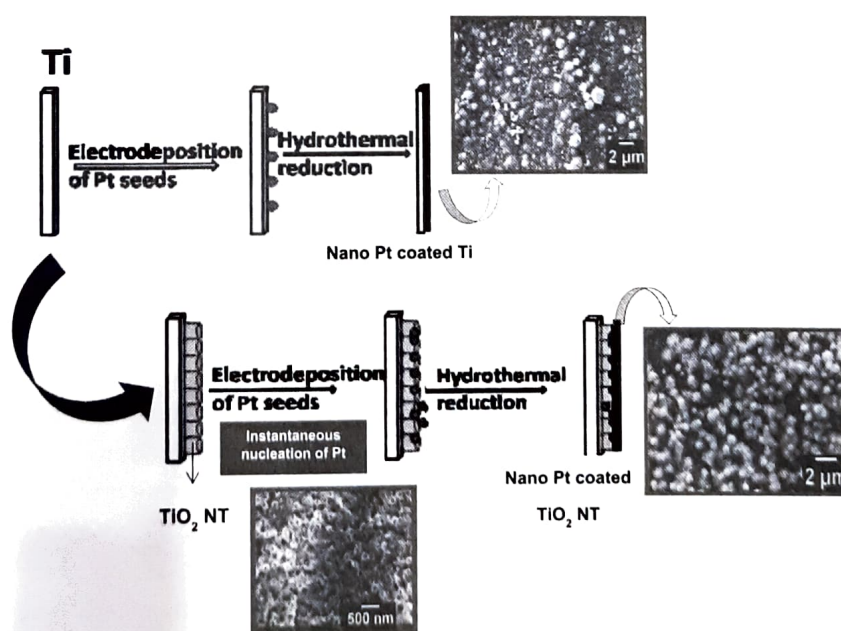


Fig. 1. Seed mediated hydrothermal reduction of Pt nanoparticles on titanium substrate and titania nanotubes.

Nano palladium particle based coatings

Another noble metal that could be an alternative to Pt is Pd. It is an ideal candidate possessing good electrocatalytic activity and it is one of the highly active catalysts after Pt in acidic and alkaline media^[20-23]. Several attempts were made to enhance the electrocatalytic activity of Pd by a simple and effective approach of dispersing smaller nanostructures of Pd on suitable support, since the electrocatalytic activity highly depends on dispersion and size/shape of metal nanoparticles. Similarly, support material should possess good surface area, excellent conductivity, high corrosion resistance and so on in the process medium and the most widely used supporting materials for dispersing Pd nanoparticles are CNT^[24], Ti^[25], TiO₂^[26] and graphene oxide^[27]. Most notable support material is Ti with its chemical stability and excellent corrosion resistance in high acidic medium make Ti and Ti based supports more suitable for the dispersion of Pt and Pd nanoparticles for electrode application. There are several methods reported in the literature for the synthesis of supported Pd nanoparticles which include chemical reduction of Pd complex, vapor-liquid-solid (VLS) growth techniques, ion exchange method, hydrothermal reduction and electrochemical synthesis. However, chemical reduction of metal salt precursor in the presence of template or seed mediated growth method^[28-30] are preferred due to simplicity, low cost and high dispersion of uniform sized nanoparticles. The experience gained from the development of Pt nanoparticle coated Ti / TiNT surfaces assured that seed mediated hydrothermal reduction method was effective for uniform and better surface coverage of metal nanoparticle. Development of Pd nanoparticle via a seeding approach is quite new and very less literatures are available so far.

Palladium seed particles were deposited chronoamperometrically from 1 mM Palladium chloride in 0.5 M H₂SO₄ for 20 s at 0.40 V. The Ti substrate with electrodeposited Pd seeds was then transferred to a Teflon lined stainless steel autoclave for hydrothermal reduction in 5 mM PdCl₂ solution along with 0.5 % formaldehyde reducing agent for 10 h at 180°C. FESEM and high resolution transmission electron microscopy (HRTEM) images confirmed the presence of solid, sharp edged cubic, triangular, truncated triangular, octahedron shaped Pd nanoparticles with an average size ranging from 20 to 80 nm in the coating. It is worthy to note here that the Pd nanoparticles coating was not as uniform as the Pt coating and the base titanium substrate remained uncovered in many spots. Nevertheless, the electrocatalytic activity of Pd nanoparticle on titanium substrate in acidic medium was confirmed by hydrogen adsorption-desorption studies^[31].

Performance evaluation of electrode coatings

The stability and durability of these three electrodes namely Pt nanoparticle coated Ti, Pt nanoparticle coated TiO₂ nanotubes and Pd nanoparticle coated Ti synthesized via seed mediated hydrothermal reduction method were evaluated. The comparison of electrode properties like adhesion of coating to substrate, ease of synthesis, stability of coating and electrocatalytic activity for Ce oxidation were studied. As described in ASTM D 3559-09, both Pt nanoparticles coated Ti and TiNT were ranked as 5B and Pd nanoparticles coated Ti as 1B. Pt nanoparticles possessed excellent adhesion to Ti and TiNT substrates whereas, Pd nanoparticles were loosely coated over Ti substrate. The performance of Pt nanoparticles coated TiNT, Pt and Pd nanoparticle coated Ti electrodes were investigated by employing it as anode in the oxidation of cerous ions under an applied current of 0.1 A in 11.5 N nitric acid. Pt nanoparticle coated TiNT electrode accomplished 100 % conversion of Ce³⁺ to Ce⁴⁺ within 2h 15 min and Pt nanoparticles coated Ti electrode completed in 2h 30 min (Figure 2), whereas both polycrystalline Pt and commercially available Pt plated titanium anodes could complete the conversion after 4.5 h. In the case of Pd nanoparticle coated Ti electrode initially electrode was found to be electrochemically active but after 30 min of the experiment the loosely adhered Pd nanoparticles detached from the Ti substrate resulting in reduced reaction rate and subsequent electrode failure.

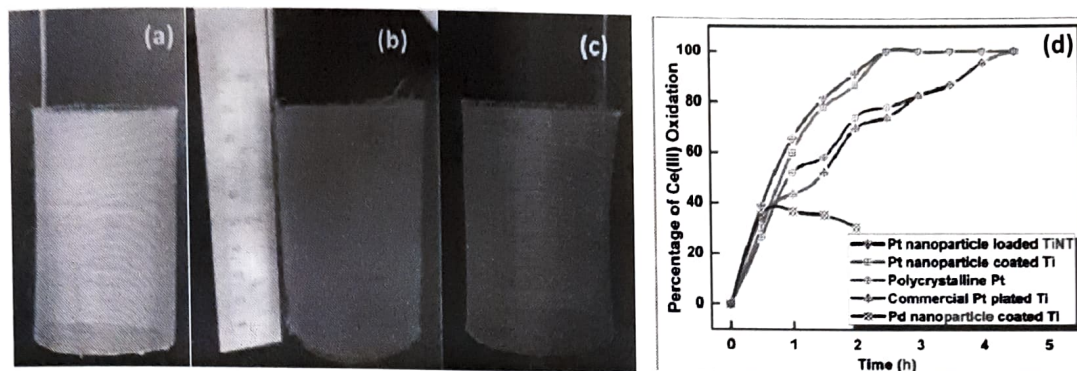


Fig. 2. Photographs of the Ti mesh (5 cm diameter and 8 cm length) electrode (a) without coating, (b) Pt nanoparticle coated Ti mesh, (c) Anodized and Pt loaded Ti mesh and (d) the performance of electrodes for the electro-oxidation of Ce in 11.5 N nitric acid (Reprinted from ref^[31] K.R. Rasmi, Ph. D thesis, Active and noble nanostructured coatings to enhance corrosion resistance of electrode materials, HBNI University, Kalpakkam, India, 2016; Figure 2a&b Reprinted with permission from ref^[8] Copyright Springer 2017)

Finally Pt nanoparticle coated Ti and TiNT electrodes were chosen for life assessment studies as anode for electro-oxidation of Ce in 11.5M nitric acid under an applied operational current density of 9 mA/cm² which is similar to reprocessing plant conditions^[8]. The life of Pt nanoparticle coated TiNT electrode was 1728 h and the coating was still intact whereas the life of Pt nanoparticle coated Ti was 1152 h and cracks were noticed in the coating after the experiment as evident from FESEM studies^[32]. Since Pt coated TiNT electrode showed excellent durability it was exposed in the simulated reprocessing solution containing a representative fraction of low-activity actinides and fission products in 11.5 N nitric acid in a mock-up of the service dissolver vessel^[33] for about 1185 h at 110°C. The morphology, chemical composition and electrocatalytic activity of the Pt nanoparticle coated TiNT electrode was evaluated after exposure. The morphological and compositional studies confirmed the presence of metallic Pt nanoparticles on the electrode surface with some localised cracking after exposure and the electrochemically active surface area of the Pt nanoparticle coated TiNT electrode after exposure was found to be twice that of polycrystalline platinum thus establishing its durability and efficiency.

Thus the development and systematic evaluation of the durability of the electrodes would pave the way to develop many binary alloys of noble metal nanoparticles like Pt-Pd, Pt-Ir alloys to generate an electrode surface with improved catalytic activity than individual noble metals. There is also scope for exploring the possibility of employing Pt nanoparticle coated Ti/TiNT electrode for other electrochemical processes in reprocessing related applications such as electrochemical reduction of uranium, destruction of soluble organic waste and electrolytic destruction of nitric acid before waste disposal.

SUPERHYDROPHOBIC COATINGS WITH CORROSION AND BIOFOULING RESISTANCES

A close observation of nature provides inspiration to poets as well as scientists; the nature is an open source and anybody can adapt its ideas. This study has drawn its motivation from the self-cleaning and superhydrophobic surface of lotus leaf. Extreme water repellent superhydrophobic coating with water contact angle more than 150° has caught the attention of corrosion researchers in the recent decade and attempts are being made to explore the possibility of using them to protect metals and alloys against corrosion.

A detailed microscopic observation of the lotus leaves in SEM and AFM showed micro-nano features namely papillae and a wax-like coating (Figure 3). Motivated by the lotus effect in which water droplets falling on the leaves bead up and roll off, superhydrophobic surface modification (Scheme 4) was carried out on engineering materials such as titanium^[34-36], chrome-moly steels^[37,38], marine steel^[39] and copper alloys^[40,41] for corrosion and biofouling resistance in aqueous environments by providing suitable surface roughness and micro chemistry. Tailor-made experimental approaches were employed depending on the material chosen. The long term stability and durability of the as developed materials were studied in detail^[42].

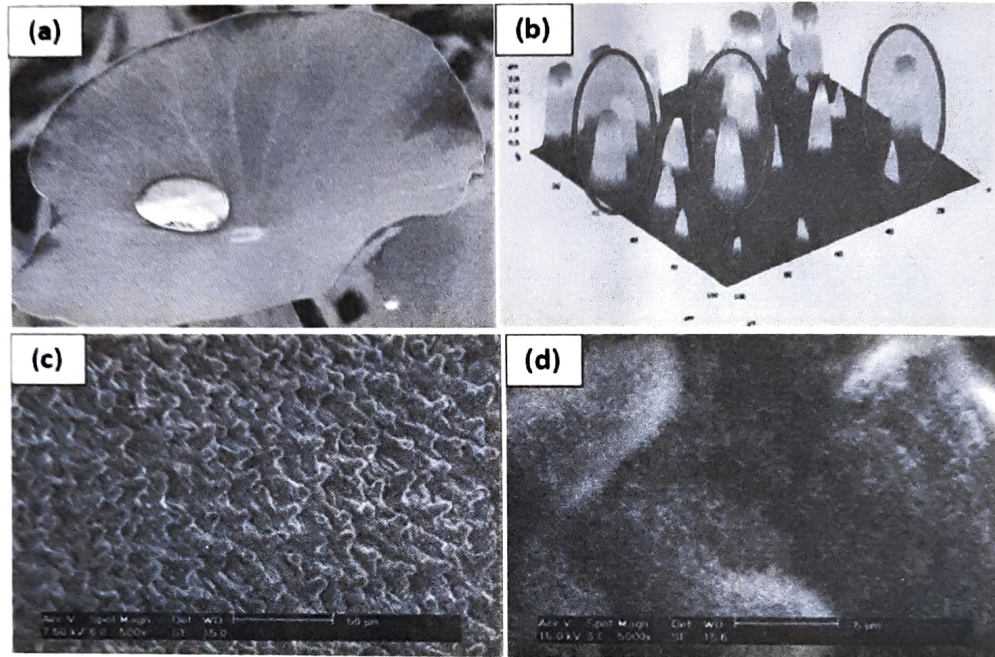
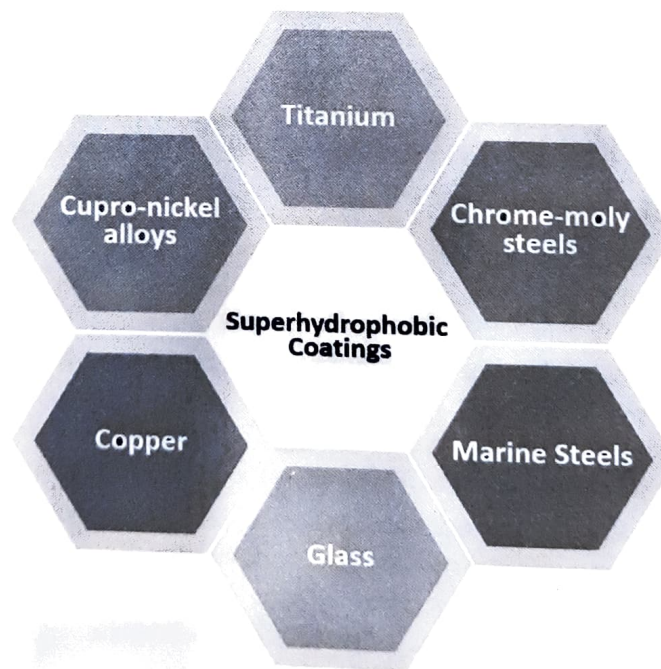


Fig. 3. (a) Photograph of water droplet on lotus leaf, (b) AFM image of lotus leaf indicating two different scale papillae, (c&d) SEM micrographs showing the distribution of the papillae and the nanocrystal wax pins on the papillae.

Scheme - 4



Titanium

SHP surface modification of titanium (Figure 4) was attempted to address the corrosion and biofouling problems of titanium which is used as condenser tubes in the seawater-cooled nuclear power plants. The main objective was to carry out a systematic study on the stability and durability of SHP coating on titanium for long term practical applications^[42]. The SHP Ti samples were prepared by abrading, pickling, anodization, dip coating in silane and heat treatment. The as-prepared SHP samples showed heterogeneous lotus leaf-like morphology on the surface with an average water contact angle of 150°. Attenuated total reflectance – infrared spectroscopy (ATR-IR)

confirmed the presence of silanol groups on the anodized titanium surface. The adhesion strength and scratch resistance of the coatings on Ti was confirmed by cross hatch tape test. The samples scored a perfect 5B as per ASTM D3359-09. In addition, the mechanical stability of the coatings was ascertained by ultrasonication, water impact tests and flowing water conditions. SHP titanium showed excellent chemical stability in chloride medium for a period of 60 days. There was minimal reduction in WCA after UV exposure for 3 h and no reduction in WCA after low temperature heat treatment at 50°C for 6 h. The bacterial adhesion studies showed one order reduction in bacterial density in the case of SHP Ti samples compared to control samples over a period of 60 days, with the SHP surfaces still maintaining minimal antibacterial activity. The shelf life of the SHP coatings on Ti was evaluated to be around 2 years in ambient conditions. SHP Ti samples were exposed in sea water kept in a flat cell and the impedance data was recorded in 15, 30, 45 and 60 days. SHP property was retained in the samples after exposing them for 60 days in sea water. The feasibility of scaling up the SHP modification procedure developed for Ti coupons to Ti with any geometry including tubes was also demonstrated. SHP modification was carried out with Ti (CP Grade 2) tubes of 4 cm length, 19 mm ID and 0.7 mm thickness. SHP Ti tubes showed a water contact angle of $147^{\circ} \pm 2^{\circ}$ on the outer side of the tube and the water rolled off the tube surface with a slight disturbance.

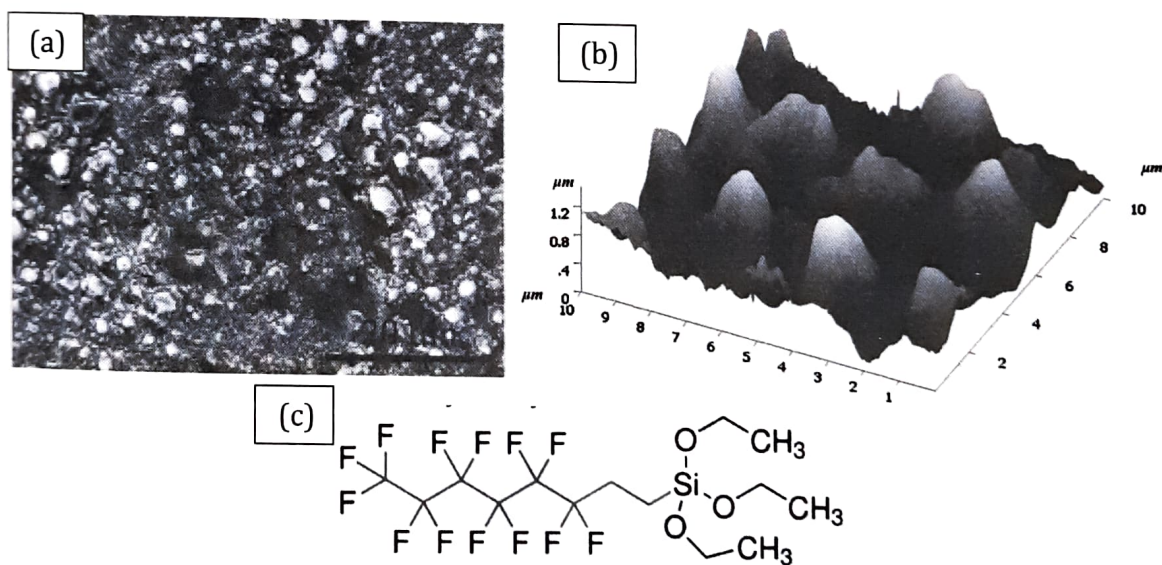


Fig.4. (a) SEM micrograph and (b) AFM image of a superhydrophobic titanium surface and (c) Molecular formula for the silane used in the surface modification of Titanium (1H, 1H, 2H, 2H Perfluorooctyltriethoxysilane, PFOTES). (Reprinted with permission from ref [36] Copyright Elsevier 2014)

Subsequent to these tests, the stability and / or coating durability of SHP silane coating on anodized Ti substrate in different environmental conditions was assessed by employing atomic force microscope (AFM) in Kelvin Probe Force mode (KPFM)^[43]. AFM topography images and surface potential images of the SHP samples before and after exposure were recorded and corroborated with the surface roughness and water contact angle values. The SKPFM mapping results (surface potential measurements) revealed that only partial removal of the SHP silane coatings from anodized Ti surface after exposure to the UV light and flowing water system. The results succinctly showed that the SHP silane coated Ti is exceptionally stable in the aggressive environments.

Chrome-Moly steels

With the successful superhydrophobic surface modification of titanium, SHP coatings were fabricated by incorporating hydrophilic silica (HS) nanoparticles in ethanolic perfluorooctyl triethoxy silane (PFOTES) solution on mod. 9Cr-1Mo substrate^[37,38]. 9Cr-1Mo ferritic steel and its modified versions are the favored steam generator tubing material in fast reactors. Even though these classes of steels have far excellent mechanical properties, high temperature corrosion resistance and high resistance to chloride induced stress corrosion cracking in water-

steam systems, they are susceptible to localized and general corrosion. Prolonged time lag was found from storage, fabrication stages to commissioning and installation stage. Hence modifying the surface to get a SHP coating that can reduce chloride ions condensation leading to general and localized corrosion in the humid coastal environments during transit, storage and installation in the coastal power plant is a need of the hour. Therefore, a SHP coating may impart good corrosion resistance to retain the integrity of the 9Cr-1Mo steel during storage period. In this regard, coatings containing optimum amounts of PFOTES and HS exhibited superhydrophobic property with high water contact angle (WCA) of $150^\circ \pm 1^\circ$ and low sliding angle of 2° . AFM and SEM studies have shown micro-nano features on the surface. The synergistic effect of these micro-nano features and the low surface energy silane coating was responsible for the observed superhydrophobicity of the samples. The surface topographic structure is an important factor that influences the surface wettability^[44]. As described by Cassie-Baxter equation^[45,46],

$$\cos \theta^* = f_s \cos \theta_s + f_v \cos \theta_v \quad (1)$$

where θ^* is the apparent WCA value of rough surfaces, θ_s and θ_v are the intrinsic WCA values of smooth flat surfaces of solid and air respectively. f_s and f_v are the fraction of the projecting solid and air on the surface respectively. If θ_v is considered to be the surface fraction area of air ($\theta_v = 180^\circ$) and $f_s + f_v = 1$ $f_s + f_v = 1$, then eq (1) can be written as

$$\cos \theta^* = f_s (\cos \theta_s + 1) - 1 \quad (2)$$

By using equation (2), the f_s value was calculated as 0.17, where $\theta^* = 150^\circ$ and $\theta_s = 102^\circ$. From this f_s value, it can be concluded that the small fraction of contact area between the liquid droplet and solid surface allows the droplet to roll off easily over the surface^[47-49]. The large fraction of air gaps trapped within the interstices of microtextured surface increased the air/water interface, which in turn effectively prevented the penetration of water droplets into the grooves.

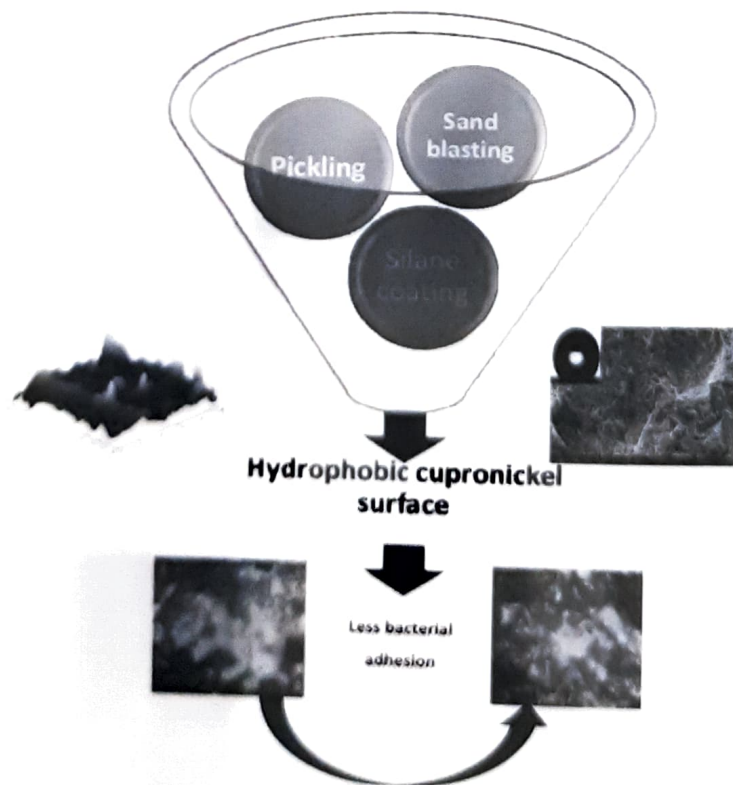


Fig. 5. Superhydrophobic surface modification of cupro-nickel alloys (Reprinted with permission from ref [40] Copyright Elsevier 2018)

The self-cleaning characteristics of the SHP mod. 9Cr-1Mo substrate surface were also examined. Coatings were contaminated by spreading saw dust on the SHP mod. 9Cr-1Mo substrate surfaces randomly. The contaminated substrate was then secured on a tilting stage (2° tilt) and water droplets (total volume $5\ \mu\text{L}$) were dropped onto the surface from a specified height. The removal of saw dust particles by the water droplets for SHP mod. 9Cr-1Mo substrate was imaged using Goniometer with a CCD camera. As discussed earlier, superhydrophobicity is a novel strategy that has been widely employed as antibacterial coating in recent times. Superhydrophobicity reduces the adhesion force between bacteria and a solid surface which enable the relatively easy removal of bacteria by conventional cleaning methods before a thick and adherent biofilm is formed on the surface. The antibacterial activity of the SHP mod. 9Cr-1Mo substrate was enhanced by an order compared to uncoated mod. 9Cr-1Mo substrate when exposed to *Pseudomonas* sp. culture. Open circuit potential (OCP) and EIS studies were carried out to evaluate the enhancement of corrosion resistance properties of SHP 9Cr-1Mo steel surfaces in 0.005M chloride environment. The OCP shifted to nobler direction indicating the good passive behavior of the SHP coating^[50,51] and the impedance values are one order more than the control samples. These results are mainly attributed to the SHP coatings which prevent the accumulation of corrosive species or water on their surface, resulting in superior anticorrosion property.

Marine steels

Lotus effect based superhydrophobic coatings were developed on marine steels^[39] to inhibit biofouling. The aim of this work is to develop superhydrophobic coatings on alloys that are used in marine environment. In this regard, DMR 249A was modified using mechanical methods such as polishing and shot / grit / glass bead blasting and finally dip coated with a low-surface energy material such as silane. The surface modification resulted in water contact angles of about 150° and tilting angles less than 5° . The surface treatment directly influenced the morphology and surface roughness of the samples, for example, glass bead blasted samples exhibited the maximum water repelling property and showed the least bacterial adhesion compared to shot blasted and grit blasted samples. The bacterial adhesion on the glass bead blasted and silane coated DMR steel samples was five orders of magnitude less than that of the as-received samples when exposed to *Pseudomonas* sp. culture. The aim of this work is to stress the unconventional use of superhydrophobic coatings based on silanes to inhibit biofouling on marine steels.

Copper alloys

Cupronickel alloys are used as condenser materials in the seawater cooled systems owing to copper toxicity towards microbes. However, there is also a possibility of copper resistant microbes forming biofilms on these alloys leading to microbiologically influenced corrosion (MIC) during prolonged service in seawater. In order to address these issues, hydrophobic cupronickel alloys were prepared by using a combination of chemical and mechanical methods such as polishing, acid pickling, sand blasting and a low surface energy silane coating^[40]. The surface profile, morphology, roughness and the water contact angle of the two different surface pretreated samples were analyzed. The bacterial adhesion studies in gram negative *Pseudomonas* sp. culture revealed that the sandblasted, pickled and silane coated cupronickel samples (WCA~ 140°) exhibited better resistance to bacterial adhesion compared to the polished, pickled and silane coated (WCA~ 135°) cupronickel samples. In comparison with the as-received samples, a significant reduction of the bacterial density on surface modified samples was observed.

Superdrophobic coating on copper was made by employing a facile and economic synthesis procedure including annealing and coating the surface with silica nanoparticles dispersed in silane solution^[41]. The annealed Cu surface was uniformly covered with spherical micron-sized copper oxide particles and significantly enhanced

surface roughness as evident from morphology studies. The composition analysis showed that an outer layer of CuO and inner layer containing mixture of CuO and Cu₂O phases have formed on the annealed Cu surface. This surface was further dip coated in silica nanoparticles dispersed silane solution resulting in dense agglomerates of silanized silica nanoparticles uniformly distributed on the surface. The as developed copper surface exhibited a superhydrophobic behavior with water contact angle (WCA) of $147^{\circ} \pm 0.1^{\circ}$ and tilting angle of 5° with the critical surface energy of 17.72 mN/m as calculated from Zisman plot. SHP Cu was immersed in de-mineralized (DM) water in ambient conditions for about 8 months and no significant reduction in water contact angles was noticed. Electrochemical studies carried out in aqueous chloride environments demonstrated the corrosion resistance of superhydrophobic copper surface as evident from the shift in open-circuit potential (OCP) values towards the nobler direction, increase in the charge transfer resistance and lower anodic current as compared with the fresh copper foil. The evaluation of the short term durability of the SHP Cu foil in aqueous chloride environments using EIS technique showed that the corrosion resistance improved with time indicating the self-healing nature of the copper oxide layers formed on the SHP Cu foil.

Glass

As a spin-off from the superhydrophobic surface modification of metals and alloys for anticorrosion and antibiofouling applications, attempts were made to synthesize one dimensional ZnO nanorods on glass substrates^[52] using solution based techniques such as successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD). The glass substrates were finally coated with a low surface energy PFOTES silane. The surfaces with water contact angle greater than or equal to 150° are called superhydrophobic surfaces and if such surfaces have contact angle hysteresis less than or equal to 10° , they are said to possess self cleaning property. The surfaces with self cleaning properties play an important role in various technical and practical applications such as self cleaning windows, antireflective and protective coatings for solar panels, water repellent textiles and low friction surfaces for fluid flow. The as developed SHP glass slides were proposed for solar panel applications. The effect of air pockets in increasing contact angle was demonstrated by measuring sliding angle and contact angle hysteresis. The fraction of solid to liquid contact area according to modified Cassie's equation was theoretically calculated to be 4%. The water repellent silane coated one-dimensional ZnO nanostructures showed a water contact angle of 148° with a sliding angle of 1° and the contact angle hysteresis of 2° . This study clearly brought out the significance of the underlying mechanism of superhydrophobic self cleaning coatings on glass substrates based on one dimensional ZnO nanorods.

SUMMARY

Electrocatalytically active Pt/Pd nano particle coated Ti electrodes with excellent corrosion resistance and high catalytic activity were developed which could be employed in reprocessing plants as anodes for electro-oxidative dissolution of spent nuclear fuel in severely corrosive boiling 11.5 M nitric acid medium.

Pt nanoparticles were deposited over titanium substrate and also loaded into titania nano tubes for electrode applications. A seed mediated hydrothermal reduction method was developed and customized to fabricate such electrodes. The electrocatalytic activity of the electrode as well as the stability and durability of the electrodes were excellent in lab as well as simulated plant conditions.

Superhydrophobic coatings were developed on titanium, chrome-moly steels, marine steels, copper alloys with reduced bacterial attachment and enhanced corrosion resistance for applications in marine environments. Superhydrophobic coatings were also developed on glass slides with self cleaning property for solar panel related applications.

REFERENCES

- [1] U. Kamachi Mudali, R.K. Dayal and J.B. Gnanamoorthy: Mixed $\text{RuO}_2/\text{TiO}_2/\text{PtO}_2$ coated titanium anodes for the electrolytic dissolution of nuclear fuels. *Nucl Tech.* 100:395–402, 1992.
- [2] U. Kamachi Mudali, V.R. Raju and R.K. Dayal: Preparation and characterisation of platinum and platinum-iridium coated titanium electrodes. *J Nucl Mater.* 277:49–56, 1999.
- [3] Baldev Raj and U. Kamachi Mudali: Materials development and corrosion problems in nuclear fuel reprocessing plants. *Prog Nucl Ener.* 48:283–313, 2006.
- [4] A. Chen and P.H. Hindle: Platinum-Based Nanostructured Materials: Synthesis, Properties, and Applications. *Chem. Rev.* 110:3767–3804, 2010.
- [5] A.L. Cheng, N.H. Kwi, N.B. Minh-Phuong, P. X. Hung, H.H. Myung, I. Muhammad, S.K. Yong, and H.S. Gi: Morphology-Controlled Synthesis and electrocatalytic Characteristics of Platinum Structures on MicroPatterned Carbon Nanotube Platforms. *J. Appl. Electrochem.* 41:1425–1431, 2011.
- [6] K.R. Rasmi, S.C. Vanithakumari, R.P. George and U. Kamachi Mudali: Synthesis and characterization of nano structured platinum coated titanium as electrode material. *J Mater. Eng. Perf.* 23:1673–1679, 2014.
- [7] K.R. Rasmi, S.C. Vanithakumari, R.P. George, C. Mallika and U. Kamachi Mudali: Development and performance evaluation of nano platinum coated titanium electrode for application in nitric acid medium. *Mater. Chem. Phys.* 151:133–139, 2015.
- [8] K.R. Rasmi, S.C. Vanithakumari, R.P. George, C. Mallika and U. Kamachi Mudali: Stability and durability study of nano Pt coated titanium for electrode application. *Trans IIM* 70:1689–1696, 2017.
- [9] B.K. Jena, C.R. Raj: Electrocatalytic Applications of Nanosized Pt Particles Self-Assembled on Sol–Gel-Derived Three-Dimensional Silicate Network. *J. Phys. Chem. C* 112:3496, 2008.
- [10] Z. Liu, X.Y. Ling, X. Su, J.Y. Lee: Carbon-Supported Pt and PtRu Nanoparticles as Catalysts for a Direct Methanol Fuel Cell. *J. Phys. Chem. B* 108:8234, 2004.
- [11] Y. Lin, X. Cui, C. Yen, C.M. Wai: Platinum/Carbon Nanotube Nanocomposite Synthesized in Supercritical Fluid as Electrocatalysts for Low-Temperature Fuel Cells. *J Phys. Chem. B* 109:14410, 2005.
- [12] F. Hu, F. Ding, S. Song, P. K. Shen, Pd electrocatalyst supported on carbonized TiO_2 nanotube for ethanol oxidation. *J. Power Sources* 163, 415, 2006.
- [13] S. Beak, D. Jung, K. S. Nahm, P. Kim: Preparation of Highly Dispersed Pt on TiO_2 -Modified Carbon for the Application to Oxygen Reduction Reaction. *Catal. Lett.*, 134:288–294, 2010.
- [14] C. Zhai, M. Zhu, D. Bin, H. Wang, Y. Du, C. Wang, P Yang: Visible-light-assisted electrocatalytic oxidation of methanol using reduced graphene oxide modified Pt nanoflowers- TiO_2 nanotube arrays. *ACS Appl. Mater. Interf.* 6:17753–17761, 2014.
- [15] Y. Lei, G. Zhao, X. Tong, M. Liu, D. Li, R. Geng: High Electrocatalytic Activity of Pt–Pd Binary Sphero-crystals Chemically Assembled in Vertically Aligned TiO_2 Nanotubes. *Chem. Phys. Chem.* 11:276–284, 2010.
- [16] C. Ruan, M. Paulose, O. K. Varghese, G. K. Mor, C. A. Grimes: Fabrication of Highly Ordered TiO_2 Nanotube Arrays Using an Organic Electrolyte. *J. Phys. Chem. B* 109:15754–15759, 2005.
- [17] D. Gong, C. A Grimes, O. K. Varghese, W. Hu, R. S. Singh, Z. Chen, E. C Dickey: Titanium oxide nanotube arrays prepared by anodic oxidation. *J. Mater. Res.* 16:3331–3334, 2001.
- [18] K.R. Rasmi, S.C. Vanithakumari, R.P. George, C. Mallika and U. Kamachi Mudali: Nanoparticles of Pt loaded on vertically aligned TiO_2 nanotube bed: Synthesis and evaluation of electrocatalytic activity. *RSC Adv.* 5:108050–108057, 2015.
- [19] H. Li, J. Wang, M. Liu, H. Wang, P. Su, J. Wu, J. Li: A nanoporous oxide interlayer makes better Pt catalyst on a metallic substrate: Nanoflowers on a nanotube bed. *Nano Research* 7:1007–1017, 2014.
- [20] M. Shao: Palladium-based electrocatalysts for hydrogen oxidation and oxygen reduction reactions. *J. Pow. Sour.* 196:2433–2444, 2011.
- [21] M. Shao, J. Odell, M. Humbert, T. Yu, Y. Xia: Electrocatalysis on Shape-Controlled Palladium Nanocrystals: Oxygen Reduction Reaction and Formic Acid Oxidation. *J. Phys. Chem. C* 117: 4172–4180, 2013.
- [22] X. Tong, M. Aindow, J. Farr: Electrocatalytic Performance of Pd Nanoparticles Supported on SiC Nanowires for Methanol Oxidation in Alkaline Media. *Fuel Cells* 11:907–910, 2011.
- [23] C.A. Rice, A. Bauskar, P.G. Pickup: Recent advances in electrocatalysis of formic acid oxidation, Electrocatalysis in fuel cells. p. 69–87, Springer, 2013.

- [24] D.J. Guo, H.L. Li: Electrochemical synthesis of Pd nanoparticles on functional MWNT surfaces. *Electrochem. Commun.* 6, 999-1003, 2004.
- [25] J. Liu, J. Ye, C. Xu, S.P. Jiang, Y. Tong: Kinetics of ethanol electrooxidation at Pd electrodeposited on Ti. *Electrochem. Commun.* 9:2334-2339, 2007.
- [26] W.E. Kaden, W.A. Kunkel, M.D. Kane, F.S. Roberts, S.L. Anderson: Size-Dependent Oxygen Activation Efficiency over Pd/TiO₂(110) for the CO Oxidation Reaction. *J. Am. Chem. Soc.*, 132:13097-13099, 2010.
- [27] X. Chen, G. Wu, J. Chen, X. Chen, Z. Xie, X. Wang: Synthesis of "Clean" and Well-Dispersive Pd Nanoparticles with Excellent Electrocatalytic Property on Graphene Oxide. *J. Am. Chem. Soc.* 133: 3693-3695, 2011.
- [28] H. Chen, G. Wei, A. Ispas, S.G. Hickey, A. Eychmuller: Synthesis of Palladium Nanoparticles and Their Applications for Surface-Enhanced Raman Scattering and Electrocatalysis. *J. Phys. Chem. C* 114:21976-21981, 2010.
- [29] T.K. Sau, C.J. Murphy: Seeded High Yield Synthesis of Short Au Nanorods in Aqueous Solution. *Langmuir* 20:6414-6420, 2004.
- [30] A.A. Umar, M. Oyama: A cast seed-mediated growth method for preparing gold nanoparticle-attached indium tin oxide surfaces. *Appl. Surf. Sci.* 253:2196-2202, 2006.
- [31] K.R. Rasmi: Ph. D thesis, Active and noble nanostructured coatings to enhance corrosion resistance of electrode materials, HBNI University, Kalpakkam, India.
- [32] K.R. Rasmi, S.C. Vanithakumari, R.P. George and U. Kamachi Mudali: Performance evaluation of platinum nanoparticle coated titanium electrodes. *NACE Mater. Perf.* 56:48-52, 2017.
- [33] S.C. Vanithakumari, K. Thyagarajan, C. Thinaharan, K.R. Rasmi, R.P. George and John Philip: On the durability of Pt coated Ti electrodes for the electro-oxidative dissolution of spent nuclear fuels. *Corro. Eng. Sci. Tech.* 55:48-56, 2020.
- [34] P.V. Mahalakshmi, S.C. Vanithakumari, Judy Gopal, U. Kamachi Mudali and Baldev Raj: Enhancing corrosion and biofouling resistances through superhydrophobic surface modification. *Curr. Sci.* 101:1328-1336, 2011.
- [35] S.C. Vanithakumari, R.P. George and U. Kamachi Mudali: Enhancement of corrosion performance of titanium by micro-nano texturing. *NACE Corrosion Journal* 69:804-812, 2013.
- [36] S.C. Vanithakumari, R.P. George and U. Kamachi Mudali: Influence of silanes on the wettability of anodized titanium. *Appl. Surf. Sci.* 292:650-657, 2014.
- [37] M. Ezhil Vizhi, S.C. Vanithakumari, R.P. George, S. Vasantha and U. Kamachi Mudali: Superhydrophobic surface modification of 9Cr-1Mo ferritic steel using PFOTES. *Surf. Eng.* 32:139-146, 2016.
- [38] M. Ezhil Vizhi, S.C. Vanithakumari, R.P. George, S. Vasantha and U. Kamachi Mudali: Superhydrophobic coating on mod. 9Cr-1Mo ferritic steel for enhancing corrosion resistance and antibacterial activity. *Trans IIM* 69:1311-1318, 2016.
- [39] S.C. Vanithakumari, Prashant Yadavalli, R.P. George and U. Kamachi Mudali: Lotus effect based superhydrophobic coatings on marine steels to inhibit biofouling. *Surf. Innov.* 3:115-126, 2015.
- [40] S.C. Vanithakumari, Prashant Yadavalli, R.P. George, C. Mallika and U. Kamachi Mudali: Development of hydrophobic cupronickel surface with biofouling resistance by sandblasting. *Surf. Coat. Tech.* 345:89-95, 2018.
- [41] S.C. Vanithakumari, R.P. George, U. Kamachi Mudali and John Philip: Development of superhydrophobic coating on copper for enhanced corrosion resistance in chloride medium. *Trans IIM* 72:1133-1143, 2019.
- [42] S.C. Vanithakumari, R.P. George and U. Kamachi Mudali: Stability and durability of superhydrophobic coatings developed on titanium. *J Mater. Eng. Perf.* 26:2640-2648, 2017.
- [43] K. Indira, S.C. Vanithakumari, U. Kamachi Mudali and C. Mallika: Probing the stability of superhydrophobic (SHP) silane coating on anodized Ti substrate using Kelvin Probe Force Microscope (KPFM). *Trans IIM* 72:3045-3055, 2018.
- [44] H. Liu, S. Szunerits, W. Xu and R. Boukherroub: Preparation of superhydrophobic coatings on Zinc as effective corrosion barriers. *ACS Appl. Mater. Interf.* 6:1150-1153, 2009.
- [45] N. Gao and Y. Yan: Modeling superhydrophobic contact angles and wetting transition. *J. Bionic Eng.* 6:335-340, 2009.
- [46] A. B. D. Cassie and S. Baxter: Wettability of porous surfaces. *Trans. Faraday Soc.*, 40:546-551, 1994.
- [47] S. Sarkar, S. Patra, S. K. Bera, G. K. Paul and R. Ghosh: Water repellent Zn nanowire arrays synthesized by simple solvothermal technique. *Mater. Lett.*, 64:460-462, 2012.

- [48] J. Jia, J. Fan, B. Xu and H. Dong: Microstructure and properties of the super-hydrophobic films fabricated on magnesium alloys. *J. Alloys Comp.* 554:142–146, 2013.
- [49] K. Nakasa, R. Wang and A. Yamamoto: Superhydrophobicity produced by vapour deposition of a hydrophobic layer onto fine protrusions formed by sputter-etching of steels. *Surf. Coat. Technol.* 210:113–121, 2012.
- [50] S. Ningshen, U. Kamachi Mudali, P. Mukherjee, A. Sarkar, P. Barat, N. Padhy and Baldev Raj: Influence of oxygen ion irradiation on the corrosion aspects of Ti-5% Ta-2% Nb alloy and oxide coated titanium. *Corros. Sci.* 50:2124-2134, 2008.
- [51] N. Padhy, S. Kamal, R. Chandra, U. Kamachi Mudali and Baldev Raj: Corrosion performance of TiO₂ coated type 304L stainless steel in nitric acid medium. *Surf. Coat. Technol.* 204:2782-2788, 2010.
- [52] S. Sutha, S.C. Vanithakumari, R.P. George, U. Kamachi Mudali, Baldev Raj and K.R. Ravi: Studies on the influence of surface morphology of ZnO nail beds on easy roll off of water droplets. *Appl. Surf. Sci.* 347:839-848, 2015.

Formation and growth of iron-zinc intermetallics during annealing treatment of galvanized steel

G.K. MANDAL¹*, M. DUTTA², TIPU KUMAR¹, AVIK MONDAL², M.G. WALUNJ¹, S. K. MISHRA¹, S. K. DAS¹, R. PAIS² and L.C. PATHAK¹

¹CSIR- National Metallurgical Laboratory, Jamshedpur - 831007, India

²Tata Steel Ltd. Jamshedpur - 831007, India

Abstract : The development of desired microstructure of galvanized sheet requires in-depth understanding of the formation and growth kinetics of various Fe-Zn intermetallic phases in the coating during post-treatment after hot dipping of the strip in liquid zinc alloy bath. Keeping this in view, annealing treatment of as-received commercial galvanized sheets, obtained from low (0.135 wt.% Al) and high (0.2 wt.% Al) aluminium containing zinc bath, is carried out to examine the microstructure of annealed sheet with varying strip annealing duration at a fixed galvannealing temperature. The effect of the bath aluminium concentration on the formation of the inhibition layer and on the formation mechanisms of various Fe-Zn intermetallics during subsequent galvannealing (GA) treatment is investigated. Strip annealing simulation is performed using Gleeble® 3800 thermo-mechanical simulator. A detailed characterization of the annealed specimens is carried out to study the galvannealed microstructure produced with varying annealing parameters for both the galvanized specimens obtained from commercial liquid zinc alloy bath with varying aluminium content. A systematic study of annealing treatment of galvanized sheet is performed to enhance the understanding of the role of reacted aluminium present at the interface of the substrate and coating in controlling the nucleation and growth kinetics of Fe-Zn phases to obtain the optimum galvannealed structure. It is observed that high aluminium galvanized bath hinders the formation of the desired sequence of Fe-Zn intermetallics in the coating during annealing treatment. However, galvannealed coating formed using low Al-containing zinc bath shows the desired sequence of various Fe-Zn intermetallics with favourable galvannealed microstructure mainly consisted of compact delta (δ) phase, particularly after annealing for 20s at 470°C.

Key Words: Galvannealing Simulation, Gleeble, Interface, Microstructure and GDOES

INTRODUCTION

There is a remarkable increase in the use of hot-dip galvannealed (GA) sheet products in recent years, particularly in automobile industries. The extensive use of galvannealed sheet is not only due to its affordability but also due to its excellent properties including good corrosion resistance and superior weldability and paintability over galvanized (GI) sheet [1-3]. The industrial production of galvannealed coating in continuous hot-dip galvanized process line requires stringent control of processing parameters for obtaining high quality coating with favorable formation of desired sequence and amount of various iron-zinc intermetallics in the phase structure [4-10]. The production of galvannealed coating involved dipping of pre-heated steel strip into a liquid zinc alloy bath containing aluminium generally less than a critical value (liquid Zn with ~0.135wt.% Al) to favour the formation of extremely thin and/or discontinuous Fe-Al inhibition layer at the substrate-coating interface [11-13]. As soon as steel strip is taken out of the liquid zinc alloy bath, the coated strip is subjected to inline annealing treatment with a suitable combination of annealing temperature and time. The annealing treatment, immediately after hot dipping of steel strip in liquid zinc alloy bath, will assist the solid-state diffusion of iron from substrate surface towards the coating for the favorable formation of various Fe-Zn intermetallic phases within the coating. Optimum galvannealed coating consists of a desired sequence and amount of a range of Fe-Zn intermetallic phases with maximum delta (δ) layer, a very thin layer (generally less than 1 μm) of brittle gamma and gamma₁ (Γ and Γ') intermetallic phases at the substrate-delta (δ) phase interface with negligible presence of zeta (ζ) crystals at the top surface location of the coating [14]. Presence of very few zeta (ζ) crystals at the top surface of the coating is preferable to improve the coating paintability. Another aim of galvannealed coated microstructure is to reduce the formation of brittle gamma and gamma₁

*Corresponding Author, E-mail: gopi@nmlindia.org

(Γ and Γ_2) intermetallic phases at the interface of substrate and coating to improve the resistance to powdering and flaking during forming operation.

Optimum galvannealing treatment strives for better control of the outward movement of iron atoms from substrate surface towards coating, which depends on the dissolution kinetics of aluminium rich interfacial layer as well as nucleation and growth mechanisms of individual Fe-Zn phases^[15]. It is noted that formation and growth kinetics of different Fe-Zn intermetallic phases strongly depends on many factors including substrate chemistry, aluminium concentration in liquid zinc bath as well as time-temperature schedule of galvannealing process^[11-16]. Therefore, it is imperative to develop a comprehensive understanding of the formation and growth mechanisms of various Fe-Zn intermetallics in the coating for better control of process parameters to achieve the desired GA microstructure.

Many investigators have studied the galvannealing treatment of galvanized coating by varying the process parameters such as bath aluminium concentration, annealing time and temperature^[1, 15, 17-20]. One of the main focus areas of most of these studies is to establish a good linkage of overall coating iron content and individual Fe-Zn intermetallic phase layer formation with galvannealing process parameters. Keeping in view the stringent requirement of process parameters to produce the desired complex microstructure of galvannealed coating further study in this direction will definitely assist to improve the understanding on formation and growth mechanisms of Fe-Zn phases.

In view of the above, present investigation is carried out to examine the microstructure of the galvannealed sheet with varying annealing duration at a fixed galvannealing temperature. Annealing experiments are performed on as-received commercial galvanized sheets obtained from low (0.135 wt.% Al) and high (0.2 wt.% Al) aluminium containing commercial zinc bath. One of the main aims of this study is to investigate the effect of the bath aluminium concentration on the formation of inhibition layer and on the formation mechanisms of various Fe-Zn intermetallics during subsequent galvannealing (GA) treatment. A systematic study of annealing treatment of galvanized sheet is performed to enhance the understanding of the role of reacted aluminium present at the interface location of the substrate and coating in controlling the nucleation and growth kinetics of Fe-Zn phases to obtain the optimum galvannealed coated structure.

EXPERIMENTAL

The as-received hot dip galvanized (GI) sheets obtained from Plant A and Plant B were used as a starting material for annealing experiments. The GI sheet obtained from Plant A was produced using iron saturated liquid zinc bath having ~0.135 wt.% aluminium. GI specimen of Plant B was obtained using a standard iron saturated liquid zinc galvanized bath containing ~0.2 wt.% aluminium. Both Plant A and Plant B specimens were obtained by dipping the steel substrate into the iron saturated Zn-Al bath for about 4s at the bath temperature of ~460°C. It is understood that specimen dipped into a liquid zinc bath containing a low concentration of aluminium (~0.135 wt.%) is expected to form discontinuous aluminium rich inhibition layer at the substrate-coating interface, whereas GI specimen obtained from high aluminium containing zinc bath will result in the formation of stable continuous Fe-Al based interfacial layer at the substrate-coating interface. Therefore, one of the main aims of this study is to investigate the effect of the bath aluminium concentration on the formation of inhibition layer and on the formation mechanisms of various Fe-Zn intermetallics during subsequent galvannealing (GA) process. The hot dip coated specimens obtained from Plant A and Plant B are refereed as AR-1 and AR-2, respectively in the subsequent text.

Figure 1 shows the schematic representation of a typical thermal cycle generally used in the plant for producing galvannealed (GA) coating. Immediately after dipping in liquid zinc alloy bath, the excess liquid zinc from the substrate surface is removed by air wiping, placed just above the commercial galvanized bath, to obtain the required coating thickness. Therefore, the temperature of the coated surface will be reduced during air wiping. Immediately after air wiping, an induction furnace is used for rapid heating of the coated strip to galvannealing temperature, which is in the range of 450-550°C. Thereafter, the coated strip is isothermally annealed inside the soaking furnace for desired galvannealing duration before air-cooling to room temperature. Based on the operating

parameters of galvannealing plant, the process window for annealing treatment of as-received GI specimens was adopted to study the development of various Fe-Zn phases within the coating by varying the annealing duration for a particular galvannealing temperature.

Based on the plant operating line speed (80-120 mpm), the average residence time for isothermal annealing treatment of as-dipped coated steel sheet in a GA plant was calculated to be in the range of 10-20s. Specimens for annealing experiments were prepared by sectioning the as-received plant specimen with pieces of dimensions 260 mm long and 50 mm wide. These pieces were used for strip annealing simulation using Gleeble® 3800 thermo-mechanical simulator. Figure 2(a) shows the pictorial view of strip annealing simulation along with the position of sample and thermocouples inside the simulation chamber of Gleeble. The as-received galvanized specimens of AR-1 were heated at a linear heating rate of 10°C/s to the isothermal annealing temperature of 470°C with varying time steps of 10, 15 and 20s to study the development of Fe-Zn intermetallic phases in the coating. Immediately after annealing at 470°C for a specific duration, the specimens were forced air-cooled. The AR-2 GI specimens were heated at a relatively faster heating rate of 50°C/s to higher galvannealing temperature of 500°C with varying isothermal holding duration of 0, 5 and 30s. The relatively faster heating rate and higher isothermal annealing temperature with a shorter holding time of 0s and 5s were chosen mainly to capture the dissolution kinetics of thin stable continuous Al-rich inhibition layer, which is expected to be present at the substrate-coating interface of AR-2 GI specimen. Keeping in the view of slower diffusion kinetics of Fe through the inhibition layer, a relative higher isothermal annealing temperature of 500°C with longer holding duration of 30s is also considered.

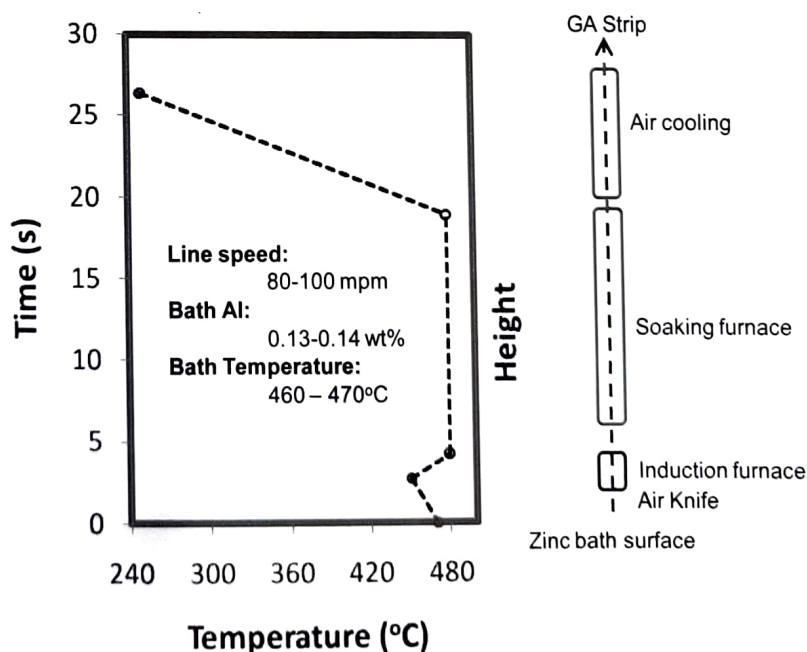


Fig. 1: Schematic representation of a typical galvannealing process

Table 1 summarizes the experimental parameters used for the annealing study. Figure 2(b) shows the picture of a typical galvannealed coating obtained after annealing experiment along with location of three thermocouples attached on the specimen surface. One thermocouple was attached at the centre point on the top surface of the specimen, the second one at 3 cm away from the centre point along the centre line of the specimen in the longitudinal direction and the third one was attached at one side of the strip about 2.5 cm away from the centre point in the width direction. Temperature variations among the thermocouples were within $\pm 2^{\circ}\text{C}$. Overall temperature variation of the specimen during annealing experiment was within $\pm 5^{\circ}\text{C}$.

Table 1: Experimental parameters for annealing study

Sample	Heating rate	Annealing temperature (°C)	Annealing time (s)	Cooling condition
AR-1	10°C/s	470	10	Forced Air
			15	
			20	
AR-2	50°C/s	500	0	Forced Air
			05	
			30	

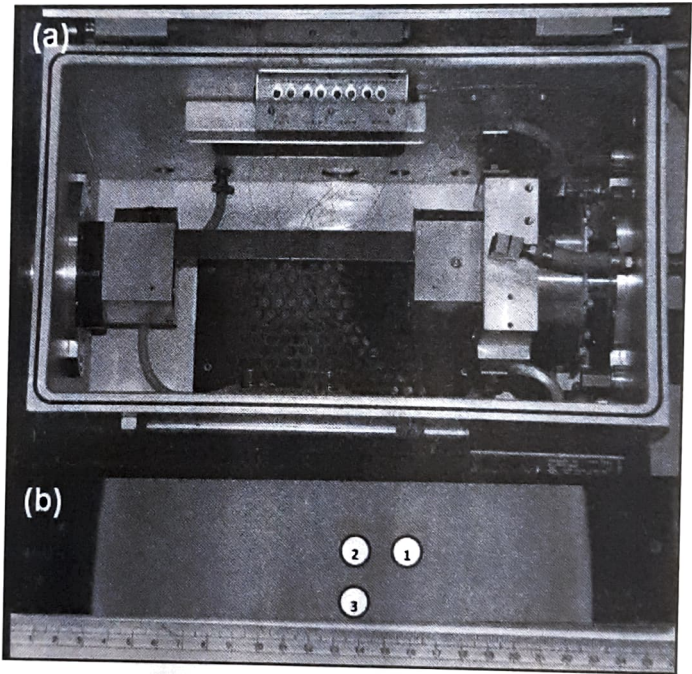


Fig. 2: Pictorial view of (a) strip annealing simulation carried out using Gleeble and (b) specimen after annealing experiment with position of three thermocouples on the specimen surface

The specimens for metallographic characterization were prepared using the standard metallographic techniques. A detailed characterization of the galvanized and galvannealed specimens were carried out using scanning electron microscopy (SEM) attached with Energy-dispersive X-ray spectroscopy (EDS) and glow discharge optical emission spectroscopy (GDOES). GDOES (LECO GDS-850A) was used for the quantitative depth profiling of various elements present in the coating. Quantitative depth profiling plots were taken from top surface of the coating at three different locations from the each specimen. An average of these three GDOES test data obtained from three different locations of the coated surface were used for the estimation of coating thickness and overall coating iron content.

RESULTS AND DISCUSSION

The low magnification cross-sectional scanning electron micrographs of the galvanized coatings (AR-1) reveal the presence of a continuous layer of coating on the substrate surface (Fig. 3). The high magnification SEM images of the plant specimens (AR-1 and AR-2), clearly reveal the coating interface, is given in Fig. 4. The SEM images clearly show the presence of a continuous layer of a coating having a thickness in the range of 5 to 7 µm on the steel substrate for both the coated specimens (AR-1 and AR-2).

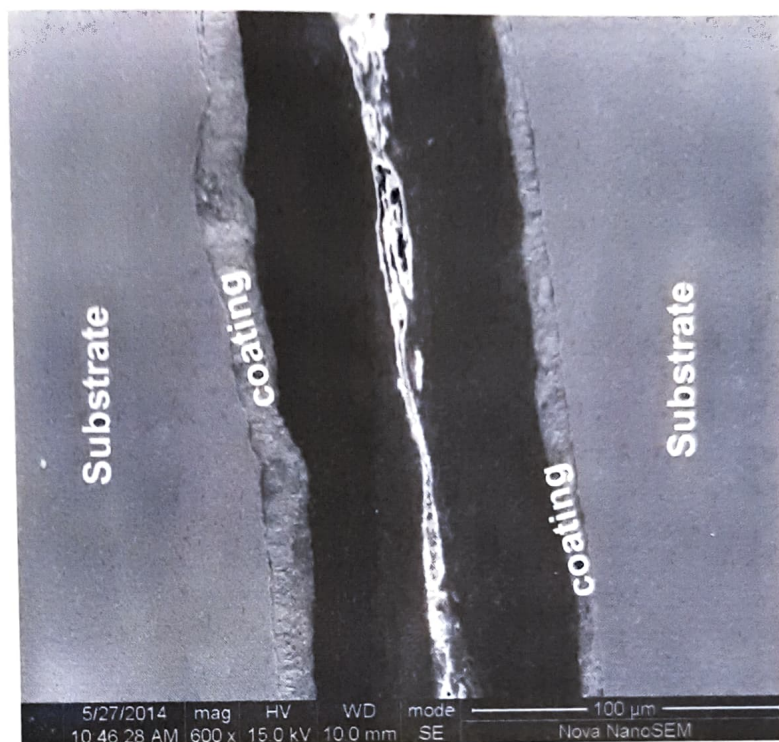


Fig. 3: The cross sectional SEM micrographs of the coatings of the plant specimen

The as-received galvanized coating of AR-1 (Fig. 4(a)) clearly demonstrates the formation of discontinuous Fe-Zn intermetallics of zeta (ζ) crystals with familiar blocky morphology at the interface between substrate and coating. The overlay coating consists of eta (η) phase of mainly pure zinc having a thickness in the range of 4-5 μm , whereas the thickness of zeta (ζ) phase at the substrate-coating interface is in the range of 1-2 μm . It is noted that the presence of zeta (ζ) crystals is completely absent at the substrate-coating interface for the coated specimen of AR-2 (Fig. 4(b)). The AR-2 GI specimen mainly consists of eta (η) layer with a very thin continuous aluminum rich interfacial layer at the interface between substrate and coating. This well-developed Al-rich interfacial layer, which is formed immediately as strip enters into the bath, completely inhibits the formation of zeta (ζ) crystals of iron-zinc intermetallics by preventing the direct contact of solid iron and liquid zinc in the bath. Figure 5 shows the SEM images obtained from the top surface of the coating for both AR-1 and AR-2 specimens. The scanning electron micrographs obtained from the top surface of the coatings clearly demonstrate the presence of only η phase (pure Zn) in both the specimens.

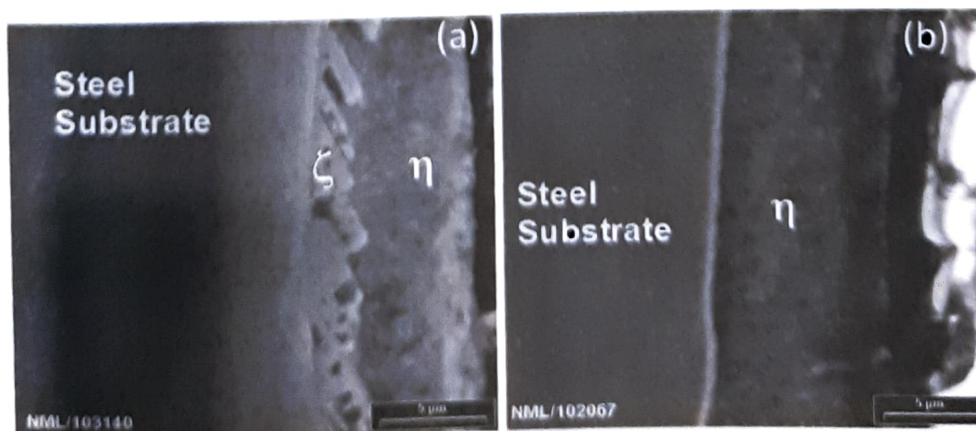


Fig. 4: The cross-sectional SEM micrographs of the coatings of the AR-1 (a) and AR-2 (b) specimens

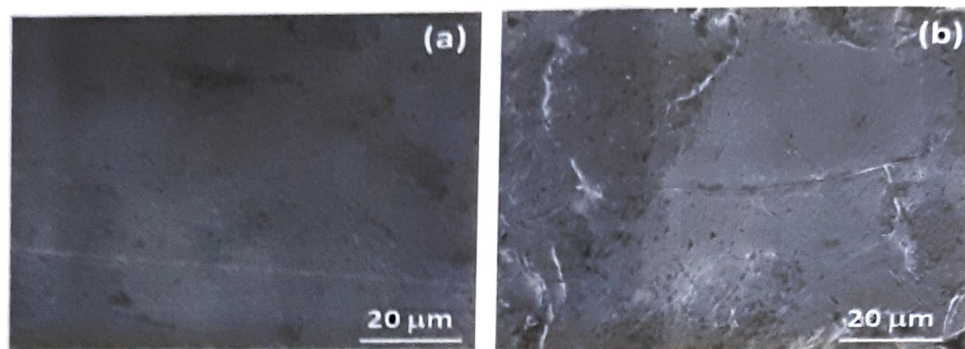


Fig. 5: Top surface of the coating for both these steels (AR-1 and AR-2) reveal the presence of only η phase (pure Zn)

An EDS analyses, conducted for elements aluminum, iron and zinc, of both the as-received specimens (AR-1 and AR-2) across the coating reveal a high intensity peak of aluminum at the interface between substrate and coating, which confirms the formation of an aluminum rich inhibition layer. The overlay coating layer is removed using an acid solution without affecting the Fe-Al based inhibition layer formed at the coating-substrate interface to examine the top surface microstructure of the Al rich layer, for both the as-received specimens. Figure 6 shows the EDS elemental mapping of Zn, Fe and Al, respectively obtained from the top surface of interfacial layer for AR-1 specimen as shown in Fig. 6(a). Elemental distribution maps demonstrate the uniform distribution of aluminium and iron throughout the inhibition layer (Fig. 6(c) & (d)). Elemental distribution map shown in Fig. 6(b) also reveals the segregation of zinc at one location on the surface, as zinc layer is not fully removed from that location of the interfacial layer by acid reaction.

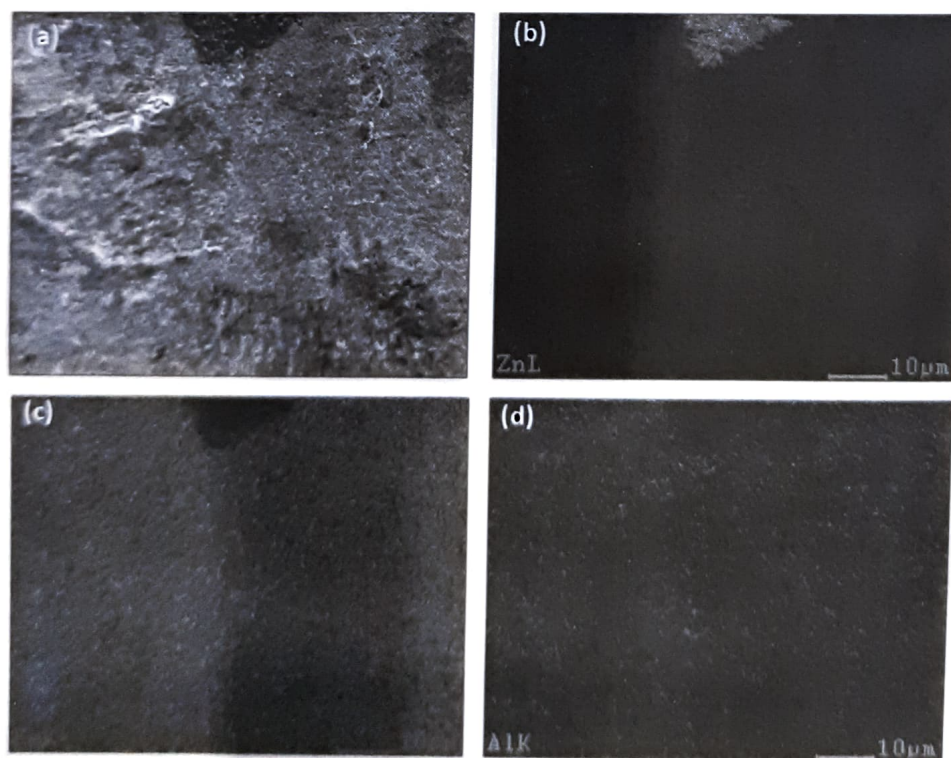


Fig. 6: X-ray mapping of the interfacial layer for the coating: (a) SEM micrograph shows the morphology of the interfacial layer, and (b)-(d) show the X-ray mapping of Zn, Fe and Al, respectively, from the region shown in (a).

The top surface morphology of the Fe-Al interfacial layer, at high magnification, for both the as-received specimens is shown in Fig. 7. It is observed that the aluminum-rich interfacial layer is not compact and continuous

for AR-1 specimen, whereas Fe-Al crystals are densely packed and continuous for AR-2 specimen. The EDS spectra obtained from region of Figs. 7(a) and (c) reveals the strong peaks of Al and Fe. However, intensity of Al peak is weak for AR-1 specimen in comparison to AR-2 specimen. The EDS analysis, therefore, indicates that the presence of higher concentration of Al at the interface for AR-2 specimen. From this analysis, it can be stated that an aluminum rich inhibition layer is formed on the substrate surface at the coating interface and this interfacial layer is expected to be compact and continuous for AR-2 specimen. For AR-1 specimen, this interfacial layer is porous and discontinuous, which will promote the formation of discontinuous zeta (ζ) crystals of Fe-Zn intermetallics at the substrate-coating interface.

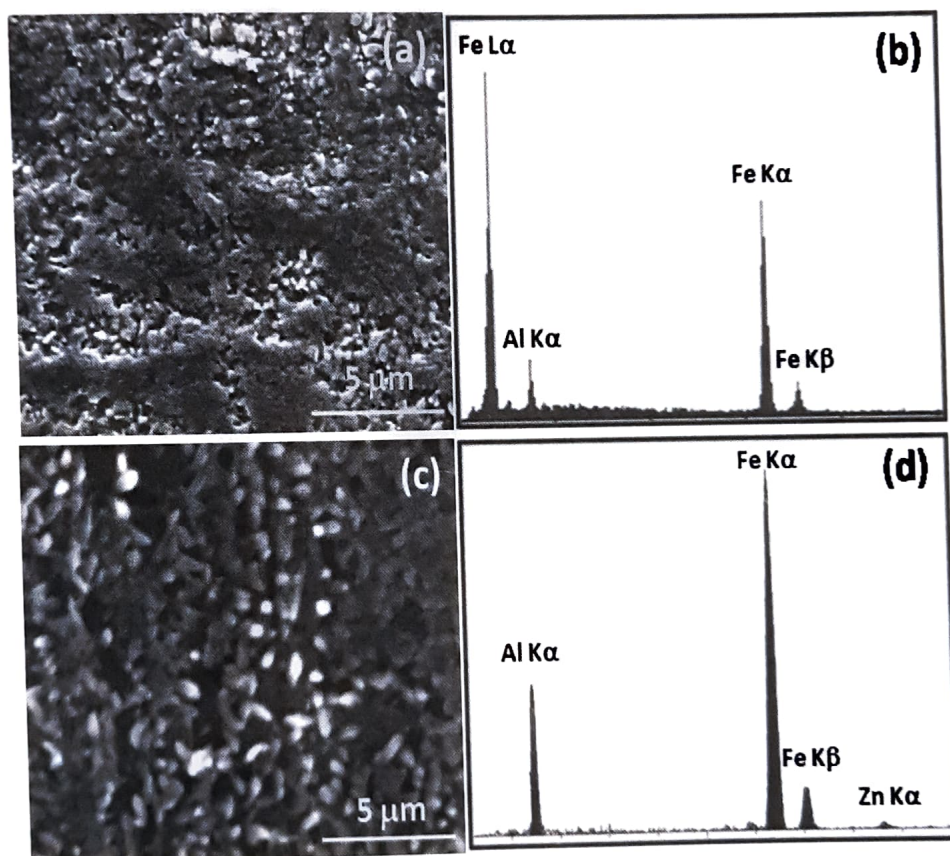


Fig. 7: SEM micrographs (a & c) and EDS analysis (b & d) obtained from top surface of the interfacial layer (a-b: Specimen AR-1; c-d: Specimen AR-2)

The presence of reacted aluminium at the coating interface is further confirmed by analysing the GDOES depth profile data obtained from top surface of both the as-received galvanized specimens. GDOES depth profile data of individual elements for the as-received GI specimens (AR-1 and AR-2) obtained from one of the location of the top surface of the coating is shown in Fig. 8. Elemental profiles indicate that peak position of Al is obtained at coating thickness of about 7.0 and 7.5 μm for AR-1 and AR-2 specimens, respectively. It is also observed that elemental profiles intersect at 50 wt.% for the elements iron and zinc, which is very close to the peak positions of Al for respective samples. Therefore, peak position of aluminium may be considered as substrate-coating interface in case of GI specimens and estimated thicknesses based on the position of Al peak may be considered as approximate thickness of the coatings, which is generally over estimated as iron concentration at this location of the coating is always on much higher side. The GDOES analysis also confirms that Al concentration at the interface location is always higher for the AR-2 specimen than AR-1 specimen. This also indirectly confirms that inhibition layer thickness in AR-2 specimen is more in comparison to AR-1 specimen.

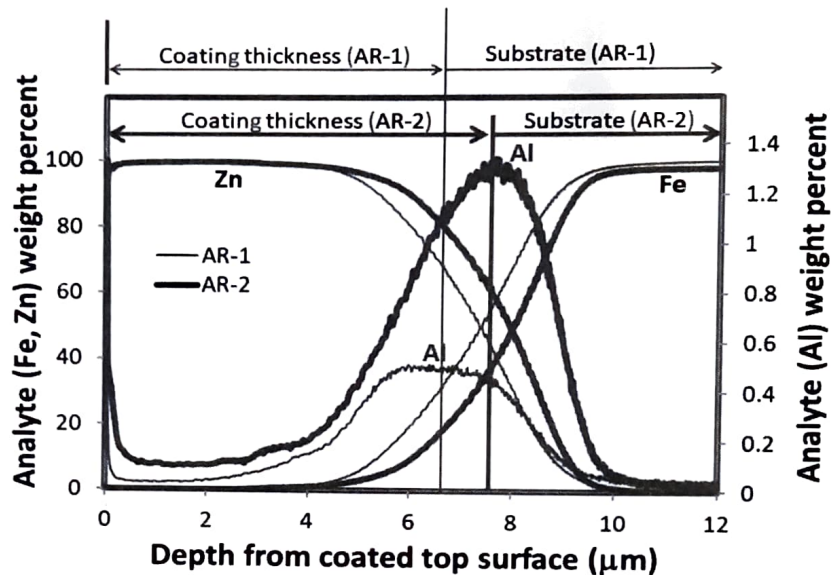


Fig. 8: GDOES plot for as-received GI specimens (AR-1 and AR-2)

Table 2 shows the details of various phases expected in Fe-Zn binary systems particularly for the GI and GA specimens including phase stoichiometry, iron content and density of individual phases [8, 21-23]. The average iron content of various individual phases and phase mixture, as mentioned in the table, is estimated based on the range of iron content in various Fe-Zn intermetallics [8, 23]. The density of individual phases and mixture of two phases is estimated by applying the inverse rule of mixture [8].

Table 2

Various phases expected in Fe-Zn binary systems particularly for the GI and GA specimens along with phase stoichiometry, iron content and density of individual phases [8, 21-23]

Phases	Stoichiometry	Wt% Fe	Average wt% Fe	Density (gm/cc)
α -Fe	Fe	100	100	7.86
η -Zn	Zn	0	0	7.14
$\eta+\zeta$			2.6	7.157
ζ	FeZn_{13}	5.2-6.1	5.65	7.177
$\zeta+\delta$			6.75	7.184
δ	FeZn_{10}	7.4-11.3	9.35	7.202
$\delta+\Gamma_1$			13.75	7.231
Γ_1	$\text{Fe}_5\text{Zn}_{21}$	16.2-18.2	17.2	7.254
$\Gamma_1+\Gamma$			19.25	7.268
Γ	$\text{Fe}_3\text{Zn}_{10}$	20.3-27	23.65	7.298

The elemental profiles, as obtained from GDOES data, are considered to estimate the overall iron and aluminium content of the coatings [8, 23]. The overall iron content of the coating can be estimated as follows:

$$[\text{wt.\% Fe}]_{\text{coating}} = 100 \times \frac{\sum M_{\varphi}^{\text{Fe}}}{\sum M_{\varphi}} \quad (1)$$

where, M_{φ} is the mass of phase layer φ (in Kg) and M_{φ}^{Fe} is the mass of Fe in phase layer φ (kg). These values are estimated as follows:

$$M_{\varphi} = V_{\varphi} \times \rho_{\varphi} \quad (2)$$

$$M_{\varphi}^{\text{Fe}} = V_{\varphi} \times \rho_{\varphi} \times f_{\varphi} \quad (3)$$

Here, V_{φ} is the volume of the φ layer and it is estimated as

$$V_{\varphi} = t_{\varphi} \times L_T \times w_T \quad (4)$$

where, f_{φ} and ρ_{φ} are average weight fraction iron and density (kg.m^{-3}) of a single phase layer or layer consists of mixture of two phases, as indicated in last two column of Table 2. L_T and w_T are overall length and width of coating (in m). t_{φ} is the layer thickness of a Fe-Zn intermetallic phase layer or a layer consisted of mixture of two Fe-Zn intermetallic phases measured from depth profile data of GDOES by superimposing composition range of individual phase layer, as mentioned in the Table 2.

In case of galvanized coating (GI), a correction for overall iron content of the coating is carried out by eliminating the contribution of iron involved in the formation of aluminium rich Fe_2Al_5 layer. It is noted that high affinity of liquid aluminium towards iron results in the formation of iron-aluminide ($\text{Fe}_2\text{Al}_5\text{Zn}_x$) layer on the strip surface during galvanizing process in case of liquid zinc bath containing Al. It is difficult to accurately estimate the iron-aluminide inhibition layer composition as this layer is extremely thin, therefore, in the present study inhibition layer is considered as Fe_2Al_5 [24-25]. By neglecting the Al present in the top surface of the coating, weight percent aluminium in the coating involved for the formation of Fe_2Al_5 layer is estimated from the elemental profile of Al obtained from the GDOES data as follows:

$$[\text{wt.\% Al}]_{\text{coating}} = \sum ([\text{wt.\% Al}] \times d_i) / \sum d_i \quad (5)$$

where, $[\text{wt.\% Al}]$ is the average weight percent aluminium within the coating depth d_i . The mass of aluminium (in kg) reacted for the formation of Fe_2Al_5 layer at the coating interface:

$$M_{\text{Fe}_2\text{Al}_5}^{\text{Al}} = ([\text{wt.\% Al}]_{\text{coating}} \times \sum M_{\varphi}) / 100 \quad (6)$$

Mass of Fe_2Al_5 layer ($M_{\text{Fe}_2\text{Al}_5}$) and mass of iron involved for the formation of Fe_2Al_5 layer ($M_{\text{Fe}_2\text{Al}_5}^{\text{Fe}}$) are as follows:

$$M_{\text{Fe}_2\text{Al}_5} = 1.82 \times M_{\text{Fe}_2\text{Al}_5}^{\text{Al}} \quad (7)$$

$$M_{\text{Fe}_2\text{Al}_5}^{\text{Fe}} = 0.45 \times M_{\text{Fe}_2\text{Al}_5} \quad (8)$$

The estimated thickness of Fe_2Al_5 layer formed at the interface

$$t_{\text{Fe}_2\text{Al}_5} = M_{\text{Fe}_2\text{Al}_5} / (\rho_{\text{Fe}_2\text{Al}_5} \times L_T \times w_T) \quad (9)$$

Here, $\rho_{\text{Fe}_2\text{Al}_5}$ is the density of Fe_2Al_5 layer, which is considered as 4720 kg/m^3 [25].

The overall Fe content of the GI coating (in wt.%)

$$[\text{wt.\% Fe}]_{\text{coating, GI}} = 100 \times (\sum M_{\varphi}^{\text{Fe}} - M_{\text{Fe}_2\text{Al}_5}^{\text{Fe}}) / \sum M_{\varphi} \quad (10)$$

Table 3 shows the estimated values of coating thickness, iron and aluminum contents as well as inhibition layer thickness estimated based on above mentioned methods using the Fe and Al depth profiles obtained by GDOES data. For the estimation of coating thickness, GI coating is considered to be consisted of only a single layer, which is a mixture of η and ζ phases, for AR-2 specimen with iron content at the substrate-coating interface is limited to 5.2 wt.%. For AR-1 specimen, overall coating thickness is estimated by assuming two layered structure of coating consisted of a mixture of overlay ($\eta+\zeta$) layer and single phase ζ layer with coating iron content of maximum 6.1 wt.% at the substrate-coating interface. The inhibition layer thicknesses estimated based on the analysis of

GDOES data are ~43 nm and ~83 nm for AR-1 and AR-2 specimens, respectively. These estimated thicknesses are reasonably good agreement with the literature data [18, 26]. Figure 9 shows that the aluminium content in the coating increases with bath Al content. Aluminum content in the inhibition layer estimated in the present study is compared with the data reported by other researchers [18, 26]. Estimated interfacial aluminium content corroborates well with the reported data of Taniyama et al. [26]. However, measured values of reacted aluminium reported by Kanamaru et al. [18] is slightly on higher side in comparison to the amount of aluminium estimated in the present study for the formation of inhibition layer. These slight differences in values are mainly due to difference in measurement techniques as well as variation in galvanizing process parameters particularly the bath temperature. Many investigators also studied the formation and growth of inhibition layer and highlighted that inhibition layer on the strip surface becomes continuous when the crystal size reaches a critical value, which is generally in the range of 40-50 nm [11, 13, 25]. Therefore, inhibition layer thickness estimated in the present investigation clearly indicates that Al rich interfacial layer formed on the strip surface will be very thin and discontinuous for AR-1 specimen, whereas this interfacial layer will be relatively thick, stable and continuous for AR-2 specimen.

Table 3

Estimated values of coating thickness, coating iron and aluminum contents as well as inhibition layer thickness for as-received GI specimens

Sample	Phase layer/s	Coating thickness (Micron)	Coating Al%	Coating Fe%	Inhibition layer thickness (nm)
AR-1	($\eta+\zeta$) & ζ	5.47	0.26	2.43	43.03
AR-2	($\eta+\zeta$)	5.23	0.58	2.13	82.93

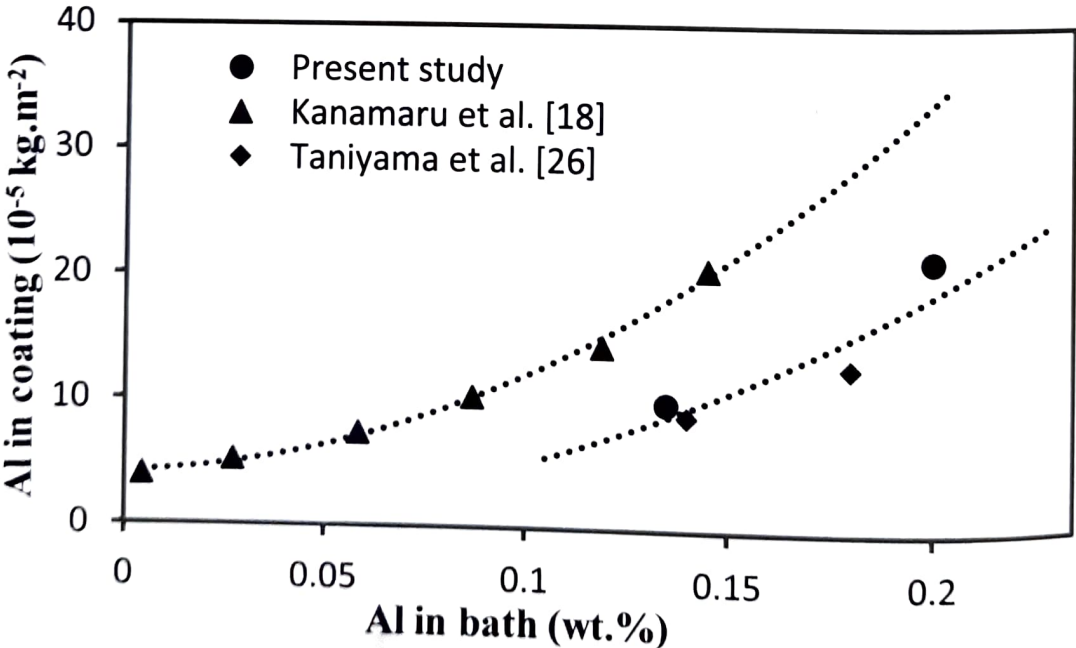


Fig. 9: Variation of Al content in coating with bath Al content

Figure 10 shows the cross-sectional SEM images of the AR-1 specimen isothermally annealed at 470°C with varying galvannealing duration of 10s, 15s and 20s. Micrographs reveal the progress of various Fe - Zn intermetallic layers as a function of annealing duration. Annealing treatment for a short duration of 10s resulted for the development of microstructure mainly consisted of delta (δ), zeta (ζ) and overlay eta (η) phases. However, at the substrate-delta (δ) phase interface a very thin discontinuous layer of gamma phase is clearly visible. Micrographs

also indicate the formation of many voids within the transverse section of the coating (indicated by an arrow in the micrographs). It is also observed that the presence of voids within the coating decreases with increase in annealing duration. It is reported that void formation in the coating occurs when eta (η) phase is consumed by the formation of zeta (ζ) Fe-Zn intermetallic phase because of change in volume due to the appearance of zeta (ζ) crystals^[7]. The decrease in voids formation with the increase in galvannealing times further indicates that coating iron content increases with increase in annealing duration as zeta (ζ) phase layer is consumed by the formation of delta (δ) phase. Specimen isothermally annealed for 15s clearly demonstrates that the coating mainly consists of delta (δ) phase and the presence of (η) phase towards the top surface region of the coating is decreased significantly due to the formation and growth of zeta (ζ) crystals. Specimen isothermally annealed for a longer duration of 20s reveals the growth of compact delta (δ) phase with the decrease in the amount of zeta (ζ) crystals and negligible presence of eta (η) phase at the top surface of the coating. It is also observed the presence of a relatively thick and continuous brittle gamma Fe-Zn intermetallic layer at the interface between substrate and coating. Therefore, it can be stated that AR-1 specimen annealed for 20s results in favourable galvannealed microstructure mainly consisted of compact delta (δ) phase. Presence of many cracks, particularly perpendicular to strip surface, is also observed in all the annealed specimens. However, the formation of cracks and other defects (mainly voids) is minimum for the coated specimen annealed for 20s.

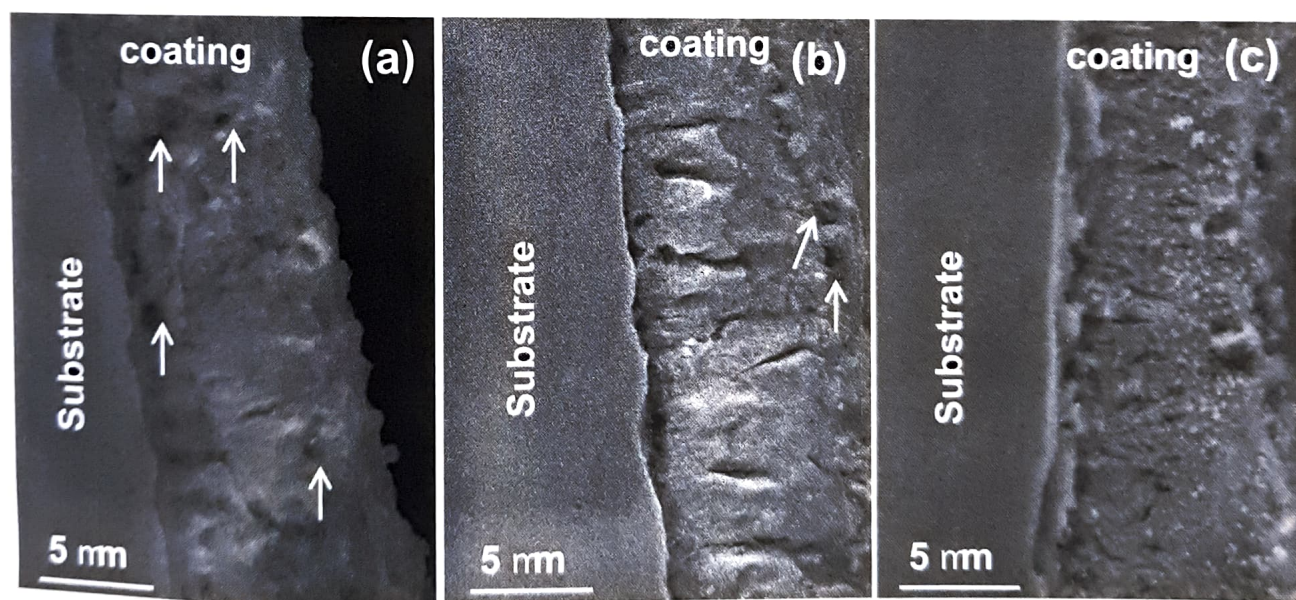


Fig. 10: Cross sectional SEM micrographs of the coating annealing at 4700C with varying galvannealing duration of 10s (a), 15s (b) and 20s (c)

Scanning electron micrographs reveal the top surface morphology of the AR-1 specimen annealed at 470°C for varying durations (Fig. 11). As-received specimen annealed for 10s reveals that the morphology of the top surface of the coating mainly consists of fine blocky zeta (ζ) crystals along with eta (η) phase. However, the amount of eta phase on the coated top surface decreases with the increase in annealing duration. Growth of zeta (ζ) crystals at the expanse of eta (η) phase can clearly be seen from the micrographs of the specimen annealed for 15s. The micrograph in Fig. 11(d), at higher magnification, clearly demonstrates that coated top surface mainly consists of a mixture of fine and coarse crystals of zeta (ζ) Fe-Zn intermetallics along with the presence of eta (η) phase at some of the location. Top surface morphology of the specimens annealed for 20s mainly reveals the blocky crystals of zeta phases with the negligible presence of eta (η) phase. Therefore, analysis of top surface confirms that with the increase in annealing time the iron content in coating increases and top surface composition changes from pure zinc to iron-zinc intermetallics.

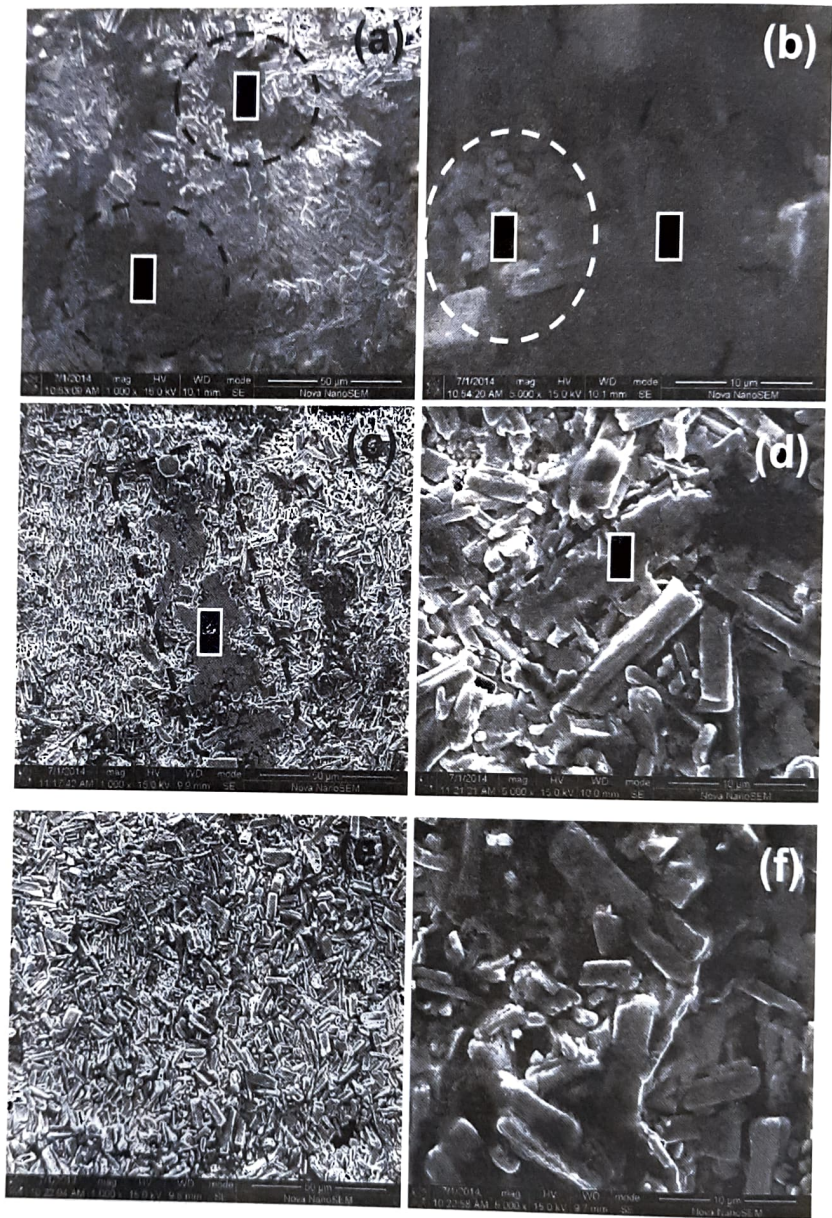


Fig. 11: Scanning electron micrographs revealing the top surface of the coating for the specimens annealed at 470°C for 10s (a & b), (c & d) 15s & (e & f) 20s

Figure 12 shows the cross-sectional SEM micrographs of the AR-2 specimen isothermally annealed at 500°C with varying galvannealing duration of 0s, 5s and 30s. It is noted that this specimen was galvanized using iron saturated liquid Zn-0.2 wt.% Al bath. Therefore, the formation of a continuous Al-rich inhibition layer at the substrate-coating interface is observed for this GI specimen. It is also expected that the presence of this continuous compact inhibition layer will slow down the diffusion assisted formation and growth kinetics of Fe-Zn intermetallic during annealing of the coating. These observations can clearly be explained by analyzing the micrographs of annealed specimens as shown in Fig. 12. Micrographs clearly demonstrate that even after 30s of annealing at a higher annealing temperature of 500°C, the coated microstructure is not fully alloyed coating rather it exhibits mainly the presence of zeta (ζ) crystals. Presence of many voids particularly at the zeta (ζ) zeta (ζ) Fe-Zn intermetallic phase. With the increase in annealing time, formation and growth of zeta (ζ) crystals are clearly visible. Specimen after annealing for 30s exhibits the presence of the mainly zeta (ζ) crystals in the

coating with the negligible presence of delta (δ) phase at the substrate-coating interface location. Figure 13 shows the SEM images obtained from the top surface of the AR-2 specimen annealed at 500°C for varying durations of 0s and 30s. The top surface morphology of the annealed specimens reveals the presence of main eta (η) phase. Presence of few zeta (ζ) crystals can also be seen at some of the locations of the top surface. The amount of zeta (ζ) crystals at the top surface is more for the specimen annealed for 30s in comparison to specimen annealed for 0s. The analysis of micrographs of both the annealed specimens (AR-1 and AR-2) clearly demonstrates that formation and growth kinetics of Fe-Zn intermetallics are very slow in AR-2 specimen in comparison to AR-1 specimen. The present study clearly demonstrates that high aluminium (0.2 wt.%) containing zinc bath results in the formation of continuous compact inhibition layer in the GI specimen, which in turn reduced the formation and growth kinetics of Fe-Zn intermetallics during annealing treatment of galvanized coating.

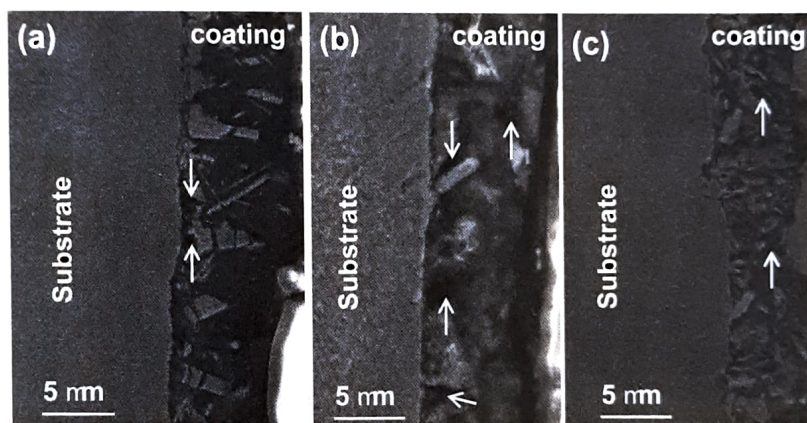


Fig. 12: Cross-sectional SEM micrographs of the coating (AR-2) annealing at 500°C with varying galvannealing duration of 0s (a), 5s (b) and 30s (c)

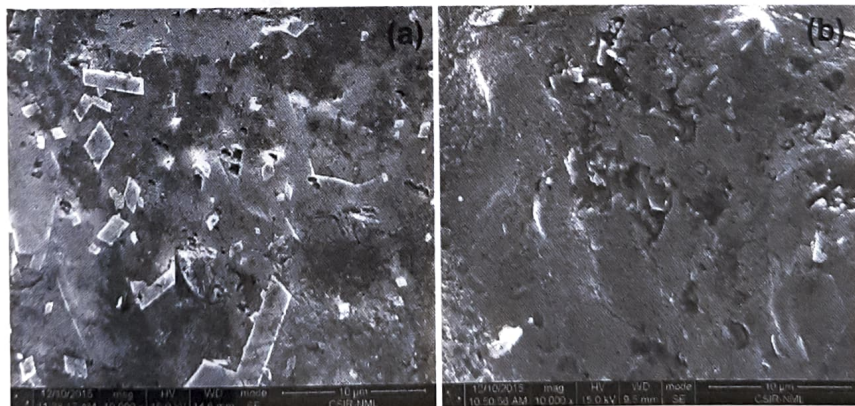


Fig. 13: SEM micrographs reveal the top surface of the coating for the specimens annealed at 500°C for 0s (a) and 30s (b)

In order to further investigate the role of inhibition layer in the formation and growth of various Fe-Zn intermetallics during annealing treatment of galvanized steel, EDS analysis was conducted along the transverse section of the coating for all the annealed specimens of AR-1 and AR-2 sheets. SEM-EDS line scan along the coating cross-section reveals no peak of aluminium at the substrate-coating interface for most of the specimens annealed at 470 and 500°C except the AR-2 specimen annealed for 0s and 5s at 500°C. Figure 14 shows the variation of aluminium concentration along the cross-section of the coating for AR-2 specimen annealed for 0s and 5s at 500°C. EDS line analysis along the transverse section of the coating clearly demonstrates that high concentration of Al at the substrate-coating interface for both the specimens obtained after annealing at 500°C for the duration of 0 and 5s, respectively. It is also noted that no peak of Al at the interface is obtained after about 5s of annealing. Based on the EDS line analysis of Al, it can be stated that thickness of the Al-rich inhibition layer, formed at the substrate-coating interface during the galvanizing process, slowly decreases with annealing duration and eventually disappear after a certain duration of galvannealing.

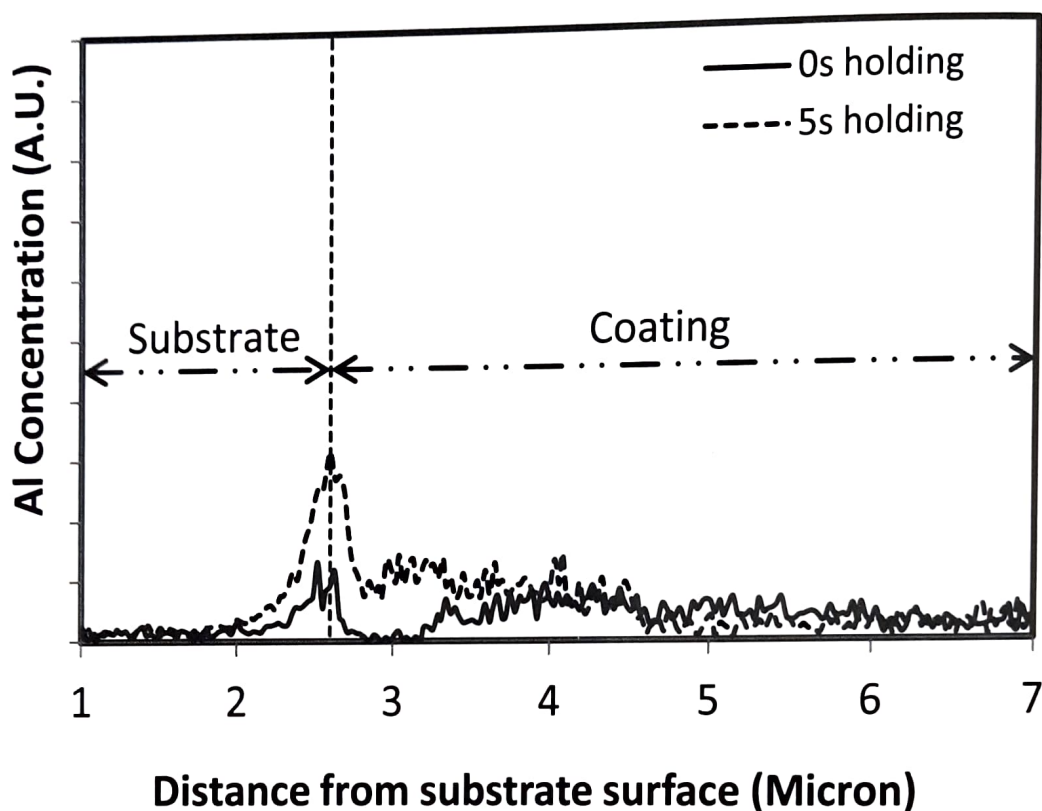


Fig 14: Variation of aluminium concentration along the cross section of the coating for AR-2 specimen annealed for 0s and 5s at 500°C

The EDS analysis across the coating cross-section also indicates higher iron content within the coating for longer annealing duration at a fixed galvannealing temperature. However, a good correlation about the overall coating iron content with galvannealing duration was difficult to obtain based on SEM-EDS analysis. Therefore, GDOES analysis was carried out mainly to find out a suitable correlation between overall iron content of the coating with annealing duration. GDOES analysis was carried out for AR-1 annealed specimens only, as fully alloyed coating was not obtained for the AR-2 annealed specimens. The GDOES plot for one of the annealed specimens obtained from a specific location of top surface is shown in Fig. 15. The layer thickness of a Fe-Zn intermetallic phase layer or a layer consisted of mixture of two Fe-Zn intermetallic phases measured from depth profile data of GDOES by superimposing composition range of individual phase layer^[8]. The average of three values, obtained from three different locations from the top surface of each specimen, is considered for the analysis of overall coating iron content. Table 4 shows the measured average coating thickness of various iron-zinc intermetallic phase layers obtained by analysing the GDOES data. From Table 4, it can be summarized that thickness of delta (δ) and gamma (Γ_1 and Γ) phase layers are comparable for all the three annealed specimens based on the fraction of thickness coverage of overall coating by individual phase regions. However, overall thickness coverage by zeta (ζ) and ($\zeta+\eta$) mixed phase layers decrease for the specimens annealed for longer duration of 15 and 20s. This observation indicates that formation of various Fe-Zn intermetallic phases in the galvannealed coating is controlled by outward diffusion of Fe from strip surface towards the coating. Decrease in zeta (ζ) and ($\zeta+\eta$) phase layer also indicate coating iron content approaches more towards optimal value for the specimen annealed for longer duration of 20s. Therefore, it can be concluded that galvannealing coating with better properties can be obtained for the specimen annealed at 470°C for 20s. This specimen also reveals that brittle gamma ($\Gamma_1+\Gamma$) phase layer thickness is limited to less than 1mm of thickness.

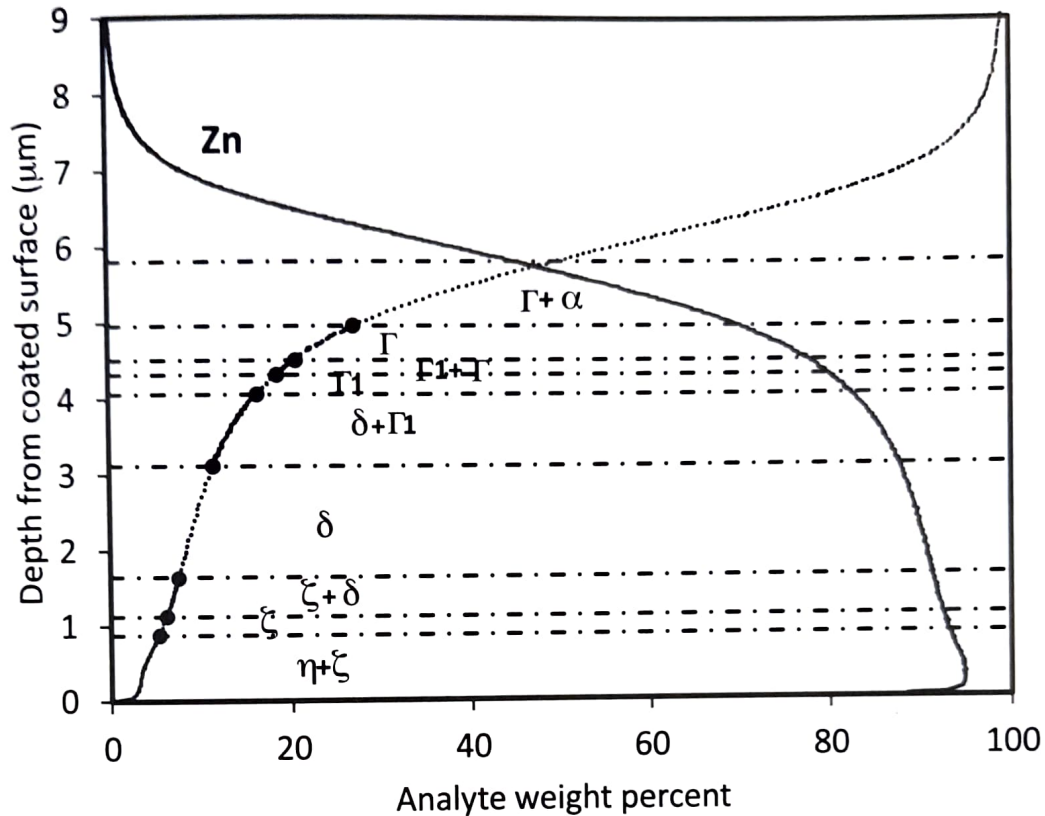


Fig. 15: GDOES plot for the specimen annealed for 10s at 470°C

Table 4: Coating thickness of various phases obtained by GDOES analysis

Phase/s	Annealing duration (s)		
	10	15	20
	Thickness of phase layers (mm)		
$\eta+\zeta$	1.053	0.882	0.764
ζ	0.308	0.218	0.216
$\zeta+\delta$	0.586	0.325	0.39
δ	1.614	1.554	1.383
$\delta+\Gamma_1$	0.937	1.367	0.972
Γ_1	0.252	0.331	0.235
$\Gamma_1+\Gamma$	0.208	0.252	0.197
Γ	0.436	0.53	0.466
Overall coating thickness (μm)	5.395	5.459	4.625

Figure 16 shows that variation of average weight percent of iron in the coating with galvannealing time. In the same figure, a model equation (Eq. 11) is also fitted by considering the rate of change of coating iron concentration is directly proportional to the difference between saturated coating iron concentration and instantaneous iron concentration in the coating^[19-20]. The integral form of the equation for the estimation of coating iron content (W_{Fe} , in wt.%) can be written as:

$$W_{Fe} = W_0 + (W_s - W_0) \{1 - \exp(-kt)\} \quad (11)$$

Here, W_0 is the initial iron content in the coating before the start of galvannealing treatment, which is 2.43 wt.% for AR-1 specimen (refer Table 2), W_s is the saturated iron content in the coating (wt.%), t is the galvannealing time (s) and k is model parameter (s^{-1}). The values of W_s and k are estimated as 13 wt.% and $0.105 s^{-1}$, respectively by best fitting the experimental data in the model equation. The estimated values of these model parameters are in good agreement with literature data^[19-20]. In Figure 16, experimental data of coating iron content obtained by Santos et al.^[20] and Lin et al.^[15] are also included. For comparison purpose, the variations of coating iron content with galvannealing time for the specimen annealed at 475°C using Zn-0.1 wt.% Al bath, as reported by Santos et al., is included^[20]. Lin et al. studied the galvannealing behaviour at 500°C with varying galvannealing time for two different grades of steel (designated as IF and IFP) using Zn-0.14 wt.% Al bath and observed the variation of coating iron content with galvannealing time. Overall coating iron content predicted based on Eq. 11 corroborates well with the present data estimated based on GDOES analysis as well as experimental data reported in literature for galvannealing duration of 10 s and more. Experimental data of coating iron content reported in literature for shorter galvannealing duration (less than 10s) are on higher side compare to predicted value based on Eq. 11. It should be noted that coating iron content just after dipping in liquid zinc bath is expected to be lower than the value (~8 wt.% Fe) reported by them. This is mainly due to application of shorter dipping time and presence of Al (0.1 to 0.14 wt.% Al) in liquid zinc bath during galvanizing process. It is also noted that during annealing treatment of galvanized steel coating iron content and formation of various Fe-Zn intermetallics in the coating is mainly controlled by solid state diffusion of iron from substrate towards the coating. Therefore, kinetics of solid state iron diffusion through various Fe-Zn intermetallic phases in the coating is expected to be sluggish.

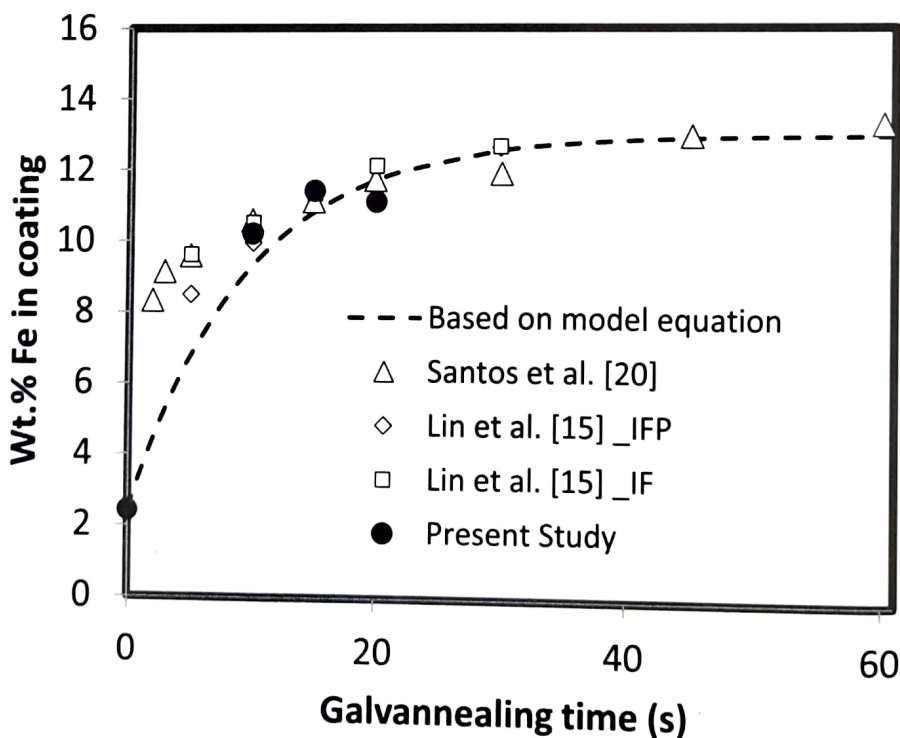


Fig. 16: Variation of average weight percent of iron in coating with galvannealing time

In the present study, galvannealing treatment of galvanized steels, obtained using low (0.135 wt.% Al) and high (0.2wt.% Al) Al containing commercial liquid zinc bath, is carried out to study the formation and growth mechanisms of various Fe-Zn intermetallics in the coating. It is observed that low Al containing Zn bath results in the formation of thin and discontinuous inhibition layer at the interface between substrate and coating of GI sheet. This inhibition layer was insufficient to prevent the direct contact between liquid zinc and solid iron. Therefore, GI sheet obtained using low Al zinc bath shows the formation of discontinuous

Fe-Zn intermetallic zeta (ζ) crystals at the interface location between substrate and coating. It is also observed that GI specimen produced using high Al zinc bath comprises of stable continuous inhibition layer at the substrate-coating interface, which completely inhibits the formation of Fe-Zn intermetallics in the coating. Present study also highlighted that formation and growth kinetics of various Fe-Zn intermetallics are relatively faster in GI specimen produced using low Al zinc bath in comparison to high Al zinc bath. Therefore, galvanized coating formed using low Al containing GI specimen shows the desired sequence and amount of various Fe-Zn intermetallics, particularly after annealing for 20s at 470°C. The sluggish kinetics of formation and growth of Fe-Zn intermetallics during galvannealing treatment of high Al containing galvanized steel is mainly due to the presence of continuous inhibition layer on the substrate surface. It is well understood that the formation and growth of different Fe-Zn phases during galvannealing treatment is primary controlled by diffusion of iron from the substrate surface towards the coating^[16, 27]. Therefore, initial formation and growth of Fe-Zn phases in the Zn coating are controlled by solid-state diffusion of iron through inhibition layer during subsequent annealing treatment just after galvanizing in liquid Zn alloy bath. The kinetics data of diffusion coefficient of Fe (m^2/s) in various phases are calculated based on the Arrhenius correlation [Eq. 12] using the values of pre-exponential constant (D_0) and activation energy (Q) obtained from available literature^[16, 25, 28-30].

$$D = D_0 \exp[-Q/RT] \quad (12)$$

where R is the gas constant (8.314 J/mol.K)

Table 5 shows the kinetics data of diffusivity of iron including D_0 and Q values obtained from the literature^[16, 22, 28-30]. In order to get an idea about the diffusivity data of iron through the inhibition layer, iron diffusion in Al matrix is considered^[25]. From the table, it is clear that there is a significant variation of diffusion of iron through different intermetallic phases. It is also noted that mobility of iron through inhibition layer will be extremely sluggish in comparison to the mobility of Fe through various Fe-Zn intermetallics, particularly in Zeta (ζ) and Delta (δ) phases. Therefore, thick, compact and continuous Al-rich inhibition layer on the substrate surface of GI coating, produced in high Al (0.2 wt.% Al) containing zinc bath, is not suitable to obtain the desired sequence and amount of various Fe-Zn intermetallics in GA coating. Fe diffusivity data clearly suggests that the stable inhibition layer will drastically reduce the formation and growth kinetics of these Fe-Zn intermetallics in the coating. On the other hand extremely thin and/or discontinuous inhibition layer formed during the galvanizing process using low aluminium (0.135 wt.% Al) zinc bath is suitable to obtain desired iron-zinc intermetallic phases in galvannealed coating using optimized annealing parameters. The present investigation also reveals that inhibition layer thickness decreases and eventually disappears with the progress of galvannealing time. Therefore, presence of extremely thin and/or discontinuous inhibition layer at the substrate-coating interface will provide better control of Fe diffusivity during the initial period of galvannealing process for the formation of desired amount and sequence of Fe-Zn intermetallics. It is also observed that overall iron content in the coating increases with increase in galvannealing time. From Fig. 16, it can be stated that overall Fe content in the coating increases with increasing rate during the initial period of galvannealing. This is mainly due to the availability of higher driving force for the Fe flux towards coating from the substrate surface due to the low concentration of Fe in the coating during the initial period of galvannealing. The increasing rate of overall iron content in the coating during initial stages of galvannealing process is also due to faster dissolution of extremely thin and discontinuous inhibition layer. Figure 16 also demonstrates that with further increase in galvannealing time overall Fe content in the coating increases at a decreasing rate. This may be due to the formation and growth of Gamma1 (Γ_1) and Gamma (Γ) layers with the progress of the galvannealing process. From Table 5, it can be stated that presence of Gamma1 (Γ_1) and Gamma (Γ) layers at the interface location of substrate and coating is expected to reduce the mobility of Fe and therefore, reduce the rate of increase of overall iron content in the coating with the progress of galvannealing duration.

Table 5 : Kinetics data of diffusivity of iron including D_0 and Q values obtained from literature ^[16, 25, 28-30]

Phase	Q (kJ/mol)	D_0 (m^2/s)	D (m^2/s)
Zeta (ζ) ^[16, 28]	99.6	$1.0 \cdot 10^{-4}$	$9.947 \cdot 10^{-12}$
Delta (δ) ^[16, 28]	106.8	$1.03 \cdot 10^{-4}$	$3.19 \cdot 10^{-12}$
Gamma _I (Γ_I) ^[14, 29]	80	$2.04 \cdot 10^{-8}$	$4.84 \cdot 10^{-14}$
Gamma (Γ) ^[14, 29]	85.35	$5.0 \cdot 10^{-9}$	$4.994 \cdot 10^{-15}$
Aluminium ^[20, 30] (Fe ₂ Al ₅ layer)	31.84	$1.7 \cdot 10^{-12}$	$9.82 \cdot 10^{-15}$

SUMMARY AND CONCLUSIONS

In the present investigation, the galvanized strip, obtained from low (0.135 wt.% Al) and high (0.2wt.% Al) Al containing commercial liquid zinc bath was annealed at a fixed galvannealing temperature with varying duration to examine the evolution of the microstructure of galvanized steel during strip annealing simulation. Strip annealing simulation was performed using Gleeble 3800 simulator. The main findings of the present investigation are as follows:

- ✓ Iron saturated galvanizing bath having 0.135 wt.% Al results in the formation of thin and discontinuous inhibition layer at the interface between substrate and coating of GI sheet
- ✓ GI sheet obtained using low Al (0.135 wt.% Al) zinc bath shows the formation of discontinuous Fe-Zn intermetallic zeta (ζ) layer at the interface location between substrate and coating
- ✓ GI specimen produced using high Al (0.20 wt.% Al) zinc bath comprises of stable continuous inhibition layer at the substrate-coating interface, which completely inhibits the formation of Fe-Zn intermetallics in the coating
- ✓ The formation and growth kinetics of various Fe-Zn intermetallics are sluggish in nature in GI specimen produced using high Al zinc bath in comparison to low Al zinc bath
- ✓ Galvannealed coating formed in low Al containing zinc bath shows the desired sequence of various Fe-Zn intermetallics with favorable microstructure suitable for producing GA coating, particularly after annealing for 20s at 470°C
- ✓ The sluggish kinetics of Fe-Zn intermetallics formation during galvannealing treatment of high Al containing galvanized steel is mainly due to the presence of thick and continuous inhibition layer on the substrate surface
- ✓ During galvannealing, inhibition layer thickness decreases and eventually disappears with the progress of galvannealing time
- ✓ Presence of extremely thin and/or discontinuous inhibition layer at the substrate-coating interface will provide a better control of Fe diffusivity during the initial period of galvannealing process for the formation of desired amount and sequence of Fe-Zn intermetallics
- ✓ It is noted that over all Fe content in the coating increases rapidly during initial period of galvannealing. However, with progress of galvannealing time, overall Fe content in the coating increases at a decreasing rate

REFERENCES

- [1] C.S. Lin, M. Meshii and C.C. Cheng: ISIJ Int., 35: 491, 1995
- [2] F.M. Queiroz and I. Costa: Surf. Coat. Tech., 201: 7024, 2007
- [3] H.Y. Ha, S.J. Park, J.Y. Kang, H.D. Kim and M.B. Moon: Corros. Sci., 53 : 2430J, 2011
- [4] Inagaki, M. Sakurai and T. Watanabe: ISIJ Int., 35: 1388, 1995
- [5] Z.W. Chen, R.M. Sharp and J.T. Gregory: Mater. Forum, 14 : 130, 1990
- [6] C.S. Lin and M. Meshii: Metall. Trans. B, 25B: 721, 1994
- [7] G.K. Mandal, S.K. Das, R. Balasubramaniam and S.P. Mehrotra: Mater. Sci. Tech., 27: 1265, 2011
- [8] A. Chakraborty and R.K. Ray: Surface & Coatings Tech. 203:1756, 2009
- [9] A. Nishimoto, J. Inagaki and K. Nakaoka: Trans. Iron Steel Inst. Jpn. 26: 807, 1986
- [10] T. Nakamori, Y. Adachi and T. Toki: CAMP-ISIJ, 5: 1637, 1992
- [11] A.R. Marder: Prog. Mat. Sci., 45: 191, 2000
- [12] V. Furdanowicz and C. R. Shastri: Metall. Mater. Trans. A, 30A: 3031, 1999
- [13] E. Baril and G. Lesperance: Metall. Mater. Trans. A, 30A:681, 1999
- [14] C. E. Jordan and A. R. Marder: Metall. Mater. Trans. A, 25A: 937, 1994
- [15] C S LIN, M MESHII and C. C. CHENG, ISIJ Int., 35: 503, 1995
- [16] A.K. Verma, S. Chandra, B.K. Dhindaw and R.D. K. Misra: Mater. Sci. Eng. A, 418 : 335, 2006
- [17] M. Onishi, Y. Wakamatsu and H. Miura: Trans. JIM, 15: 331, 1974
- [18] T. Kanamaru and M. Nakayam: Mater. Sci. Res. Int., 1: 150, 1995
- [19] V.S.S Lopes, M.A. de Faria and P.R. Rios: ISIJ Int., 39: 1204, 1999
- [20] D.R. dos Santos, U.R. Seixas and P.R. Rios: ISIJ Int., 38: 1393, 1998
- [21] T.B. Massalski, Phase Diagrams, ASM Metals Handbook, 3: 206, 1992
- [22] J.H. Hong, S.J. Oh and S.J. Kwon: Intermetallics 11: 207, 2003
- [23] J.M. Long, D.A. Haynes and P.D. Hodgson: Mater. Forum 27 : 62, 2004
- [24] Z.W. Chen, R.M. Sharp and J.T. Gregory: Mater. Sci. Technol. 6: 1173, 1990
- [25] G.K. Mandal, R. Balasubramaniam and S.P. Mehrotra: Metall. Mater. Trans. A, 40A: 637, 2009
- [26] A. Taniyama and M. Arai: Mater. Trans., 45: 2482, 2004
- [27] Syahbuddin, P.R. Munroe, C.S. Laksmi and B. Gleeson: Mater. Sci. Eng. A 251: 87 1998
- [28] U. Chakkingal: Microstructural evolution in galvanized coating during galvannealing, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1994
- [29] Y. Wakamatsu, K. Samura and M. Onishi: J. Jpn. Inst. Met., 41: 664, 1977
- [30] S.R. Teixeira, P.H. Dionisio, E.F. DA Silveira, F.L. Freire, Jr., W.H. Schreiner and I.J.R. Baumvol: Mater. Sci. Eng., 96: 267, 1987

Metallic gold thin film micropattern on polydimethylsiloxane film for flexible electronic sensors and circuits

A. KAKATI¹ and S. DAS^{2*}

¹Advanced Technology Development Center, Indian Institute of Technology Kharagpur, West Bengal, 721302, India

²School of Medical Science and Technology, Indian Institute of Technology Kharagpur, West Bengal, 721302, India

Abstract: This work illustrates the importance as well as major challenges related to the development of malleable metallic Au thin film micropattern on soft elastomeric film and then presents a fabrication technique to overcome these challenges for developing reliable, flexible electronic sensors and circuits. A self-assembled molecular adhesive layer has been introduced between the polydimethylsiloxane (PDMS) and the thin metal film to increase the adhesion and then analyzed the multilayer structure. The contact angle measurement showed that the introduction (3-mercaptopropyl) trimethoxysilane (MPTMS) molecular adhesive layer increases the hydrophilicity of the PDMS film for a more extended period and Au film on MPTMS coated PDMS shows superior film quality. The random buckles formed on the thin Au film have been successively manipulated using controlled heating after micropatterning. The SEM analysis of the Au thin film confirmed that the deposited film is granular and filled with nanogaps. The electrical characterization of the deposited showed that the sheet resistance of the metal thin is higher compared to the Au thin film on Si surface. This investigation is beneficial for realizing reliable, flexible electronic devices and circuits on soft polymer.

Keywords: Contact angle, flexible sensor, microfabrication, microstructure, optical lithography, PDMS.

INTRODUCTION

Recent advancements in the field of flexible electronic sensors and systems demand thin metal film to be fabricated on a flexible or a stretchable substrate for sensing elements as well as connecting circuits^[1]. Flexible sensors with unique stretchability have vast potential applications in various fields such as health monitoring, man-machine interface, robotic skin, wearable devices, etc.^[2,3,4]. Au is a highly conductive biocompatible ductile noble metal and is suitable for thin film microstructure on soft elastomeric material. Similarly, PDMS is an established elastomeric MEMS material and compatible with most of the traditional microfabrication processes^[5]. Moreover, PDMS is a highly flexible, relatively cheap, chemically nonreactive biocompatible soft material that makes it a prominent material for biomedical and electronic skin applications^[6,7]. Although the Au strain gauge sensor developed on PDMS film shows much higher sensitivity due to low Young's modulus of the substrate film, it also faces three significant problems. First, the high strain sensitivity of these sensors is driven by the formation of microcracks in a direction perpendicular to its stretching, which creates some local debonding of the film from the elastomer substrate^[8]. Although this debonding is local and has less impact on reversibility, it influences the linearity of the strain response. Second, miniaturization of the resistor becomes critical as the width of the resistor film must always be broader than the microcrack dimension. Third, the Au thin film fabricated on an elastomeric film has random buckles on its surface^[5]. Thus, the formation of a crack on a randomly oriented film becomes a complex shape and will contribute to nonlinear strain response behavior^[9]. Moreover, PDMS is a hydrophobic in nature and the thin metal film deposited on its film has poor adhesion. Therefore, any electronic device developed with these material shows poor reliability, especially in flexible and stretchable applications^[10]. Therefore, reliable thin metal thin film deposition on PDMS film becomes critical for maintaining the quality of any fabricated electronic devices. In this work, we deposit Cr/Au film on PDMS film coated with a molecular adhesive layer and then study the quality of the film and simultaneously try to fabricate an array Au thin film microelectrode with connecting microlines on PDMS film. Moreover, manipulation of the random buckles by heat treatment will be investigated for the reliable microelectronic device.

* Correspondence Author E-mail: sou@smst.iitkgp.ac.in

EXPERIMENTAL PROCEDURES

Substrate preparation

A 150 μm thick PDMS film was prepared with Sylgard 184 kit from Dow Corning Corp. by thoroughly mixing the base and curing solution (10:1) and spin coating over a glass slide at a speed of 500 rpm for 20s. The sample was cured by heating the sample at 90°C for two hours. A 2 μm thick polyvinyl alcohol (PVA) was used as a sacrificial layer between the glass slide and the PDMS film. The cured PDMS film was treated with O_2 plasma at 150 mTorr chamber pressure, 40 W plasma power for 30 s and subsequently immersed in a 5 mM solution of (MPTMS) for one hour. The MPTMS coating was used as a molecular adhesive layer for reliable metal thin film over hydrophobic PDMS substrate film^[11]. The sample was rinsed in deionized water (DI) and dried by blowing N_2 gas. The hydrophilicity of the MPTMS coated PDMS was tested and compared with bare PDMS film, and only O_2 plasma-treated PDMS film.

Thin-film deposition

The Au material was sputtered on the top of the Cr layer over the surface-modified PDMS sample. The base vacuum of the sputtering chamber was kept below 3×10^{-6} mbar of pressure before Ar gas was injected into the deposition chamber. The chamber was first flushed with Ar gas and then maintained a constant Ar pressure of 2.6×10^{-3} mbar for the entire period of deposition. The PDMS samples were kept at 2.36" above the target material on the substrate holder plate. Both Cr and Au target material have 4" diameters and 99.99% purity.

Microstructure patterning

The Cr and Au thin film sputtered over PDMS film were micropatterned with a conventional photolithography technique. The fabrication process starts with coating positive photoresist (HPR 504, from Fujifilm) on the PDMS sample using a spin coater (3000 rpm for 20s) followed by soft baking at 90°C for 30 min. The sample was subsequently exposed to UV light inside a Mask aligner (Karl Suss MJB3 Mask Aligner) for 7.5 sec. The exposed samples were then developed in a developer solution hard 429 (Fujifilm). The samples were subsequently post baked at 120°C for 25 min for hardening the patterned photoresist. The Au and then Cr thin films were sequentially removed by immersing in Au and Cr etchant (Transene), respectively. The remaining photoresist was removed by dipping in acetone followed by cleaning in deionized water and then dried with N_2 gas. The PDMS samples were then heated at 160°C for 15 min and then cooled down to room temperature for allowing the random buckles developed due to mismatch Young's modulus during the sputtering process to an ordered parallel structure^[9]. The PDMS film was released by immersing in hot water (60°C, 2 hours) from the underlying glass substrate. Finally, the micropatterned film was dried with N_2 gas and prepared for characterization.

Testing and Characterization

The contact angle was measured by capturing the image of the water droplet by a high-resolution CCD camera and 'Screen Protractor' software. The surface morphology of the Au thin film was analyzed by both optical (Leica DM2700M) and scanning electron microscope (Zeiss Sigma FE-SEM -03-85). The sheet resistance of the deposited Au film was measured with the four-probe technique, and the thickness of the film was measured with a surface profiler (DEKTA150).

RESULTS

Contact Angle measurement

In order to study the effect of liquid deposited MPTMS layer on the surface energy of the PDMS film, static contact angle measurement experiment was performed using the sessile drop method after liquid deposition. The samples were thoroughly dried using an N_2 blower before placing a 4-6 μL of deionized (resistivity 18 $\text{M}\Omega\text{ cm}$)

water droplet on its surface for the hydrophobicity/hydrophilicity test. The contact angle of MPTMS deposited PDMS was compared with untreated PDMS (freshly prepared PDMS sample without surface modification), and O_2 plasma (150 mTorr, plasma power 40 W, for 30s of time) treated PDMS sample. As the surface free energy of solid is associated with the chemical composition on its surface^[11], the variation of the contact angle reflects the change in chemical composition on its surface. When the PDMS surface was exposed under O_2 plasma, the hydrophobic surface temporarily becomes hydrophilic^[11]. Therefore, a variation of the contact angle was measured at a different time interval after surface modification. Variation of the measured contact angle for similar samples is plotted with an error bar and is shown in figure 1. The experiment was performed with three samples at a time for each of the three sets. The measured contact angle of a liquid droplet on the liquid MPTMS layer deposited PDMS was found to be 28° after 10 min and saturates at $37 \pm 3^\circ$ after 5 hours of surface treatment. The O_2 plasma-treated PDMS sample has shown hydrophilic nature just after plasma treatment and becomes hydrophobic with a contact angle of $92 \pm 3^\circ$ after 2 hours. The water droplet contact angle on bare PDMS was observed at $108 \pm 3^\circ$ throughout that period.

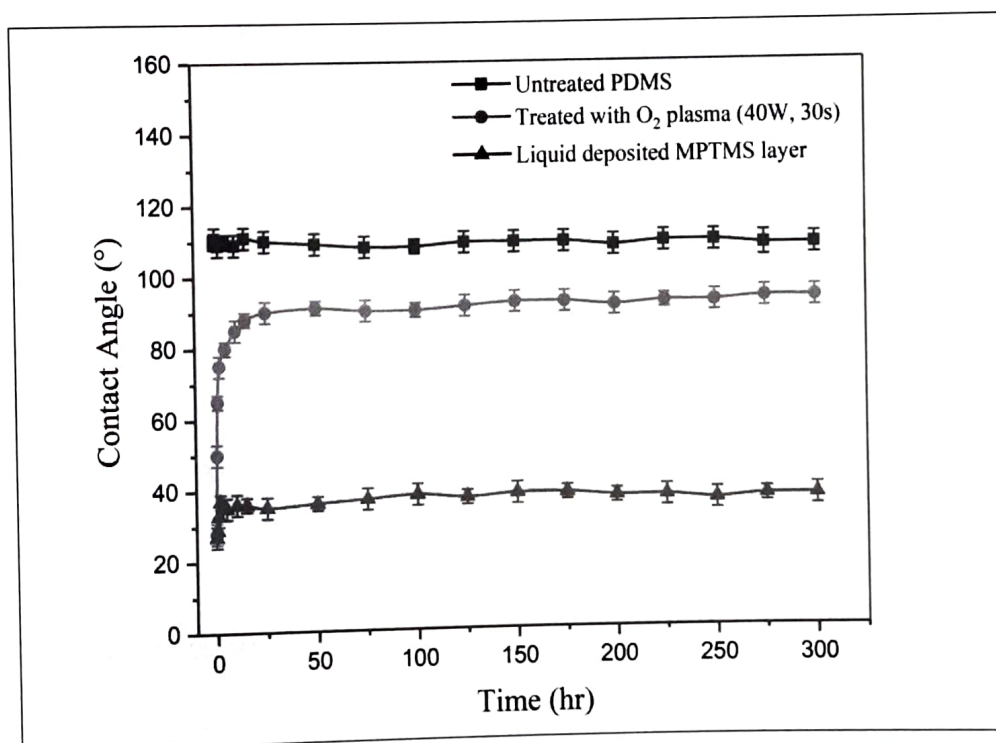


Fig. 1: Variation of contact angle of a water droplet at different time intervals for untreated PDMS, O_2 plasma-treated PDMS, and MPTMS layer deposited PDMS sample.

Thin-film adhesion study

To observe the adhesion between the deposited metal film on PDMS macroscopic adhesion experiment was performed. The test was conducted using two different adhesive tapes; tape 1 has low adhesion compared to Tape 2 and thus could be released easily from the deposited Au surface. The adhesion tests were performed for sputtered deposited Au film, Cr/Au film on O_2 plasma-treated PDMS, and Cr/Au film on MPTMS layer deposited PDMS. Figure 3 shows the optical images of the transfer of Au film to the adhesive tapes after peeling up from its surface. It is quite clear from the experimental results that the Au thin film on PDMS substrate has the lowest adhesion compared to the other two films. It is observed that introducing intermediate Cr film increases the adhesion of the Au thin film, and the sample was able to clear the Tape 1 test but fails in the Tape 2 test. On the other hand, sputtered Cr/Au film on MPTMS layer deposited PDMS film qualifies both the test. The macroscopic adhesion test results support the published works, which suggest that introducing MPTMS molecular adhesive layer increases the adhesion between the PDMS and the thin metal film.

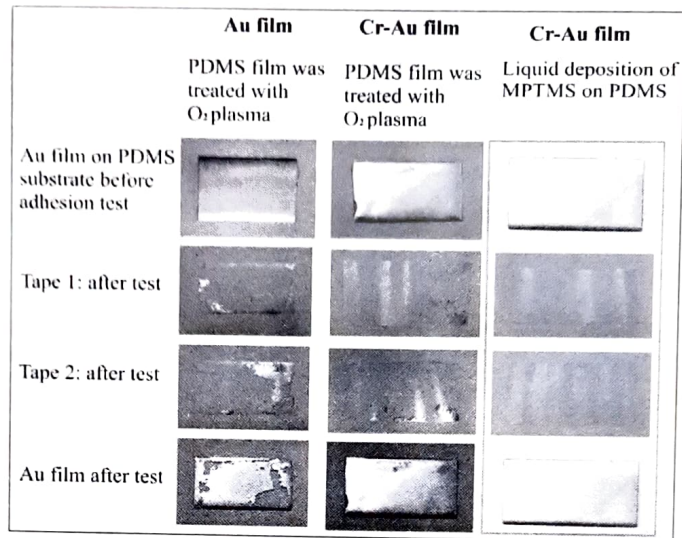


Fig. 2 : Photograph of the Au thin film over PDMS before and after the double tape test on O₂ plasma-treated sample, Cr/Au film on O₂ plasma-treated sample, and MPTMS coated sample.

Bucklemanipulation study

The fabricated Cr/Au thin film microstructure on PDMS with magnified images at the contact pad and central microline region of a single resistor is shown in figure 3. The magnified images show that the formation of ordered buckles on the surface of the metal film resistor. The ordered buckles after heating the patterned structure can be explained by studying the various stresses associated with the fabrication process. In this process, the Cr/Au thin film was deposited on a smooth PDMS film at 60°C using sputtering, which cooled down to 25°C after deposition. The deposited metal film experiences an equibiaxial compressive during this process due to different coefficients of thermal expansion of the PDMS and metal film, leading to random buckles [9]. After patterning the thin film using photolithography process, the length and the width of microline changes. The subsequent heating to 160°C and cooling made the equibiaxial stress to become directional, i.e., compressive stress along the width of the microline is different from the length [9]. This directional stress forces the buckles to transform into an ordered structure on the metal surface. Therefore, this method does not require any rigid structure or pre-strained PDMS film for ordering the random buckles [13] that formed due to mismatch Young's modulus and coefficient of thermal expansion after deposition.

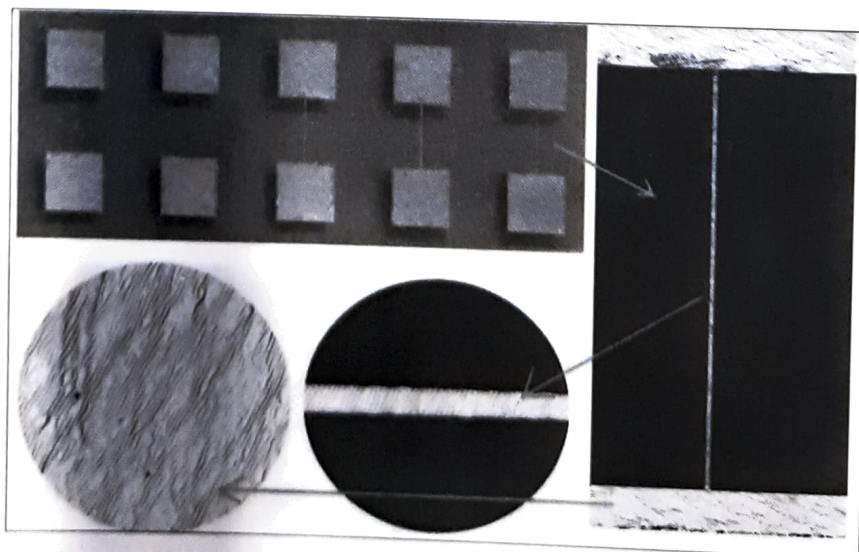


Fig. 3: Optical micrograph of Au thin film microline on a flexible PDMS substrate with magnified images of a micro-resistor.

Electrical characteristics study

The details of the optimized deposition conditions and electrical properties are presented in table 1. It is observed that at constant deposition, the film thickness increases linearly with the sputtering time on the PDMS sample. The results indicate that the measured sheet resistance of the Au film is higher than the bulk metal^[9]. The experimental results also show that an increase in the film thickness exponentially decreases the sheet resistance of the Au film, which resembles the reported literature^[14]. The Au thin film surface deposited over the PDMS film using dc magnetron sputtering is shown in figure 4. This SEM image shows that the surface of the Au film is granular, and the average diameter of the grain size is ~40 nm. The Au thin film surface is filled with nanoholes and nanocracks in between these grains. This nanohole and nanogaps are responsible for the high resistivity of the thin Au film on the elastomeric substrate compared to a bulk Au film^[8]. When tensile strain is applied on a strain sensor with Au thin film as a resistor on PDMS film, the nano-cracks between granular islands widens and contribute to high normalized resistance, and suitable for high strain sensitivity.

Table 1: The deposition parameters of Cr/Au sputtering & film properties.

Film type	Working pressure (mbar)	Sputtering power (W)	Sputtering time (s)	Film thickness (nm)	Sheet resistance $\Omega / \square$
Cr	0.0025	54	40	3.15 ± 0.5	
			60	5.05 ± 0.6	
Au	0.0025	60	150	102 ± 2.5	1.843 ± 0.285
			180	118 ± 3.0	1.035 ± 0.250
			230	154 ± 4.5	0.48 ± 0.115
			270	183 ± 4.0	0.331 ± 0.055
			300	202 ± 4.5	0.265 ± 0.045

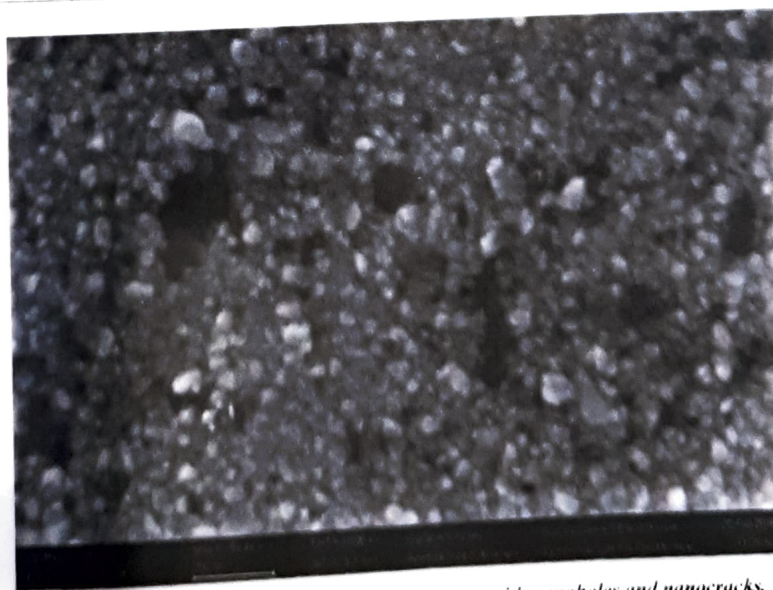


Fig. 4: SEM image of granular Au thin film surface with nanoholes and nanocracks.

DISCUSSION

Experimental observation of the Cr/Au thin metal film on PDMS shows that the deposited metal film is filled with granular Au islands occupied with nanoholes and nanogaps. These NanoRacks and nanoholes lead to the high sheet resistance of the metal film compared to bulk metal. Introducing MPTMS molecular adhesive layer in-between the PDMS and Cr/Au film enhances the adhesion between them, which leads to superior film quality.

The surface analysis of the Cr/Au thin film over PDMS film exposed the effect on buckling surface due to the heat treatment on the patterned thin film. Heating the patterned sample demonstrates a simple buckle manipulation technique of thin metal film on soft elastomer without using any prestrain film or ridge guided surface. Figure 5 shows arrays of Au thin film microelectrodes fabricated on a PDMS film for impedance measurement and is useful in biomedical and robotics skin applications. To increase the flexibility of the device, the connecting line is curvedly designed.

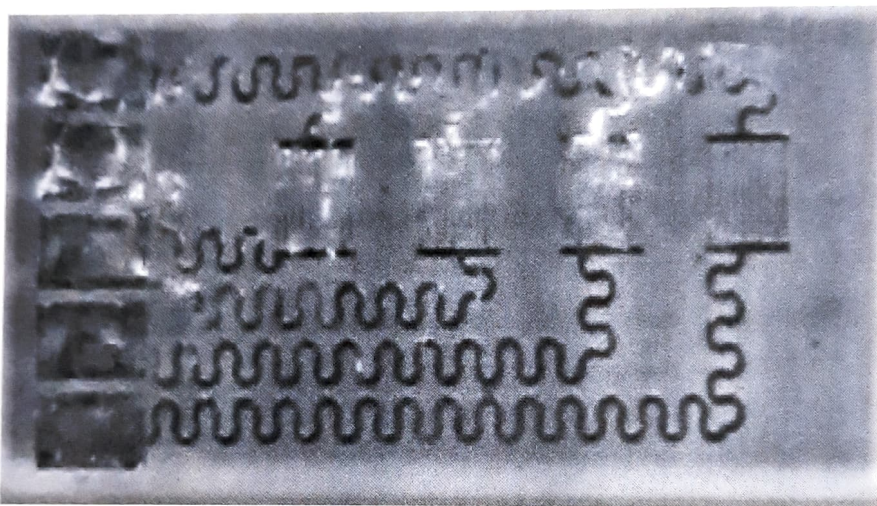


Fig. 5: Photograph of a flexible circuit with arrays of Au thin film microelectrode and curved connecting lines on PDMS substrate for dielectric property measurement.

CONCLUSIONS

The research work presents the fabrication and characterization of the metallic gold thin film micropattern deposited over PDMS elastomeric film for flexible electronic sensor and circuit applications. It is observed that the deposition of self-assembled MPTMS molecular adhesive over the PDMS surface increases the adhesion between a thin metal film with PDMS film. The contact angle measurement of the water droplet placed on the MPTMS layer coated PDMS surface indicates that the hydrophilicity of the modified PDMS surface significantly increases and lasts for an extended period compared to O_2 plasma-treated PDMS surface. Subsequently, the Au thin film was sputtered on bare PDMS, O_2 treated PDMS, and MPTMS molecular adhesive layer coated PDMS with the same deposition conditions using dc magnetron sputtering. Macroscopic adhesion study using a double tape peel-up test confirmed that the deposition of the molecular adhesive layer over the PDMS substrate showed better adhesion with the sputtered Au film compared to the other two PDMS samples. The deposited Cr/Au film was efficiently patterned for microstructure on the PDMS substrate using traditional photolithography and wet etching process, unlike the shadow mask technique that is mostly used for Au thin film deposition on elastomeric PDMS. The stronger adhesion between the thin metal film with the PDMS makes direct patterning using photolithography techniques possible. The random buckles formed on the Au metal film were successively manipulated. The SEM micrograph confirms the Au thin film on the PDMS film is granular and led to the high sheet resistance of the thin metal film. The research is beneficial for the reliable fabrication of sensors and circuits with an Au thin film on elastomeric PDMS film.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Ministry of Electronics and Information Technology (MeitY), Govt. of India, for supporting this work. The authors wish to acknowledge the Central Research Facility (CRF) and Microfabrication Laboratory, Indian Institute of Technology Kharagpur, for providing a fabrication characterization facility.

REFERENCES

1. J. A. Rogers, T. Someya, and Y. Huang: Materials and mechanics for stretchable electronics. *Science* 327: 1603-1607, 2010
2. A. Kakati and S. Das. Chameleon skin inspired Au nanodisk patterned strain responsive PDMS film. In 2018 IEEE SENSORS, 1-4, 2018
3. A. Kakati and S. Das. Nano-structured gold strain gauge arrays on PDMS for highly sensitive NEMS pressure sensor skin. 12th IEEE International Conference on Nano/Micro Engineered and Molecular Systems (NEMS), 611-614, 2017
4. Y. Wang, T. Yang, X. Li, X. Zang, M. Zhu, K. Wang, D. Wu, and H. Zhu: Wearable and highly sensitive graphene strain sensors for human motion monitoring. *Advanced Functional Materials* 24: 4666-4670, 2014
5. B. H. Jo, L. M. Van Lerberghe, K. M. Motsegood, and D. J. Beebe. Three-dimensional micro-channel fabrication in polydimethylsiloxane (PDMS) elastomer. *Journal of micro electro mechanical systems* 9(1): 76-81, 2000
6. A. Kakati, D. Maji, S. Das. Unveiling the wet chemical etching characteristics of polydimethylsiloxane film for soft micromachining applications. *Journal of Micromechanics and Microengineering* 27(1): 015033, 2016
7. A. Kakati and S. Das. E-Beam Patterned Gold Nanostructure Matrix on PDMS for Plasmomechanical Pressure Sensor Skin. 21st International Conference on Miniaturized Systems for Chemistry and Life Sciences (MicroTAS 2017), at Savannah, Georgia, USA 2017
8. S. P. Lacour, D. Chan, S. Wagner, T. Li, and Z. Suo. Mechanisms of reversible stretchability of thin metal films on elastomeric substrates. *Applied Physics Letters* 88(20): 204103, 2006
9. A. Kakati, and S. Das. Self-transformed parallel structures in strain sensitive Au thin film micropattern embedded on soft elastomer. *Journal of Micromechanics and Microengineering* 30 (11): 115004, 2020
10. T. Fujii. PDMS-based microfluidic devices for biomedical applications. *Microelectronic Engineering* 61: 907-914, 2002
11. I. Byun, A. W. Coleman, and B. Kim. Transfer of thin Au films to polydimethylsiloxane (PDMS) with reliable bonding using (3-mercaptopropyl) trimethoxysilane (MPTMS) as a molecular adhesive. *Journal of Micromechanics and Microengineering* 23(8): 085016, 2013
12. D. Bodas, and C. Khan-Malek. Hydrophilization and hydrophobic recovery of PDMS by oxygen plasma and chemical treatment-A SEM investigation. *Sensors and Actuators B: Chemical* 123 (1): 368-373, 2007
13. D. Maji, D. Das, J. Wala, and S. Das: Buckling assisted and lithographically micropatterned fully flexible sensors for conformal integration applications. *Scientific reports* 5: 17776, 2015
14. K. Chopra, L. Bobb, and M. Francombe. Electrical Resistivity of Thin Single-Crystal Gold Films. *Journal of Applied Physics* 34(6): 1699-1702, 1963

Vacuum based coatings for engineering applications

V. VASUDEVA RAO¹ and V. RAVINDRA^{2*}

¹ Cryogenic Engineering Centre, IIT Kharagpur

² School of Energy Science & Engineering Centre, IIT Kharagpur

Abstract: In the present modern age, vacuum based coatings are employed in every field of technology to reduce size and improve performance. The present paper briefly describes the physical concepts involved in vacuum coating for different applications along with technical details of necessary vacuum equipment.

Keywords: Vacuum, PVD, CVD, Sputtering, Coating applications

INTRODUCTION

Vacuum based coating is the deposition of a two-dimensional film on a surface in a vacuum (or low-pressure plasma) environment. These coatings are finding several engineering applications related to public life. These include laptops, mobile phones, LED-TVs, coated spectacles, solar-PV coatings, solar thermal coatings, diamond coated machine tools, decorative coatings and coatings on household items like utensils & packaging materials. Further, several industrial products and processes depend on metallic coatings for wear-resistance, corrosion resistance, thermal resistance, electrical transport, optical efficiency etc^[1]. Vacuum environment gives advantages of reducing the boiling point of the material to be deposited (power saving) and increases the time to form the monolayer (less contamination like oxidation).

Vacuum coatings are broadly classified into two types: Physical vapour deposition (PVD) and Chemical vapour deposition (CVD). In Physical vapour deposition (PVD) material to be deposited as the coating is melted to create vapour for coating using resistively heated filament/ boat of refractive metal such as Mo, Ta, W, Nb under high vacuum. One can use several metallic vapour sources evaporating sequentially or simultaneously for controlling the thickness of individual layers by suitable shutters connected to process controllers for creating a composite film with required properties for an engineering application^[2]. In CVD process, the material being deposited comes from a chemical vapour precursor that is decomposed by reduction or thermal decomposition—mostly on a hot surface. In contrast to PVD methods where the substance to be deposited is either solid or liquid, in CVD the substance is already in the vapour phase when admitted to the vacuum system. To deposit it, the substance must be thermally excited, i.e. by means of appropriate high temperatures or with a plasma.

Physical vapour deposition (PVD) coating techniques are mostly confined to making relatively thin films at a vacuum level of 10^{-4} to 10^{-9} mbar, whereas chemical vapour deposition (CVD) is used both for thin films as well as thick coatings up to 1 mm at relatively low vacuum levels. The present paper concentrates more on vacuum based PVD coatings and their engineering applications.

VACUUM BASED COATING UNITS FOR THIN FILM DEPOSITION

Vacuum coating units are specialized equipment consisting of modern vacuum pumps (Turbo, Cryo, Diffusion, Roots and Rotary), vacuum measuring gauges (Pirani, Penning, Bayard Alpert ionization gauge, RGA) and process controllers (mass flow controllers, temperature controllers, pressure controllers, HV/RF controllers). In addition, the manufacturers of specialized vacuum coating systems should be aware of vacuum chamber manufacturing (material selection, welding, brazing) and vacuum troubleshooting procedures (cleaning and leak detection)^[3].

In most of the vacuum based PVD systems (Fig 1a), the distance between the vapour source and the substrate material (on which deposition takes place) is less than the mean free path at the operating vacuum so that there will be no scattering of the depositing vapor molecule, till they arrive at the substrate to form thin film coating.

* Correspondence Author E-mail - vvrao@cryo.iitkgp.ac.in

Vacuum compatible high current feed-throughs are connected to the base plate of the vacuum chamber for electric heating of boats and substrates. Substrate heating/cooling attachment in PVD units helps to grow crystalline / amorphous film. With the recent availability of large capacity Ultra-high Vacuum (UHV) Pumps, high quality thin films are being made by Molecular beams created through evaporation from hot solid sources without melting (effusion cells). Such coating units extending the PVD to UHV conditions are called molecular beam epitaxy units (Fig 1b).

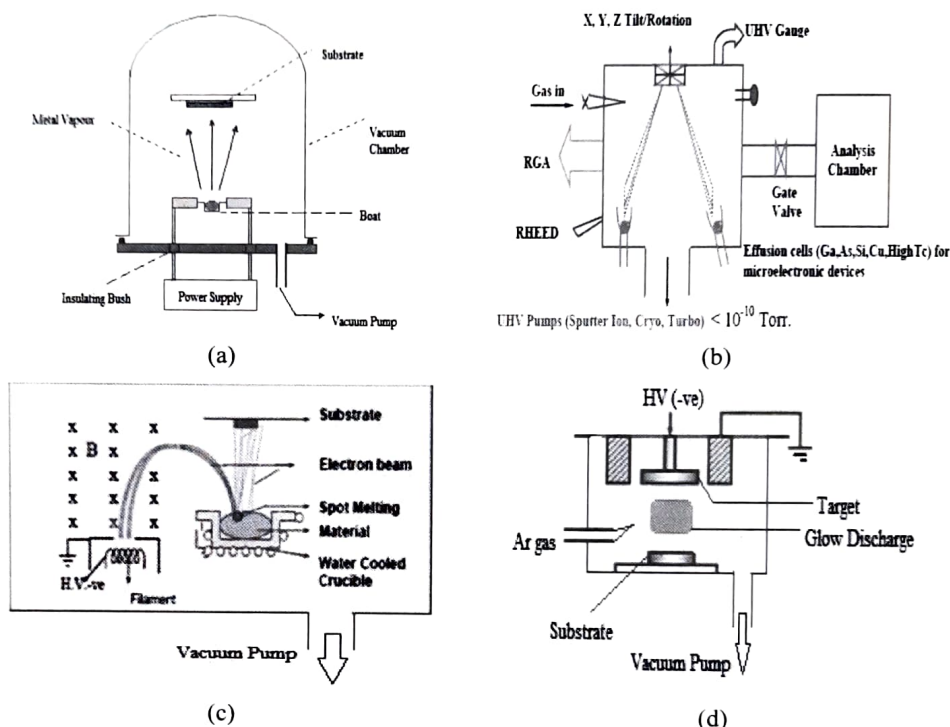


Fig.1: Schematic diagrams of (a) thermal evaporation (PVD), (b) Molecular Beam Epitaxy (MBE) (c) e-beam deposition and (d) Sputtering deposition

Unlike electrical heating, electron beam heating (Fig 1c) and sputtering process (Fig 1d) can also be used for a deposition without melting the total source material. These methods also reduce contamination from support material and minimize the consumption of costly materials with high melting points. In electron beam deposition under vacuum, a concentrated e-beam is focused on a spot of the source material by suitable electric and magnetic fields for evaporation without any heating of bulk material.

In DC sputtering, a controlled discharge is created between the substrate (anode) and the source material (cathode) to be coated. The positive ions in discharge plasma are accelerated towards the cathode and act as machine tools to dislodge (sputtering) the material from the cathode through momentum transfer at the surface. These sputtered atoms from the cathodic target get deposited as a film/coating onto the substrate attached to the anode (usually grounded). We cannot use DC sputtering for non-conducting targets and hence, one uses RF sputtering for sputtering the non-metallic target for film deposition. Both DC and RF sputterings can be extended to high vacuum conditions by adding magnetic confinement of plasma (magnetron sputtering).

ENGINEERING APPLICATIONS OF VACUUM COATINGS

Recently, the importance of relatively thick coatings using PVD is increasing for special engineering applications like thermal barrier coatings, corrosion protective coatings, wear resistant coatings & diamond like hard coatings under the broad discipline known as 'Surface Engineering'^[4]. Similarly, metallization coatings, optical layers and conducting films are finding applications in several modern technologies. These aspects are briefly explained in this section.

Wear/Corrosion resistance coatings

Gold coloured TiN coatings are used successfully on machine tools for improving their wear/ corrosion resistance properties. Coatings may be crystalline or amorphous depending on the processing conditions. These hard coatings increase the cutting efficiency and life of machine tools^[5]. Hard coatings also are used to minimize fatigue-wear in ball bearings and to improve the scratch resistance of moulded plastic lenses and plastic aeroplane canopies. Vacuum coatings at surfaces are also effective in creating protection from an aggressive chemical environment. For example, carbon coatings are used on metals to be implanted in the human body. Similarly deposited coatings of cadmium, aluminium, and Al:Zn alloys are used for preventing galvanic corrosion of steels.

Vacuum coatings for metallization application

The aluminium metallization of polymer webs used in manufacturing power capacitors typically requires the system to be pumped out to 10^{-6} mbar range and when the deposition starts the pressure typically rises into the 10^{-4} mbar region. Roll-to-roll metallization, also known as web coating, is the process of creating patterned metal layers on a roll of flexible polymer film. Such flexible metallised polymer rolls are subsequently being slitted to the required dimensions on a slitting machine. Capacitor films for high power application are usually metal coated thin polymer films using thermal evaporation (PVD). These thin film materials are very sensitive to the alignment of the polymer rolls with respect to evaporating metal source in a high vacuum chamber ($\sim 10^{-4}$ torr) and control of proper speed & tension of web is very crucial. These thin metallised web coatings may tear under tension (required for moving the roll). This problem can be solved by running the tape on several support wheels to have multiple short free span lengths.

Blanket metallization is used to shield mobile phones from electromagnetic interference (EMI). Similarly, in semiconductor based electronic devices, aluminium or gold films are used as electrodes on silicon. However, as these microelectronic circuits are processed at high-temperatures, an electrically conductive titanium nitride film is deposited on silicon surface before the metal electrode is deposited to prevent the metallic diffusion into silicon.

High Tc superconducting coatings

The recent development of high Tc superconducting tapes (2G-HTS) based on Yttrium Barium Copper Oxide (YBCO) coating are becoming technologically important. These 2G-HTS tapes in sufficient length are manufactured by depositing YBCO films on flexible metal substrates with different buffer and protection layers in high vacuum conditions. The deposition methods include pulsed laser deposition (PLD) and metal-organic chemical vapour deposition (MOCVD). These HTS tapes can carry very high currents without any electrical resistance. Intense efforts are going on around the world to use these coated superconducting tapes in electrical power, medical and nuclear applications^[6]. Further, the HTS superconducting films by sputtering and MBE methods are going to play an important role in realising superconducting quantum computing.

Optical coatings

Vacuum based optical coatings are used in ophthalmic optics, lenses for cameras/optical instruments, optical filters, antireflection (AR) coatings and special mirrors. They are usually deposited in multiple layers to get desired transmission or reflection properties of glass or plastic substrates. The thickness and refractive index of individual coatings are controlled precisely and matched to each other. Quartz crystal thickness monitors are used to monitor the deposition rates and accumulated thicknesses of various layers. The vacuum system for these optical coaters consists of high vacuum pumps (Turbo molecular/Cryo/Diffusion) backed by a combination of a rotary vane pump and roots pump. Aluminium films are also widely used as front-surface reflectors for headlights along with an over-coat of the protective polymer film.

Packaging and Decorative Coatings

Recently, aluminium metal coatings on flexible polymer films and papers are being developed on a large scale for food packaging to reduce the water vapor transmission rate and oxygen transmission rate. Metallization for decorative purposes is also becoming a large market based on metallization of three-dimensional articles such as moulded polymer decorative fixtures and cosmetic containers. These coatings consist of a reflective aluminium coating deposited on a smooth base coat, followed by a dyed lacquer so that the coating gets the desired colour and texture along with corrosion/wear resistance. Similarly, gold coloured titanium nitride (TiN) and brass coloured zirconium nitride (ZrN) coatings with good scratch resistance are used on door hardware, plumbing fixtures and fashion items.

Coatings for solar thermal / PV applications

Both selective absorbing coatings and highly reflecting coatings are extensively used in harvesting solar energy in the form of heat. These coatings are useful for concentrating solar power (CSP) technologies which have a great promise in meeting the energy requirements of the world. The CSP technologies are classified into four types: Parabolic trough collector (PTC), Parabolic dish concentrator, linear Fresnel reflector and solar tower (ST). Among these, PTC and ST technologies are gaining more prominence. While the parabolic trough technology is a line focus technology, the solar tower is a point focus technology. In PTC we use highly reflective aluminium coatings on parabolic collector which focusses the solar energy on to an absorber tube located along the focal axis. The absorber tube is coated with multiple layers of different materials to effectively absorb the focussed solar radiation for conversion into useful heat^[7].

Thin film based photovoltaic (PV) solar panels utilize one of the four technologies based on (i) Cadmium Telluride (CdTe), (ii) Amorphous silicon (A-Si), (iii) Copper Indium Gallium Selenide (CIGS) and (iv) Gallium Arsenide (GaAs) coatings. These panels are much smaller compared to conventional bulk silicon based panels. While GaAs and CIGS are yet to become cost effective, CdTe and A-Si have already penetrated the market with mass production strategies. The CdTe thin film solar cells are made on glass support consisting of several sub-layers. The deposition sequence of these sublayers is as follows:

A conductive tin oxide (ITO) is first deposited on glass support (substrate), followed by a transparent layer of Cadmium Sulphide (CdS) with high electrical resistivity.

A thin layer of CdTe is then applied, so that sunlight induced electrical carriers are generated at the interface between CdS and CdTe layers. A suitable thermal activation treatment is given at this stage to optimize the crystalline structure and electrical properties of solar cell.

Finally, a metallic compact layer is deposited for draining the carriers into the external circuit, followed by encapsulation and panelling.

The deposition methods adopted for CdS/CdTe solar panels include thermal evaporation, sputtering, close-spaced sublimation and vapour transport deposition^[8].

CONCLUSIONS

It is very clear from the above studies, that public life in modern society involves several engineering applications of vacuum based coatings. This paper briefly presents the scientific principles of vacuum coating and their applications in various fields.

ACKNOWLEDGMENTS

The authors would like to acknowledge the companies, Pfeiffer Vacuum India Pvt Ltd and TDK India Pvt Ltd for sharing their experiences on coating equipment. The help in typing and editing of this article by Mr PappuSubba Rao is also acknowledged.

REFERENCES

- [1] Bishop, C.A. Vacuum Deposition onto Webs, Films and Foils: Third Edition (Elsevier Inc.), 2015.
- [2] Chopra, K.L. Thin Film Phenomena, (McGraw Hill, New York), 1969
- [3] Rao, V.V., Ghosh, T.B. and Chopra, K.L. , Vacuum science and technology, (Allied Publishers), 1998.
- [4] Subramanian, C., Strafford, K. N., Wilks, T. P., and Ward, L. P., On the design of coating systems: Metallurgical and other considerations. Journal of Materials Processing Technology, 56: 385–397, 1996.
- [5] Grainer, St. and Blunt, J., Engineering coatings – Design and applications. (Cambridge: Abington Publishing), 1998.
- [6] Wang, Y., Fundamental Elements of Applied Superconductivity in Electrical Engineering. (John Wiley and Sons), 2013.
- [7] Xu, K. et al, A review of high-temperature selective absorbing coatings for solar thermal applications. J. of Materiomics 6: 167–182, 2020.
- [8] Rahmana, K.S., et al, Influence of deposition time in CdTe thin film properties grown by close spaced sublimation (CSS) for photovoltaic application. Results in Physics 14: 102371, 2019.

Multifunctional properties of electrodeposited nickel composite coating containing nanosized monoclinic zirconia particles

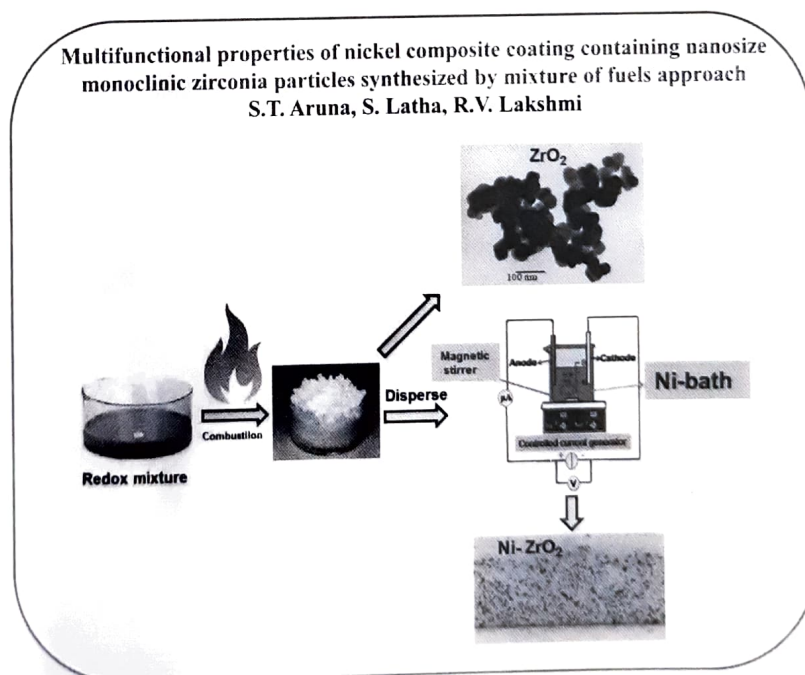
S.T. ARUNA*, S. LATHA and R.V. LAKSHMI

Surface Engineering Division, Council of Scientific and Industrial Research-National Aerospace Laboratories, HAL Airport Road, Bangalore 560017, India

Abstract : Nickel-based composite coatings containing ceramic particles as the distributed phase have been widely used in aerospace and automotive industries. In the present work, a Ni-composite coating containing nanosized monoclinic zirconia (ZrO_2) powder is prepared by solution combustion (SC) method. The SC method is modified to get phase pure white zirconia powder by using the mixture of fuels approach. Since the synthesized powder contained agglomerated particles, the powder is ball milled and dispersed in a nickel sulphamate bath. The Ni and Ni- ZrO_2 coatings are electrodeposited at 0.75 A/dm^2 for 6 h. The Ni- ZrO_2 composite coating exhibits a microhardness of 750 KHN(50 gf) as against 270 KHN(50 gf) observed for plain Ni coating. The Ni- ZrO_2 coating exhibits improved corrosion resistance and wear resistance compared to plain nickel coating as confirmed by potentiodynamic polarization and continuous salt spray tests. The as-deposited hydrophobic Ni- ZrO_2 coating transforms to superhydrophobic upon depositing a thin layer of fluoroalkyl silane on the coating. Thus, the synthesized zirconia particles when incorporated in the Ni matrix impart multifunctional properties to the electrodeposited Ni coating.

Keywords: Electrodeposited; composites; nickel; zirconia; corrosion; wear; superhydrophobic

Graphical Abstract



INTRODUCTION

Nickel-based composites containing reinforced particles are playing a pivotal role in aerospace and automotive industries owing to their high specific strength, excellent mechanical properties, good thermal stability, good toughness, chemical inertness, high wear resistance and corrosion resistance [1]. Silicon carbide has been the most widely used reinforcement mainly owing to its high hardness and higher wear resistance [2-4]. Further, to extend the application of electrodeposited Ni composite coatings for higher temperatures, oxide

* Corresponding Author Email: aruna_reddy@nal.res.in

particles have been explored in lieu of SiC particles. The important reinforcement or distributive phases that have been explored in the literature are Al_2O_3 [5], TiO_2 [6], Fe_2O_3 [7], CeO_2 [8], ZrO_2 [9], diamond [10], graphite [11], carbon nanotubes (CNTs) [12], etc. The research arena of electrodeposited composite coatings continues to expand. More recent papers are focused towards utilizing graphene/graphene oxide [13-19] and a mixture of phases [20] as distributive phases in Ni matrix. There has been renewed interest in using non-oxide ceramics such as TiC and TiN as fillers in electrodeposited Ni composite coatings on tungsten carbide cutting tools [21]. Among the different distributed phases studied, zirconia is an important ceramic material as it is known for its excellent high temperature mechanical properties, thermal shock resistance, wear and oxidation resistance, low thermal conductivity and reasonable match in thermal expansion coefficient to that of metals [22]. Pure ZrO_2 has a monoclinic crystal structure at room temperature and undergoes transitions to tetragonal and cubic phases at increasing temperatures. It is observed that in most of the reported Ni- ZrO_2 composite coatings [23-27] commercially available zirconia powder is being used and seldom the phase of zirconia is mentioned. A recent publication shows the prospects of using Ni- ZrO_2 nanocomposite on the surface of the copper plate of crystallizer, an important equipment used for continuous casting production at 280°C [28].

In the present study, electrodeposited Ni composite coating containing monoclinic zirconia as the distributive phase exhibiting multifunctional properties is described. The monoclinic zirconia powder has been prepared by solution combustion technique. The process has been modified to get phase pure, carbon free monoclinic zirconia powder. The powder has been characterized for phase purity and morphology. The synthesized powder has been used as the filler in electrodeposited Ni composite coating. The obtained coating has been characterized for microstructure, phase, mechanical, and wear and corrosion properties. The wettability of the coatings has also been studied.

EXPERIMENTAL

Preparation and characterization of ZrO_2 powder

Solution combustion method, which is one of the most popular methods for the synthesis of nanosize oxides, has been utilized for the synthesis of zirconia powder [29]. For the preparation of phase pure and carbon free white zirconia powder, the redox mixture composition used for solution combustion was optimized (Table-1). The temperatures measured during solution combustion synthesis using a K-type thermocouple are also tabulated in Table-1. Phase pure white zirconia powder was prepared by a mixture of fuels approach as follows: 0.031 M of ZrOCl_2 was dissolved in water to which 10 mL of nitric acid was added and stirred well. To the clear solution, 62.06 g urea, 21.72 g ammonium acetate and 37.5 g ammonium nitrate were added. The clear solution was transferred to alumina crucible and placed in a furnace pre-heated to 350°C . The solution boils, froths, catches fire and gives voluminous white oxide powder. It was found that a combination of mixture of fuels and oxidizers facilitated the formation of pure white zirconia particles devoid of carbon traces and which may be attributed to the higher flame temperature observed with this composition.

Table-1. Solution combustion synthesis parameters used for the preparation of monoclinic zirconia powder.

S. No.	Mole ratio of Oxidizers		Mole ratios of Fuels			Flame temp. ($^\circ\text{C}$)	Nature of combustion	Powder color
	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	NH_4NO_3	Glycine	Urea	Ammonium acetate			
1	0.031	---	0.069	---	---	238	Flameless	Black
2	0.031	---	0.034	0.052	0.028	317	Flameless	Black
3	0.031	---	0.035	0.052	0.056	330	Flameless	Black

S. No.	Mole ratio of Oxidizers		Mole ratios of Fuels			Flame temp. (°C)	Nature of combustion	Powder color
	ZrOCl ₂ ·8H ₂ O	NH ₄ NO ₃	Glycine	Urea	Ammonium acetate			
4	0.031	---	0.017	0.077	0.028	325	Flameless	Black
5	0.031	0.012	---	0.103	0.028	330	Flameless	Dull white
6	0.031	0.025	---	0.103	0.028	350	Flameless	Dull White
7	0.031	0.025	---	0.103	0.028	400	Dull flame with orange sparks	Dull White
8	0.031	0.031	---	0.103	0.028	450	Flame with orange sparks	White
9	0.031	0.047	---	0.103	0.028	700	Bright flame	Pure white

The phase purity and crystallite size of the synthesized powder was determined using a powder X-Ray diffractometer (Bruker D8 Advance, CuK α radiation). The monoclinic phase present in the synthesized zirconia powder was identified from XRD pattern using JCPDS card: 37-1484. The morphology of the synthesized zirconia powder was obtained by Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss). The particle size distribution of the powders was measured using a particle size analyzer (Mastersizer 2000, Malvern instruments). The transmission electron micrograph (TEM) of the zirconia particle was measured using JEOL-JEM 100SX transmission electron microscope.

Development of electrodeposited Ni-ZrO₂ composite coating

Nickel sulfamate plating bath with the composition as detailed in Table-2 was used for depositing Ni and Ni-ZrO₂ coatings. About 200 mL of Ni-sulfamate plating bath containing 20 g of synthesized ZrO₂ particles was taken in a glass beaker and its pH was adjusted to 4. A pure nickel sheet with a dimension of 2.5 cm x 12 cm was used as anode and a polished brass substrate with similar dimension as the anode was employed as cathode. The brass substrate was degreased with acetone and cathodically cleaned by dipping it in a mild alkali (20% NaOH) at 0.0645A/dm² and dipped in 10% H₂SO₄. It was finally washed with distilled water. The above electrolyte bath containing zirconia particles was magnetically stirred with ~600 rpm for 15 hours before the deposition and during co-deposition to confirm proper dispersion of particles in the bath. The co-deposition was carried out on the brass substrate area of 2.5 cm x 3.75 cm using a current density of 0.75 A/dm² for a duration of 6 h to obtain a deposit thickness of ~40 μ m according to Faraday's laws. These parameters were chosen based on the optimized parameters of the previous study^[30].

Table-2. Composition of the nickel sulfamate bath used for electrodeposition.

S. No.	Plating bath chemicals	Supplier	Composition
1.	Nickel sulfamate solution (50 g Ni/L)	Grauer & Weil, India	300 g/L
2.	Nickel chloride	S.D Fine	10 g/L
3.	Boric acid	S.D Fine	30 g/L
4.	Sodium lauryl sulfate	S.D Fine	0.2 g/L
5.	Zirconia powder	In-house synthesized	100 g/L

Characterization of developed Ni-ZrO₂ composite coating**Phase, microstructure, surface roughness and microhardness of Ni and Ni-ZrO₂ composite coatings**

The XRD patterns were indexed as per the JCPDS no. 4-850. The relative texture coefficients (RTC(hkl)) were calculated for electrodeposited Ni and Ni-ZrO₂ composite coatings based on their XRD patterns^[31]. The texture and preferred orientation of Ni and Ni-ZrO₂ films was calculated by employing relative texture coefficient RTC_{hkl} (eqn. 1):

$$RTC_{hkl} = \frac{I_{hkl} / I_{hkl}^0}{\sum_1^3 I_{hkl} / I_{hkl}^0} \cdot 100\% \quad \dots\dots\dots (1).$$

where I_{hkl} are the relative intensities of the (hkl) reflections, $\sum I_{hkl}$ is the sum of all the peak intensities corresponding to (111), (200), and (220) peaks of Ni. In the equation I_{hkl}^0 refers to the relative intensities of a randomly oriented nickel powder sample.

The surface microstructure of as deposited coatings was observed using FESEM. The surface roughness of the coatings was also analyzed using 3D-profilometer (Nanomap 500LS, AEP Technology)

To prepare, the samples for cross-sectional imaging and microhardness determination the as-deposited Ni and Ni-ZrO₂ coatings were coated with Cu backup layer. Then the coating along with the substrate was cut and mounted in a Bakelite matrix. Then the samples were ground with various grades of emery followed by metallographic polishing (down to 0.05 μ m) using alumina slurry. The Knoop microhardness was measured on the cross-section at ten different locations using a load of 50 gF (Micromet 2103, Buehler). The microstructure of the cross section of Ni-ZrO₂ coating was recorded using a microscope.

Corrosion studies

The corrosion studies of Ni and Ni-ZrO₂ coatings on brass substrates were conducted in deaerated 3.5 wt% (0.6 M) NaCl solution (200 $\pm$ 2 ml) using an electrochemical workstation (CHI 604 2D). The test was conducted using Ni and Ni-ZrO₂ coated brass coupons with an active area of 1cm² each as working electrodes, platinum foil as counter electrode and a standard saturated Calomel electrode as the reference electrode. The details of potentiodynamic polarization have been already reported^[32]. The corrosion potential (E_{corr}), corrosion current density (i_{corr}) and polarization resistance (R_p) were deduced from the Tafel plot and are summarized in Table-3. The polarization resistance was obtained using the Stern-Geary equation^[33].

$$R_p = \left[\frac{b_a b_c}{2.303(b_a + b_c)} \right] \left[\frac{1}{i_{corr}} \right] \quad \dots\dots\dots 2$$

Where b_a and b_c are Tafel slopes or the Tafel constants, expressed in mV/dec.

Corrosion rates (CR) were calculated by the following equation:

$$CR = \frac{1.13 i_{corr} \times Eq. \text{ wt. of Ni}}{\text{Density of Ni}} \quad \dots\dots\dots 3$$

The samples were also subjected to accelerated corrosion by placing them in a highly corrosive conditions (5% NaCl solution) in a continuous salt spray chamber (Ascott Sxp 120,) as per ASTM B117 standard. The coatings were also tested for 2400 h.

Table-3 : Relative texture coefficients of Ni and Ni-ZrO₂ electrodeposited coatings.

Sample	Relative Texture Coefficient (%)		
	(111)	(200)	(220)
Ni	15.54	56.35	28.09
Ni-ZrO ₂	39.84	33.30	26.84

Wear studies

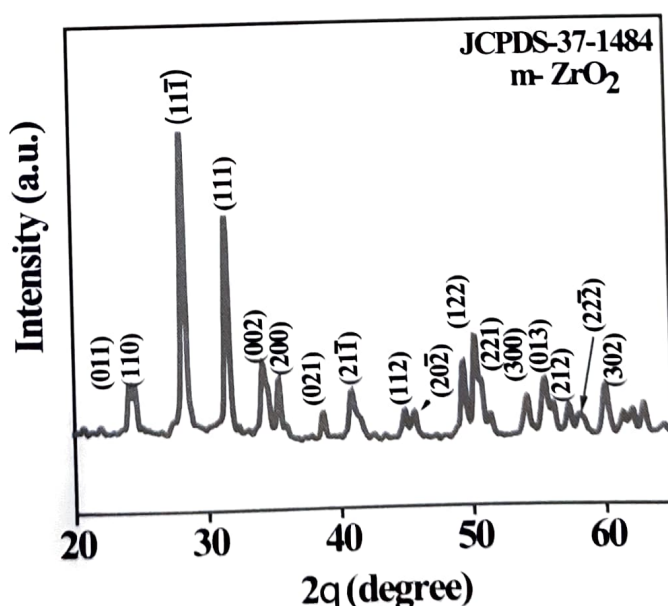
The wear resistance of the electrodeposited Ni and Ni-ZrO₂ composite coatings on brass pin (radius 6 mm) was investigated using a pin-on-disk wear tester (DUCOM, India) under ambient conditions of temperature and humidity (30°C, 50% RH) at an applied load of 9.8 N. The counterpart was hardened EN31 steel disk with a hardness of 750 HV. Complete details regarding the wear studies have already been reported [32]. The wear coefficient was calculated using the Holm-Archard relationship [34, 35].

Water repellent property of Ni and Ni-ZrO₂ composite coatings

The brass substrates coated with Ni and Ni-ZrO₂ coatings were surface modified with a low surface energy material like 1 wt% of fluoro alkyl silane (FAS-17, ABCR GmbH) ethanolic solution using a paint spray gun. The FAS treated coatings were dried at 80 °C for 1 h. The water contact angles (WCA) on the surface of as-deposited and FAS treated Ni and Ni-ZrO₂ coatings were measured at room temperature using a contact angle meter (Surface Electro Optics, Phoenix) by sessile drop method by placing 8 µL water drops on the surface of the coatings. The average value of five WCA measurements at different positions of each coating is reported as the final WCA.

RESULTS AND DISCUSSION**Powder characterization**

Figure 1 shows the XRD pattern of as calcined ZrO₂ powder. The XRD peaks correspond to monoclinic zirconia phase and peaks corresponding to either tetragonal or cubic phases of zirconia were not observed. The crystallite size as calculated from Scherrer equation was 26 nm.

**Fig. 1. Powder XRD pattern of solution combustion synthesized zirconia powder.**

The particle size distribution curve of zirconia powder (Fig. 2) exhibits a uniform distribution of particles. The average agglomerated particle size was $2.875\ \mu\text{m}$ with 90% of the particles below $9.5\ \mu\text{m}$ and 10% of the particles below $0.876\ \mu\text{m}$.

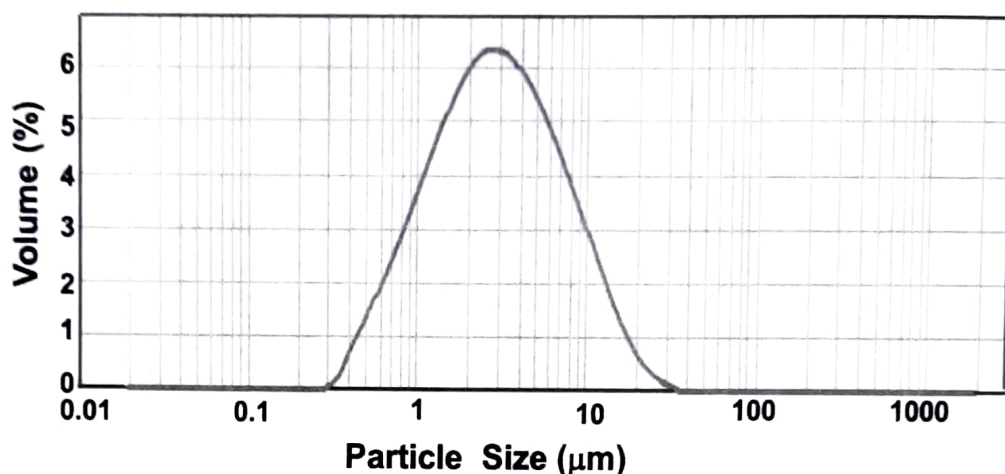


Fig. 2. Particle size distribution of ball-milled ZrO_2 powder.

The FESEM image of as prepared zirconia powder showed flaky structure (not shown). The FESEM images of ball-milled zirconia powder is shown in Fig.3a. The FESEM image of zirconia powder exhibited smaller agglomerated particles. The particle size seems to vary from 50-100 nm with some bigger agglomerated particles. The TEM image clearly shows distinct particles with the majority of the particles having $< 50\ \text{nm}$ size (Fig.3b).

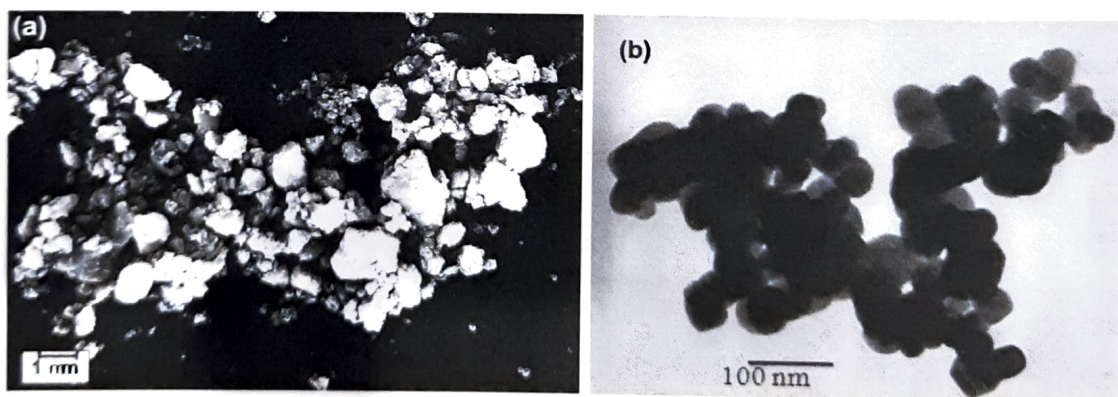


Fig. 3. (a) FESEM and (b) TEM images of ball milled ZrO_2 powder.

Phase, microhardness, microstructure and surface roughness of Ni and Ni- ZrO_2 coatings

Figure 4 shows the XRD patterns of electrodeposited Ni and Ni- ZrO_2 coatings. It is evident from the XRD patterns that pure nickel coating exhibited intense peaks at 44° and 51° corresponding to Ni (111) and (200) planes respectively. The XRD pattern of Ni- ZrO_2 composite coating showed ZrO_2 peak which clearly indicates the incorporation of large number of particles in the coating.

There was also a slight change in the relative texture coefficients for Ni and Ni- ZrO_2 composite coatings (Table-III). The preferred orientation through an axis $[hkl]$ was selected by values of $\text{RTC} \geq 25\%$ such that when the RTC approaches the value of 100%, the strength of the preferred orientation becomes maximum amount. The (200) peak intensity was highest for Ni and for Ni- ZrO_2 the peak intensity was highest for (111). The preferred orientation in Ni was [200] and in case of Ni- ZrO_2 , [111] was the preferred orientation.

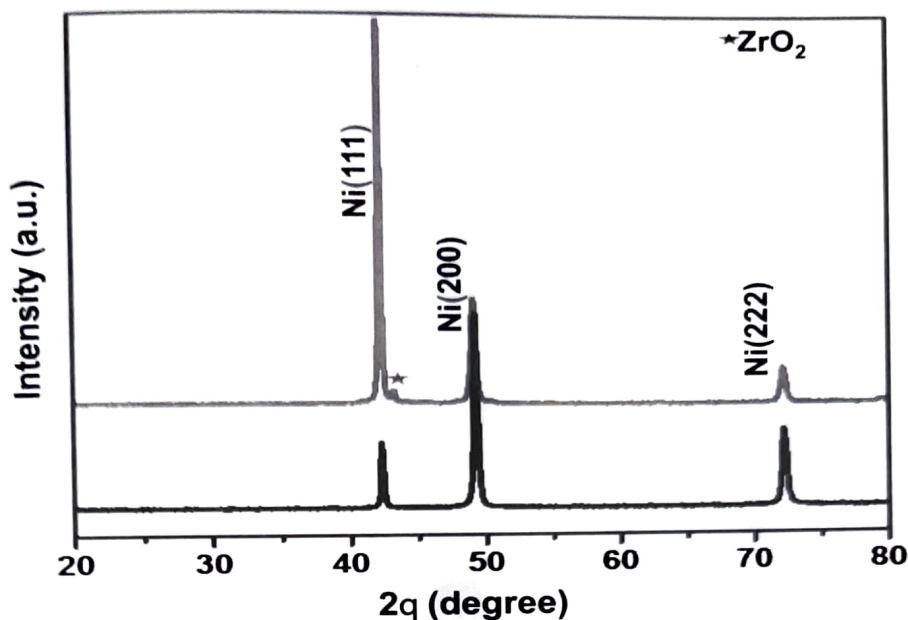


Fig. 4. XRD patterns of electrodeposited (a) Ni and (b) Ni-ZrO₂ composite coatings.

The Ni crystallite sizes as calculated from Scherrer formula were 32 and 24 nm for Ni and for Ni-ZrO₂ it was 38 and 19 nm respectively for the peaks corresponding to (111) and (200) respectively. From this, it is evident that there is not much of a change in the crystallite size of nickel with the incorporation of zirconia particles. The optical micrograph of Ni-ZrO₂ coating is shown in Fig. 5. It shows a uniform distribution of particles. The presence of agglomerated particles is also evident.

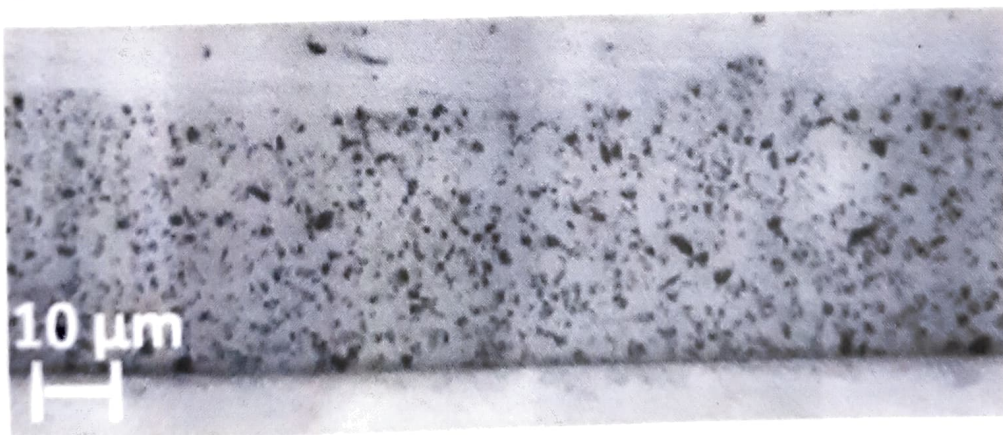


Fig. 5. Optical micrograph of Ni-ZrO₂ coating electrodeposited at 0.75 A/dm².

The Ni-ZrO₂ composite coating exhibited a microhardness of 750±10 KHN (50 gf) and Ni electrodeposited under similar conditions exhibited a microhardness of 270±10 KHN(50 gf). Since the grain refinement was not remarkable in case of Ni-ZrO₂, the dispersive strengthening effects would have dominated resulting in higher microhardness of the composite. Thus the enhancement of microhardness of Ni-ZrO₂ composite coating can also be related to the dispersion-strengthening effect caused by ZrO₂ particles in the composite coatings, which obstruct the motion of dislocations in the Ni matrix [36].

Figure 6 shows the surface topography of Ni and Ni-ZrO₂ composite coating. Ni coating shows more uniform surface and Ni-ZrO₂ coating shows the presence of some protrusions clearly indicating a rough surface. The surface roughness was 628 and 193 nm respectively for Ni-ZrO₂ and Ni coatings.

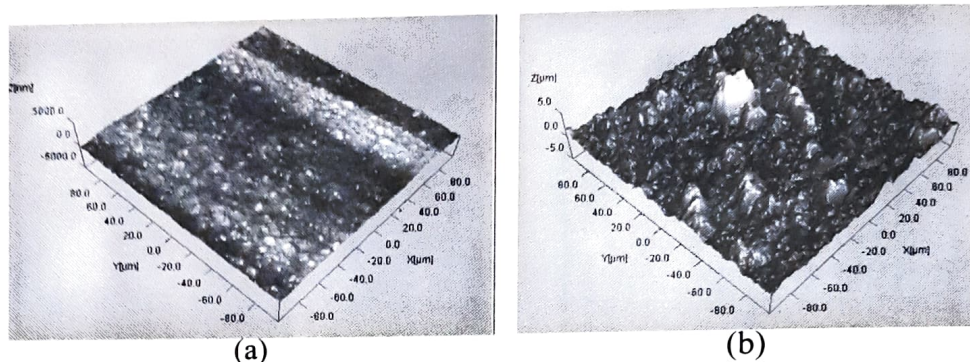


Fig. 6. 3D-image showing the surface roughness and topography of electrodeposited (a) Ni and (b) Ni-ZrO₂ coatings.

The pure nickel deposit exhibited a rather regular surface (not shown), whereas the composite coating developed an uneven surface containing nodular features (Fig.7). The zirconium oxide particles are clearly seen on the surface. Also, white zirconia particles are homogeneously distributed on the surface.

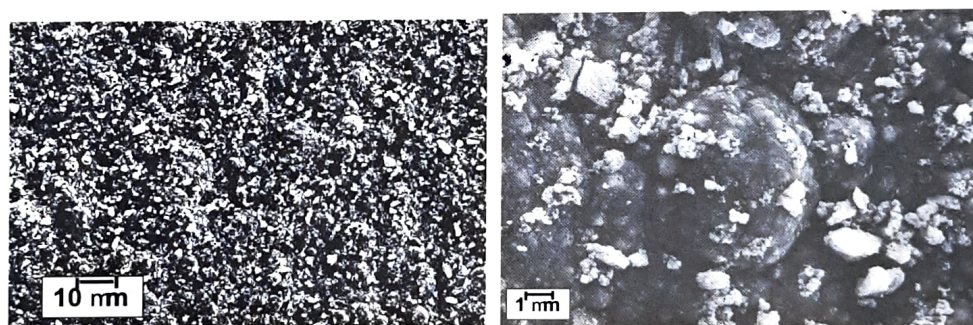


Fig. 7. FESEM image of electrodeposited Ni-ZrO₂ composite coating at two different magnifications.

The X-ray mapping images of Ni, Zr and O elements present in Ni-ZrO₂ composite coating are shown in Fig.8. The X-ray mapping clearly shows incorporation of a large fraction of zirconia particles in the Ni-ZrO₂ coating. The average EDAX data recorded on various spots of Ni-ZrO₂ coating surface (Fig.8) are tabulated in Table-4. The EDAX results indicate a higher wt% of ZrO₂ incorporation.

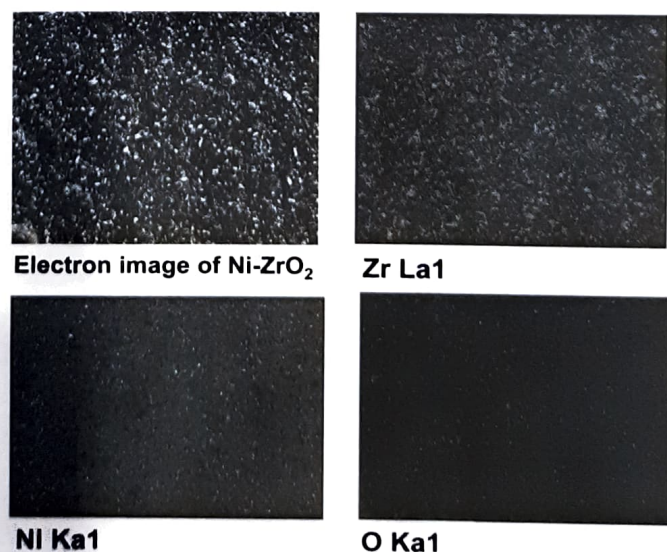


Fig. 8. Electron image of Ni-ZrO₂ coating and X-ray mapping images of Ni, Zr and O elements present in Ni-ZrO₂ coating.

Table-4 : EDAX results taken on Ni-ZrO₂ coating surface.

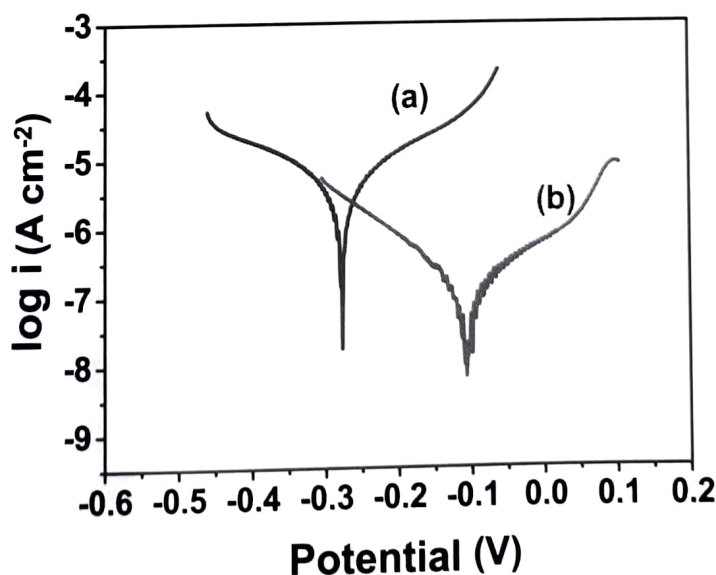
Element	Weight %
O	4.73
Zr	16.93
Ni	78.35
Total	100.00

Potentiodynamic polarization and EIS studies

The Tafel plots corresponding to Ni and Ni-ZrO₂ composite coatings are shown in Fig. 9 and the obtained polarization parameters are listed in Table-5. When compared to plain nickel coating, the corrosion potential of the Ni-ZrO₂ coating moved towards more positive side, suggesting enhanced corrosion resistance of the coating. The corrosion current density (*i*_{corr}) is a crucial parameter which indicates the kinetics of the corrosion reaction. Lower the corrosion current density value, higher will be the corrosion protection. The corrosion current density value for the Ni-ZrO₂ coating was very low (0.161 $\mu\text{A}/\text{cm}^2$) compared to plain Ni (28.65 $\mu\text{A}/\text{cm}^2$) indicating improved corrosion resistance of the Ni-ZrO₂ coating. This observation was further substantiated by the observed higher polarization resistance (*R*_p) value (189 $\text{k}\Omega\text{ cm}^2$) for Ni-ZrO₂ coating.

Table-5 : Potentiodynamic polarization results of Ni and Ni-ZrO₂ composite coatings.

Sample	OCP(V) vs. SCE	E _{corr} (V) vs. SCE	<i>i</i> _{corr} ($\mu\text{A}/\text{cm}^2$)	<i>R</i> _p ($\text{k}\Omega\text{ cm}^2$)	<i>b</i> _a (V/dec)	<i>b</i> _c (V/dec)	Corrosion rate (g/h)
Ni	-0.482	-0.471	28.65	1.44	0.157	0.2375	1.07×10^{-4}
Ni-ZrO ₂	-0.105	-0.107	0.16	189	0.163	0.1239	6.02×10^{-7}

**Fig. 9. Tafel plots of electrodeposited (a) Ni and (b) Ni-ZrO₂ coatings.**

Plain brass substrate and Ni-ZrO₂ coated substrates were subjected to continuous salt spray test for 168 h and prolonged 2400 h salt spray. There were no corrosion products on the Ni-ZrO₂ surface. The Ni-ZrO₂ coating was intact even after 2400 h of salt spray test. There were no visible changes on the surface of the Ni-ZrO₂ coating which indicates better corrosion resistance of the coating. This has been already confirmed by potentiodynamic polarization study.

Wear resistant property of Ni-ZrO₂ coatings

The wear data of Ni and Ni-ZrO₂ composite coatings are summarized in Table-6. It can be observed from the table that Ni-ZrO₂ coating is exhibiting better wear resistance (lower wear loss). It is also gratifying to note that Ni-ZrO₂ composite coating shows lower coefficient of friction and lowest wear rate compared to plain nickel. The lower wear rate can be attributed to the higher and uniform incorporation of zirconia particles in the nickel matrix. The higher fracture toughness of monoclinic zirconia particles could have also resulted in improved wear resistance as the wear resistance of zirconia increases with the fourth power of its fracture toughness^[37].

Table-6. Comparative wear properties of Ni and Ni-ZrO₂ coatings.

Coating	Average coefficient of friction	Wear loss (μm)	Wear volume loss(mm ³)	Wear coefficient	Wear rate (mm ³ /Nm)
Pure Ni	0.789	90	0.12647	1.39×10^{-8}	5.59×10^{-5}
Ni-ZrO ₂	0.515	14	0.00307	8.67×10^{-10}	1.36×10^{-9}

Superhydrophobic property of Ni and Ni-ZrO₂ coatings

In the present study, the WCA of as deposited and FAS treated Ni and Ni-ZrO₂ surfaces were measured and are shown as histogram (Fig. 10). Although there was not much variation in the WCA of as-deposited Ni (89°) and Ni-ZrO₂ (95°) coatings, there was a drastic rise in the WCA of FAS treated Ni-ZrO₂ coating. Ni-ZrO₂ coating exhibited superhydrophobic property with a WCA~157° and Ni showed hydrophobic property with a WCA~109°. The higher WCA observed in Ni-ZrO₂ coating may be attributed to its higher surface roughness (628 nm) consisting of hierarchical micro and nano roughness due to the combination of matrix and zirconia particle roughness. The formed coating contains trapped air pockets leading to Cassie Baxter state resulting in superhydrophobicity. The obtained WCA value is higher than that reported in the literature for Ni-TiO₂ (140°) surface treated with trimethoxy(propyl)silane solution^[6].

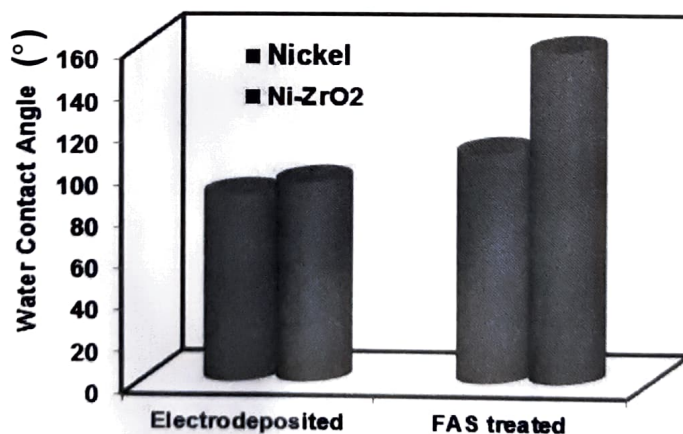


Fig.10. Histogram showing the water contact angle of as deposited and FAS treated Ni and Ni-ZrO₂ electrodeposited coatings.

CONCLUSIONS

In the present study, electrodeposited Ni-ZrO₂ coating exhibiting multi-functional properties was developed. Nanosized monoclinic zirconia powder was prepared by solution combustion method using a mixture of fuels and extra oxidizer. The obtained powder was subjected to ball-milling before electrodeposition to reduce the agglomeration of the particles. The coating electrodeposited at 0.75 A/dm² was used for corrosion and wear studies. The Ni-ZrO₂ coating exhibited improved corrosion and wear resistance compared to plain Ni coating. The Ni-ZrO₂ coatings also exhibited a lower coefficient of friction and lower wear loss compared to plain Ni

coating. The Ni-ZrO₂ coating also exhibited a higher water contact angle and can find potential use in applications requiring hydrophobic property. Thus, the developed Ni-ZrO₂ is a multi-functional coating exhibiting a synergistic combination of higher microhardness, improved wear resistance and corrosion resistance and superhydrophobic property.

ACKNOWLEDGMENTS

The authors thank Director and Head, SED, CSIR- NAL for their constant encouragement. The authors also thank Mujibir, A. Sreenivasan, Muni Prakash, Siju, and Dinesh for the help received in electrodeposition, corrosion testing, wear testing, FESEM, microhardness and contact angle measurement studies respectively. The author thanks Dr. Shay Tirosh from Bar-Ilan University for the TEM study.

REFERENCES

- [1] F.C. Walsh, S. Wang, N. Zhou: The electrodeposition of composite coatings: Diversity, application and challenges. *Curr Opin Electrochem*, 20: 8-19, 2020.
- [2] L. Ghelani, M. Naoun, L. Aissani, A. Abbassi, S. Boulahrouz: Electrodeposition and mechanical characterization of Ni/SiC composite coatings, *J. Nano- and Electron Phys* 11 (3): 03016, 2019.
- [3] G. Gyawali, K. Hamal, B. Joshi, A. Rajbhandari, S. Wahn Lee: Microstructural and electrochemical analysis of Ni-SiC composite coatings prepared in presence of additives, *Mater Lett* 126: 228-231, 2014.
- [4] S.T. Aruna, C. Anandan, V.K.W. Grips: Effect of probe sonication and sodium hexametaphosphate on the microhardness and wear behavior of electrodeposited Ni-SiC composite coating, *Appl Surf Sci* 301: 383-390, 2014.
- [5] O. Yilmaz, M. Erdogan, I. Karakaya: Combined effects of ALS and SLS on Al₂O₃ reinforced composite nickel coatings, *Surf Eng* 36 (5): 477-484, 2020.
- [6] M. Salehi, M. Mozammel, S.M. Emarati: Superhydrophobic and corrosion resistant properties of electrodeposited Ni-TiO₂/TMPSi nanocomposite coating, *Colloids Surf A: Physicochem Eng Asp* 573: 196-204, 2019.
- [7] I.U. Haq, K. Akhtar, T.I. Khan, A. Ali Shah: Electrodeposition of Ni-Fe₂O₃ nanocomposite coating on steel, *Surf Coat Technol* 235: 691-698, 2013.
- [8] S.T. Aruna, C.N. Bindu, V. Ezhil Selvi, V.K. William Grips, K.S. Rajam, Synthesis and properties of electrodeposited Ni/ceria nanocomposite coatings, *Surf Coat Technol* 200 (24): 6871-6880, 2006.
- [9] Z. Geng, Y. Liu, H. Zhang: Tribological properties of electrodeposited Ni-ZrO₂ nanocomposite coatings on copperplate of crystallizer, *Surf Eng* 35 (10): 919-926, 2019.
- [10] I. Makarova, I. Dobryden, D. Kharitonov, A. Kasach, J. Ryl, E. Repo, E. Vuorinen: Nickel-nanodiamond coatings electrodeposited from tartrate electrolyte at ambient temperature, *Surf Coat Technol* 380: 125063, 2019.
- [11] J. Lapinski, D. Pletcher, F.C. Walsh: The electrodeposition of nickel-graphite composite layers, *Surf Coat Technol* 205 (21-22): 5205-5209, 2011.
- [12] T.Borkar, S. Harimkar: Microstructure and wear behaviour of pulse electrodeposited Ni-CNT composite coatings, *Surf Eng* 27 (7): 524-530, 2011.
- [13] R. Zhang, G. Cui, X. Su, X. Yu, Z. Li: A novel functionally graded Ni-graphene coating and its corrosion resistance, *J Alloys Comp* 829: 154495, 2020.
- [14] A. Siddaiah, P. Kumar, A. Henderson, M. Misra, P.L. Menezes: Surface energy and tribology of electrodeposited Ni and Ni-graphene coatings on steel, *Lubricants*, 7 (10): 87, 2019.
- [15] L.D Xiang, Q. Shen, Y. Zhang, W. Bai, C. Nie: One-step electrodeposited Ni-graphene composite coating with excellent tribological properties, *Surf Coat Technol* 373: 38-46, 2019.
- [16] J. Wang, W. Lei, Y. Deng, Z. Xue, H. Qian, W. Liu, X. Li: Effect of current density on microstructure and corrosion resistance of Ni-graphene oxide composite coating electrodeposited under supercritical carbon dioxide, *Surf Coat Technol* 358: 765-774, 2019.
- [17] S. Singh, S. Samanta, A.K. Das, R.R. Sahoo: Tribological investigation of Ni-graphene oxide composite coating produced by pulsed electrodeposition, *Surf Interf* 12: 61-70, 2018.

- [18] G. Cieřlak, M. Trzaska: Preparation and properties of nanocrystalline Ni/graphene composite coatings deposited by electrochemical method, *Pol J Chem Technol* 20 (1): 29-34, 2018.
- [19] N. Chronopoulou, D. Vozios, P. Schinas, E.A. Pavlatou: Electrodeposition and characterization of electroplated Ni/Graphene composite coatings, *Mater Today: Proceed* 5 (4): 27653-27661, 2018.
- [20] H.S.Maharana, P.K. Katiyar, K. Mondal: Structure dependent super-hydrophobic and corrosion resistant behavior of electrodeposited Ni-MoSe₂-MWCNTcoating, *Appl Surf Sci* 478: 26-37, 2019.
- [21] A. Saini, B.S. Pabla, S.S.Dhami: Preparation and characterization of electrodeposited Ni-TiC, Ni-TiN, and Ni-TiC-TiN composite coatings on tungsten carbide cutting tool, *Proceed Inst Mechan Eng. Part J: Eng and Tribology*, 233: 1688, 2019.
- [22] P.F. Manicone, P. Rossi Iommetti, L. Raffaelli: An overview of zirconia ceramics: Basic properties and clinical applications, *J Denti* 35 (11):819-826, 2007.
- [23] Z. Peng, P. Shi, Y. Deng: Corrosion rate of Ni-ZrO₂ nano-coatings forecasted by GRNN, *ACM Int Conf. Proceed Series*, 236-241, 2020.
- [24] W. Ge, T. He, M. Wang, J. Li: Nano-grain Ni/ZrO₂ functional gradient coating fabricated by double pulses electrodeposition with enhanced high temperature corrosion performance, *Coatings*, 10 (4): 332, 2020.
- [25] A.K. Kasar, M.U. Bhutta, Z.A. Khan, P.L. Menezes: Corrosion performance of nanocomposite coatings in moist SO₂ environment, *Int J Advan Manuf Technol* 106 (11-12): 4769-4776, 2020.
- [26] B. Bostani, N. Parvini Ahmadi, S.Yazdani, R. Arghavanian: Synthesis and characterization of functionally gradient Ni-ZrO₂ composite coating, *Prot Met Phys Chem Surf*, 54 (2): 222-229, 2018.
- [27] B. Bostani, R. Arghavanian, N. Parvini Ahmadi, S.Yazdani: Fabrication and properties evaluation of functionally graded Ni-NCZ composite coating, *Surf Coat Technol* 328: 276-282, 2017.
- [28] Z. Geng, Y. Liu, H. Zhang: Tribological properties of electrodeposited Ni-ZrO₂ nanocomposite coatings on copperplate of crystallizer, *Surf Eng* 35 (10): 919-926, 2019.
- [29] S.T. Aruna, A.S. Mukasyan: Combustion synthesis and nanomaterials, *Curr Opin Solid State Mater Sci* 12 (3-4): 44-50, 2008.
- [30] S.T. Aruna, A. Kiran, M. Shilpa: Reclamation of thermal power plant waste as a distributed phase in electrodeposited Ni composite coating, *Surf Eng* 35 (12): 1042-1047, 2019.
- [31] S. Spanou, E.A. Pavlatou, N. Spyrellis: Ni/nano-TiO₂ composite electrodeposits: Textural and structural modifications, *Electrochim Acta*, 54: 2547-2555, 2009.
- [32] S.T. Aruna, V.K. William Grips, K.S. Rajam: Ni-based electrodeposited composite coating exhibiting improved microhardness, corrosion and wear resistance properties, *J Alloys Comp*, 468: 546-552, 2009.
- [33] M. Stern Geary: Electrochemical polarisation: A theoretical analysis of the shape of polarization curves, *J Electrochem Soc*, 104: 56-63, 1957.
- [34] R. Holm: *Electric Contacts*, Almquist and Wiksells, Stockholm, Section 40, 1946.
- [35] J.F. Archard: Contact and rubbing of flat surfaces, *J Appl Phys* 24: 981-988, 1953.
- [36] Y. Zhou, H. Zhang, B. Qian: Friction and wear properties of the co-deposited Ni-SiC nanocomposite coating, *Appl Surf Sci* 253(20): 8335-8339, 2007.
- [37] T. E. Fischer, P.A. Michael, S. Jahanmir: Influence of fracture toughness on the wear resistance of yttria-doped zirconium oxide, *J Amer Ceram Soc* 72(2): 252-257, 1989.

Techniques for investigation: Semiconductor/electrolyte interface processes in photoelectrochemical cell for solar water splitting

DIPIKA SHARMA, SAKSHI GUPTA and B. R. MEHTA*

Thin Film Laboratory, Department of Physics, Indian Institute of Technology, New Delhi-110016, INDIA

Abstract: Photoelectrochemical water splitting process for solar hydrogen production has attained great consideration due to acceptance of hydrogen as a sustainable and environmentally friendly energy carrier. The key functional components of a PEC cell are the semiconductor electrode and semiconductor-electrolyte interfacial junction. The semiconductor-electrolyte interface, the other crucial functional unit of PEC cell is rarely investigated. The nature of the charge carrier's movement at the semiconductor/electrolyte interface is fundamental for the optimization of semiconductor electrode performance for efficient hydrogen generation. To understand the above processes at the interface, various techniques are being used to investigate the electrochemical reactions and photocatalytic response of a stable photoelectrode. In this review, the charge transfer kinetics and various methods used to investigate the e^-/h^+ transfer processes at the semiconductor/electrolyte interface are reviewed and discussed.

Key words: Techniques for investigating the processes occur at Semiconductor-Electrolyte Interface.

INTRODUCTION

In the search for a sustainable society which uses energy based on renewable solar energy, an efficient approach is needed to convert solar light into chemical fuel. Hydrogen is being considered as a favorable future fuel carrier on account of its high potential in terms of diversified supply and negligible emission of carbon and greenhouse gases. Photoelectrochemical water splitting reaction using solar light is the most convenient route for hydrogen production to fulfil the future energy requirements^[1-8]. The main functional units of PEC cell are the semiconducting materials and semiconductor-electrolyte interface junction shown in Fig.1.

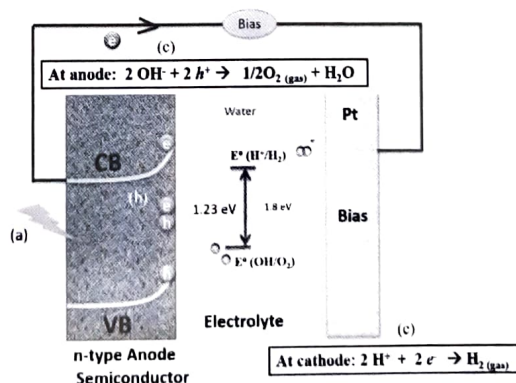


Fig. 1 Schematic illustration of PEC water splitting process with n-type semiconductor as photoanode under applied bias. The main processes involved are (a) light absorption (b) electron-hole pair separation and movement and (c) redox reactions on the corresponding surfaces.

A huge wealth of data is available in the development of efficient semiconducting materials by various modification strategies to improve the PEC response. The role of semiconductor/electrolyte interfacial junction in photoelectrochemical behavior of semiconducting materials is rarely analyzed. The nature of e^-/h^+ transferal processes at the semiconductor/electrolyte junction is fundamental to optimize the semiconductor electrode performance for efficient hydrogen generation.

TECHNIQUES / EXPERIMENTAL METHOD FOR INVESTIGATING THE INTERFACIAL PROCESSES OCCUR AT SEMICONDUCTOR/ELECTROLYTE JUNCTION

There is a wide number of experimental techniques have been used to analyze the interfacial process of semiconductor-electrolyte interface. Some of these methods are described below and summarized in Table 1.

* Corresponding Author Email: brmehta@physics.iitd.ac.in, dipika.sharma286@gmail.com

Table. 1. Experimental techniques to understand the interfacial processes of Semiconductor/Electrolyte junction:

Technique	Used for
Current-Voltage Curves	provide anodic and cathodic behavior of semiconductor with band edges position estimation
Electrochemical Impedance Spectroscopy : Bode plot/ Nyquist plot	To study the kinetics of interfacial processes of photoelectrochemical cell such as charge transfer resistance.
Mott- Schottky Analysis	To study the interfacial properties such as flatband potential, donor density and space charge region width.
Photocurrent Transients	To study the rate of photogenerated charge transfer at semiconductor/electrolyte junction
Optical Techniques: a) Photoluminescence b) Electroluminescence c) Transient and Time-Resolved Measurements	Recombination processes and presence of surface state
Scanning Probe Methods: a) Scanning Electrochemical Microscopy b) Scanning Tunneling Microscopy c) Conducting Atomic forcemicroscopy (CAFM).	To study the surface phenomena that affect the charge diffusion at the electrode surface and structural imperfections.

I-V Curves

Current-voltage plots obtained in three electrode photoelectrochemical cell are the basic characterization method of semiconductor/electrolyte interface, used to understand the interfacial e^-/h^+ transport. These curves provide a rough estimation of anodic and cathodic behavior of semiconductor with band-edge alignment positions and other processes such as stability, photo corrosion at the surface of semiconductor. Under illumination, higher current value than dark indicating the photogeneration of minority charge carriers under the illumination of the interface. I-V curves under illumination also give an idea of the kinetics of charge transfer and nature of the interface^[9-10]. The current-potential curve also provides valuable information about open circuit potential. However, when no detailed models are accessible, I-V curves alone provide the qualitative information of the SE interface.

Electrochemical Impedance Spectroscopy (EIS): Bode plot/ Nyquist plot:

Electrochemical Impedance Spectroscopy (EIS) is responsive to charge accumulation and charge passage kinetics at the interface of semiconductor and electrolyte. EIS measurements of a sample are conducted for a large range of frequencies and the obtained spectrum is evaluated in the complex plane^[11]. The real and imaginary parts of impedance are measured at different angular frequencies, and an equivalent circuit is suggested to investigate the physical nature of the elements on the basis of their dependence on external parameters such as voltage, temperature, and electrolytic solution. The frequency dependence of the EIS measurements is often attributed to the capacitance of the surface state present and space charge layer capacitance to measure the combined space charge/surface state/semiconducting material capacitance^[12].

Diez-Garcia et al. (2016) developed a theoretical model based on the kinetic mechanism for thin calcium ferrite electrodes involved in water splitting. They concluded that direct transfer was taking place of the electrons from the conduction band to electrolytic solution and majority of the carrier recombination took place in the bulk of

the material. EIS helps us study the behaviour of photoelectrodes and find methods for improvements in their properties^[13].

Bertoluzzi et al. (2012) discussed a model that explains the kinetics of charge carriers in a thin semiconductor film which is undergoing photoelectrochemical water splitting in order to differentiate between charge transfer processes and trap-assisted recombination. This could be used to understand the current potential curve during photogeneration. It is possible to identify the physical processes that contribute to limiting the current density at a low value of potential, lower e^-/h^+ pair separation and effective charge movement from the traps^[14].

Impedance spectroscopy can be used to provide important parameters influencing photoelectrodes with a comparatively simple measurement. Klahr et al. (2012) performed impedance spectroscopy to figure out the mechanism of photocurrent production by varying the light intensity, potential bias and electrolyte pH for hematite photoelectrodes^[15].

Trinh et al. (2014) conducted the study of the presence of adsorbate intermediates at the interface of semiconductor/electrolytic solution. The complex differential capacitance was calculated by the synchronized measurement of the electrochemical impedance of competing absorbates. By assuming that the electrochemical mechanism observes Tafel kinetics and by applying the linearized currents, the impedance response can be calculated^[16]. Wijayantha et al. (2011) characterized the electron transfer kinetics and recombination at the time of oxygen evolution at illuminated polycrystalline $\alpha\text{-Fe}_2\text{O}_3$ electrodes. The rate constant for electron transfer has been observed to increase with the increase in potential. Therefore, the change in potential of the Helmholtz layer has an impact on the activation energy for the oxygen evolution reaction (OER). This complex potential dependence demonstrates the non-ideal nature of the $\alpha\text{-Fe}_2\text{O}_3$ electrolyte interface due to the photogenerated surface species^[17]. There are many reports that discuss the EIS in more detail^[18-21].

Mott Schottky Analysis:

Semiconductor/electrolyte interface is electrically charged and has an associated interfacial capacitance due to the presence of ions on the liquid side and e^-/h^+ towards semiconductor. The width of the space charge region is more towards semiconducting material than that of electrolyte resulting in the difference or generation of the electrostatic potential at the semiconductor/electrolyte interface. Presence of any surface states at the semiconductor surface also leads to the difference in the applied potential and interfacial capacitance across the space-charge region. The difference in the electric potential between electrode surface (flatband) and electrode bulk resulting into the band bending and capacitance of space charge region. The magnitude of band bending tells about the electronic properties of surfaces and provide the estimations about the energy levels of the semiconductor/electrolyte junction. The interface capacitance and potential variation across the space charge region follows the Mott-Schottky equation given below^[22-23]:

$$\frac{1}{C^2} = \left(\frac{2}{q \epsilon_s \epsilon_0 N A^2} \right) (V_{app} - V_{fb} - \frac{kT}{q})$$

Here q is the charge, V_{app} is the applied potential and V_{fb} is the flat band potential, N is the donor density, ϵ_s is the dielectric constant of material, ϵ_0 is electronic charge, k is Boltzmann constant, T is the temperature, and A is the area of the electrode. According to the Mott-Schottky relation, the measurement of interface differential capacitance and its linear plot vs applied potential offer the determination of (i) donor and acceptor concentrations in semiconductor from the slope of this linear plot (ii) valuation of flat-band potential from extrapolation of the linear plot of $1/C^2$ vs applied potential, the extensively used analysis in the presence both dark and light conditions. These plots of capacitance and potential have been obtained by different models of electrochemical impedance spectroscopy by Mántia et al (2010), Hankin et al (2019), Gelderman et al 2007^[24-26].

In addition to this Mott Schottky analysis is useful in many other applications. Albery et al. (1996)^[27] showed that the curved part analysis of Mott-Schottky plots can provide the potential distribution at the semiconductor/electrolyte interface. Adan-Mas et. al. 2017^[28] suggested that the Mott-Schottky model also useful in the correct selection of potential values to carry out the EIS measurements. In Gelderman et al. 2007^[26], used polycrystalline ZnO electrode, exposed the many crystal planes and suggesting that different V_{fb} values were obtained on account of different conductivity values along different crystallographic planes.

There have been found some deviations in the linear Mott-Schottky behaviour due to the complex nature of the nanostructured semiconductor and water interface.

Pareek et. al. 2014^[29] observed the deviation in the flat-band potential with applied frequency and electrolytic pH values. An increase in applied frequency reduces the flat band potential showing the dependence of the frequency of capacitance at higher frequencies. The pH of the solution affects the redox potential and thus the flat band potential. Mantia et al. 2010 explained the frequency dependence of the capacitance. This is seen in Mott-Schottky plots which affect donor density and flat band potential. In the low band bending region, the slope is constant for all frequencies but the effect of frequency increases with increasing potential^[24].

Cen et. al. 2016 showed a non-linear Mott-Schottky plot for non-uniform donor density distribution with decreasing slope towards higher potential^[30].

Transient photocurrent spectroscopy

Transient photocurrent measurements are performed by passing a current through a sample illuminated by white light. At the electrode, pulses of coloured light perturbations are passed. The light source is modulated periodically while the current through the system is observed. The transient delays are fitted to models and time constants determined. Dumortier et al. developed a model for transient current measurements in TiO_2 photoanode and Pt cathode^[31]. They found two different pathways for the cell reaction by numerical modelling and transient phenomena. There was the charging of surface states and the transfer process of H^+ ions at the TiO_2/Na ion interface.

Using transient photocurrent measurements, possible decay mechanisms of the photoelectrode can be determined by observing the recombination rate of photogenerated e^-/h^+ in the semiconductor. Thus, photoelectrodes can be characterised, especially the charge accumulation at the SEI. This was done by Le Formal et al. in their investigation of photocurrent transient behaviour of $\alpha-Fe_2O_3$ photoanodes^[32]. Ngami et al. investigated the charge transfer process at the semiconductor electrolyte interface of TiO_2 electrodes. They found that the oxidation of specifically absorbed OH^- ions is causing the transients. This can give insights into electrode kinetics^[33].

Laskowski et. al. studied catalysed photoanodes and concluded that the photocurrent transients are influenced by the presence of surface state and their formation or other presence other catalytic activity^[34].

Optical Techniques Specific to Semiconductors

The generation of charge carriers at the semiconductor under illumination condition and their effect and movement towards the semiconductor/electrolyte interface has led to the formation of new techniques to study the photo effects at semiconductors. Some of the more relevant techniques are: a) Photoluminescence b) Electroluminescence c) Time resolved and transient measurements, and d) Transient absorption spectroscopy

Photoluminescence:

“Photoluminescence is the emission of light which is caused by the irradiation of a substance with external light. In particular, PL spectra and their intensity dependencies can be used”;

- “to determine the band gap energy and/or the wavelength of maximum gain

- to determine the composition of ternary or quaternary layers
- to determine impurity levels (which can e.g. lead to the emission of light with longer wavelengths than otherwise possible)
- to investigate recombination mechanisms"

Photogenerated charge carriers at semiconductor/electrolyte interface yield photoluminescence (PL) by radiative recombination. It is a competitive process with the photocurrent generation and allows us to study the photo effects at semiconductor surface. Several researchers have studied the photoluminescence of the energy research materials on their surface modifications in accord with the "dead-layer" model given by Smandek et al. 1989^[35].

Ellis et al. 1983 studied the energetics of n, p type GaAs/electrolyte interface to calculate the width of space charge layer and capture velocity of surface minority charge carriers^[36]. Po-Yen Kunget al. 2015^[37] utilized the organic pigments photo-sensitizers and produce down-conversion photoluminescence spectra to excite Surface plasma response of silver nanoparticles.

Electroluminescence

"Electroluminescence (EL) is an optical phenomenon and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field". In this phenomena e^-/h^+ pair recombine from semiconductor and donor and acceptor present in the electrolyte under externally applied potential and release energy in the form of photons. This technique is more complex and specific to materials or systems than photoluminescence. Electroluminescence (EL) spectrum are more often recovered in conjunction with photoluminescence. Ouyang, J. et al. 1989 observed the identical PL and EL peaks for Mn-doped ZnS indicating the same luminescent center and shift in EL peaks with other dopants indicating the specificity for each material^[38]. A Krier et. al. 2000 shown the In As electroluminescence spectra of InAsSbP/InAs interface, results indicated the staggered type alignment at the interface^[39].

Time-resolved and transient measurements

Pulsed/chopped illumination and transient measurements of photocurrent and luminescence spectra is an advanced technique to understand in depth the interfacial charge transport. Willig et al. recorded the transients photoluminescence spectra of n-SnS₂ modified with Dye and investigate the transfer rate of electron towards the conduction band^[40].

Transient absorption spectroscopy

TAS is the advanced technique based on pump-probe in which transient absorption in visible/or near IR region using pulsed laser source are measured to study the basic processes of photoelectrochemical water splitting reaction such as trapping, transport, and lifetime of photogenerated electron/holes (charge carriers) pairs in semiconductors^[41-42]. The change in intensity of the transient absorption signal provides the kinetics of charge carriers under light condition. Moreover, this technique can also use to study the position of trapped electron and holes at surface and or bulk. In situ TAS measurement during photoelectrochemical water splitting reaction allows the direct determination of photoexcited charge carrier kinetics in the semiconductor. At Microsecond scale TAS transient measurements are carried out using a laser flash photolysis (LFP)spectrometer and nanosecond laser pump and flash lamp probe^[43-44]. Charge transfer process and their kinetics study at the n-type semiconductor/electrolyte interface for water oxidation process has been investigated using μs -TAS by R. Qian et al. 2019 and M. Lorenc et al. 2002^[45-46]. M. Barroso et al. 2013 recorded the μs -TAS spectra of Fe₂O₃ and indicated the presence of potential dependency irrespective the fabrication technique^[47]. Furthermore, pico and femtoseconds transient absorption spectroscopy measurements can be used to study ultrafast kinetics of interfacial charges of semiconductor/electrolyte junction. I. Grigioni et al 2018 demonstrated that direct detection of photogenerated electrons in the semiconductor by using mid-infrared (IR) probes is possible. They have also

demonstrated the lifetime for photo-excited electron in pristine WO_3 and BiVO_4 semiconductor and observed longer lifetime for photoexcited electrons in WO_3 than in BiVO_4 [48].

Scanning Probe Methods

The emergence of scanning probe techniques such as scanning tunnelling microscopy (STM), Scanning Electrochemical Microscopy and atomic force microscopy (AFM) in the recent years received attention on account of their capability of exploring the atomic structure of the semiconductor surface and presence of other redox species. A large number of surface states can drastically modify the behaviour of the semiconductor/electrolyte interface by pinning the Fermi level. Moreover, the band bending which takes place at a semiconductor-electrolyte interface makes it sensitive to the presence of light. These scanning probe techniques can be used to explore the atomic structure of the semiconductor surface and adsorbed layers at the interface.

Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy (STM) by Binnig and Rohrer is an emerging technique for investigating the semiconductor/electrolyte interface properties. In this probe tip scanned across the surface, which generates a small current between tip and surface through "tunneling" process and imaging surface at the atomic level. Besides the imaging at the atomic level, this technique has the potential to investigate the electrochemistry of the semiconductor/electrolyte interface. STM applications for investigating the semiconductor/electrolyte interfaces are mainly of two types a) in situ monitoring of changes occur at the material surface due to in contact with the electrolyte and b) determination of the kinetics of interfacial energetics at semiconductor/electrolyte interface. Bard et al. 1987 etched the nanometer scale features of GaAs surface immersed in solution under illumination condition by moving the tip across the surface [49]. Thundat et al. 1990 demonstrated topographical changes at the surfaces occurred due to electrochemical reactions by scanning tunnelling microscopy under uniform potential. Combining STM topographs with other probe techniques provide useful information. The STM tip was used to make localized structures by utilizing photoelectrodeposition and photocorrosion. These results suggest promising applications in lithography [50].

Scanning Electrochemical Microscopy (SECM)

Scanning electrochemical microscopy was developed by Bard and his co-workers. It is a high- resolution electrochemical scanning probe technique [51]. The probe is a pipette with two channels for the electrodes in electrolytic solutions. A meniscus is formed at the tip of the pipette due to the electrolyte. The probe undergoes small oscillations perpendicular to the substrate, creating an ac current caused by the change in the dimensions of the electrolyte contact and dc current. The pipette geometry significantly controls the dc conductance current, measured by microscopy.

In SECM, mass transport to the substrate surface occurs through diffusion. If the analyte is charged, changing the potential difference between the electrodes is used to manipulate the ion migration. The movement of the analytes to the semiconductor electrolyte interface can be controlled precisely. Therefore, SECM can be used to study fast heterogeneous electron transfer kinetics. Bard's group used this microscopy technique to study the SEI energetics of GaAs. They investigated the differences between n-type GaAs and p-type GaAs and looked at the valence band energy closely. Zhang et al. (2016) also investigated the interfacial charge kinetics while in feedback mode to be able to develop a simulation for oxygen evolution in photoelectrochemical cells [52]. Snowden et al. (2012) used FEM modelling to quantitatively study surface kinetics and mass transport using SECM by measuring the conductance and working electrode current simultaneously [53]. Kinetic measurements in the scale of interface dimensions and high-resolution voltammetric imaging can be performed as well. The simulations helped to understand the role of migration and diffusion.

Ma et al. (2019) used a scanning electrochemical microscope to study water oxidation of Au-modified hematite. The probe used was made up of optical fibre to radiate the photoanode with visible light. Characterisation techniques, X-ray photoelectron spectroscopy and scanning electron microscopy, were used to study Au-modified and unaltered hematite samples. In the Au modified hematite, Au metallic nanoparticles were embedded in the hematite structure^[54]. Zhang et al. (2018) reviewed the development of SECM and the principles it worked on. He discussed recent advances such as interfacial reaction kinetics and screening of photoelectrodes and photocatalysts. The quantisation of intermediates during the reaction was used to judge the effectiveness of catalysts and develop novel composite photoanodes and high-efficiency devices.^[55]

Atomic force microscopy (AFM)

Photoconductive atomic force microscopy (pc-AFM) is used for characterisation of structural and optoelectronic properties with nanoscale resolution. Photocurrent maps of pc-AFM provide information about properties across the film and give insight into the charge transport mechanism. Eichhorn et al. 2018 applied pc-AFM for optoelectronic properties in nanostructured BiVO₄ thin-film and analysed its charge-transport limitations. The current distribution was observed to be non-uniform across the film with a higher photocurrent at facet boundaries and planes and lower photocurrent at the grain boundaries. The understanding of interaction at nanoscale dimensions is essential to know the charge carriers transfer from heterogeneous photoelectrode^[56].

Potential-sensing electrochemical atomic force microscopy (PS-EC-AFM) is utilised to probe the electronic and interface properties of electrochemical systems. Contact-based PS-EC-AFM directly measures the electrochemical surface potential while the electrochemical system is in operation. Laskowski et al. 2020 used this technique to quantitatively assess the surface voltage of metal-oxyhydroxide catalyst films on metal-oxide photoelectrodes. PS-EC-AFM spatially resolves the electronic properties of semiconductor electrode interfaces at nanoscale^[57].

In this technique, a conductive tip attached to an electrically insulated cantilever is in direct contact with the sample film. Force feedback is utilised for the management of tip-substrate interactions by observing cantilever deflections for stable electrical connection between substrate and the AFM nanoelectrode tip. The advantage of a small tip being in contact with the electrolyte is that capacitive and surface electrochemical processes are minimized. It is assumed that the Fermi levels of the tip and catalyst coincide so that the surface of the catalyst can be probed. Photoelectrochemical water splitting reaction is caused by the accumulation or depletion of charge carriers at the surface of the semiconductor and interfacial electrochemical potential gradients lead to charge transfer. The nanoscale conducting tip of the cantilever senses the surface electrochemical potential of electrocatalysts. Liu et al. 2019 studied morphology and mechanical adhesive properties upper-layer using AFM to understand the component's roles at the nanoscale. It was possible to visualise all the nanoparticles of oxide overlayer present over BiVO₄ surface. Surface structural properties of the sample can be deduced by using the topography images with adhesion maps^[58].

SUMMARY

In summary, the understating of semiconductor/electrolyte interface of photoelectrochemical water splitting process is reliant on the advancement of the experimental techniques. Powerful potentiometric and microscopic techniques are being developed to understand the in-depth charge carrier kinetics at the interface of the PEC cell. These techniques play an important role to apprehend the numerous reactions at the semiconductor/electrolyte interface affects the efficiency of the PEC cell such as charge transport, recombination rate, and photocorrosion and photovoltage generation. However, none of the single technique can provide a complete understanding of the mechanistic aspects of the semiconductor/electrolyte interface. Thus, a combination of these techniques can be an effective and powerful tool to understand and develop new vital knowledge of the interfacial process of the PEC water splitting reaction.

ACKNOWLEDGMENTS

Author (Dipika Sharma) gratefully acknowledges the financial support received from IIT Delhi for Institute Post Doc fellowship.

REFERENCES

- [1] A. Fujishima, A. T. Rao, D. Tryk: Titanium dioxide photocatalysis. *J. of Photochemistry and Photobiology C Photochemistry Reviews* 1: 1-21, 2000.
- [2] D. Sharma, S. Upadhyay A. Verma A. V.R. Satsangi, R. Srivastav, U.V. Waghmare, S. Dass: Nanostructured Ti-Fe₂O₃/Cu₂O heterojunction photoelectrode for efficient hydrogen production. *Thin Solid Films* 574: 125-131, 2015.
- [3] T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell: Photo-electrochemical hydrogen generation from water using solar energy: Materials-related aspects. *Int. J Hydrogen Energy* 27: 91-102, 2002.
- [4] D. Sharma, V. R. Satsangi, R. Shrivastav, U.V. Waghmare, S. Dass: Nanostructured BaTiO₃/Cu₂O heterojunction with improved Photoelectrochemical Activity for H₂ Evolution: Experimental and First-Principles Analysis. *Applied catalysis B: Environmental* 189: 75-85, 2016.
- [5] M. Gratzel: Review article photoelectrochemical cells. *Nature* 414: 33-44, 2001.
- [6] A. Fujishima, K Honda: Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238-378, 1972.
- [7] D. Sharma, B.R. Mehta: Nanostructured TiO₂ thin films sensitized by CeO₂ as an inexpensive photoanode for enhanced photoactivity of water oxidation. *Journal of Alloys and Compounds* 749: 329-335, 2018.
- [8] R. K. Upadhyay, D. Sharma: Fe doped BaTiO₃ sensitized by Fe₃O₄ nanoparticles for improved photoelectrochemical response. *Materials Research Express* 5: 015913, 2018.
- [9] S. R. Morrison: *Electrochemistry at Semiconductor and Oxidized Metal Electrodes*. Plenum New York. 1980.
- [10] R.H. Wilson: Electron transfer processes at the semiconductor-electrolyte interface. *CRC Crit. Rev. Sol. State Mater. Sci.* 10, 1980.
- [11] D. Cahen, Y.W. Chen, R. Noufi, R. Ahrenkiel, R. Matson, Micha Tomkiewicz: n-Cu In Se₂ photoelectro chemical cells. *Solar Cells* 16: 529-548, 1986.
- [12] M. Tomkiewicz: Impedance spectroscopy of rectifying semiconductor-electrolyte interfaces. *Electrochimica Acta* 1631-1635, 1990.
- [13] M. I. Díez-García, R. Gómez: Investigating Water Splitting with CaFe₂O₄ Photocathodes by Electrochemical Impedance Spectroscopy. *ACS Appl. Mater. Interfaces* 8: 33, 21387-21397, 2016.
- [14] L. Bertoluzzi, J. Bisquert: Equivalent Circuit of Electrons and Holes in Thin Semiconductor Films for Photoelectrochemical Water Splitting Applications. *J. Phys. Chem. Lett.* 3: 2517-2522, 2012.
- [15] B. Klahr, S. Gimenez, F. Fabregat-Santiago, T. Hamann, J. Bisquert: Electrochemical and photoelectrochemical investigation of water oxidation with hematite electrodes. *Energy Environ. Sci.* 5: 7626 (2012).
- [16] D. Trinh, M. Keddama, X. R. Nóvoac, V. Vivie: Characterization of adsorbates by transient measurements in Scanning Electrochemical Microscopy. *Electrochimica Acta* 131: 28-35, 2014.
- [17] K. G. U. Wijayantha, S. Saremi-Yarahmadia, L. M. Peter: Kinetics of oxygen evolution at α -Fe₂O₃ photoanodes: a study by photoelectrochemical impedance spectroscopy. *Phys. Chem. Chem. Phys.* 13: 5264-5270, 2011.
- [18] W. H. Leng, Z. Zhang, J. Q. Zhang, C. N. Cao: Investigation of the Kinetics of a TiO₂ Photoelectrocatalytic Reaction Involving Charge Transfer and Recombination through Surface States by Electrochemical Impedance Spectroscopy. *J. Phys. Chem. B* 109: 15008-15023, 2005.
- [19] S. Gimenez, H. K. Dunn, P. Rodenas, F. Fabregat-Santiago, S. G. Miralles, E. V. Barea, R. Trevisan, A. Guerrero, J. Bisquert: Carrier density and interfacial kinetics of mesoporous TiO₂ in aqueous electrolyte determined by impedance spectroscopy. *Journal of Electroanalytical Chemistry* 668: 119-125, 2012.
- [20] K. Shimizu, A. Lasia, J. Boily: Electrochemical Impedance Study of the Hematite/Water Interface. *Langmuir* 28: 7914-7920, 2012.
- [21] T. Lopes, L. Andrade, H. A. Ribeiro, A. Mendes: Characterization of photoelectrochemical cells for water splitting by electrochemical impedance spectroscopy. *International Journal of Hydrogen Energy* 35: 11601-11608, 2010.

- [22] D. Sharma, V. R. Satsangi, R. Shrivastav, U. V. Waghmare, S. Dass: Improved Photoelectrochemical Water Splitting Performance of $\text{Cu}_2\text{O}/\text{SrTiO}_3$ Heterojunction Photoelectrode. *J. Phys. Chem. C* 118: 25320–25329, 2014.
- [23] D. Sharma, R. K. Upadhyay, B. Satpati, V. R. Satsangi, R. Shrivastav, U. V. Waghmare, S. Dass: Electronic band-offsets across $\text{Cu}_2\text{O}/\text{BaZrO}_3$ heterojunction and its stable photo-electro-chemical response: First-principles theoretical analysis and experimental optimization. *Renewable Energy* 113: 503–511, 2017.
- [24] F. La Mantia, H. Habazakib, M. Santamariac, F. D. Quartoc: A Critical Assessment of the Mott–Schottky Analysis for the Characterisation of Passive Film Electrolyte Junctions. *Russian Journal of Electrochemistry* 46: 1306–1322, 2010.
- [25] A. Hankin, F. E. Bedoya-Lora, J. C. Alexander, A. Regoutz, G. H. Kelsall: Flat band potential determination: avoiding the pitfalls. *J. Mater. Chem. A* 7: 26162–26176, 2019.
- [26] K. Gelderman, L. Lee, S. W. Donne: Flat-Band Potential of a Semiconductor: Using the Mott–Schottky Equation. *Journal of Chemical Education* 84: 685–688, 2007.
- [27] W. J. Albery, G. J. O'Shea, A. L. Smith: Interpretation and use of Mott-Schottky plots at the semiconductor/ electrolyte interface. *J. Chem. Soc., Faraday Trans. 92*: 4083–4085, 1996.
- [28] A. Adán-Más, T. M. Silva, L. Guerlou-Demourgues, M. F. Montemor: Application of the Mott-Schottky model to select potentials for EIS studies on electrodes for electrochemical charge storage. *Electrochimica Acta* 289: 47–55, 2018.
- [29] A. Pareek, P. P. Pramod, H. Bors: Characterization of Nano-Titania Modified CdS /Polysulfide Electrolyte Interface by Utilizing Mott Schottky and Electrochemical Impedance Spectroscopy *Electroanalysis* 26: 2403–2407, 2014.
- [30] J. Cen, Q. Wu, D. Yan, J. Tao, K. Kisslinger, M. Liu, A. Orlov: Photoelectrochemical water splitting with a SrTiO_3 ; Nb/SrTiO_3 n^+-n homojunction structure. *Phys. Chem. Chem. Phys.* 19: 2760–2767, 2017.
- [31] M. Dumortier, T. Bosserez, J. Ronge, J. A. Martens, S. Haussener: Combined Experimental-Numerical Analysis of Transient Phenomena in a Photoelectrochemical Water Splitting Cell. *J. Phys. Chem. C* 120: 3705–3714, 2016.
- [32] F. Le Formal, K. Sivula, M. Grätzel: The Transient Photocurrent and Photovoltage Behavior of a Hematite Photoanode under Working Conditions and the Influence of Surface Treatments. *J. Phys. Chem. C* 116: 26707–26720, 2012.
- [33] G. Nogami, Y. Nishiyama: Determination of Charge Transfer Rate at the Semiconductor Aqueous Electrolyte Interface by Photocurrent Transients. *Electrochem. Soc.: Electrochemical science and Technology* 135: 3038–3044, 1988.
- [34] F. A. L. Laskowski, J. Qiu, M. R. Nellist, S. Z. Oener, A. M. Gordon, S. W. Boettcher: Transient Photocurrents on Catalyst-Modified n -Si Photoelectrodes: Insight from Dual-Working Electrode Photoelectrochemistry. *Sustainable Energy Fuels* 2: 1995–2005, 2018.
- [35] B. Smandek, G. Chmiel, H. Gerischer: Photoluminescence as an In-Situ Technique to Determine Solid State and Surface Properties of Semiconductors in an Electrochemical Cell- Application of the “Dead Layer Model. *Phys. Chem.* 93: 1094, 1989.
- [36] A. B. Ellis: In Chemistry and Structure at Interfaces: New Laser and Optical Techniques. *Angewandte Chemie International Edition – Wiley*, 26: 1198–1199, 1987.
- [37] Po-Yen Kung, Li-Wen Huang, Tin-Wei Shen, Wen-Lin Wang, Yen-Hsun Su, and Melody I. Lin: Down-conversion photoluminescence sensitizing plasmonic silver nanoparticles on ZnO nanorods to generate hydrogen by water splitting photochemistry. *Appl. Phys. Lett.* 106: 023114, 2015.
- [38] J. Ouyang, Fu-Ren F. Fan, and A. J. Bard: Semiconductor Electrodes: Photoluminescence and Electroluminescence from Manganese-Doped ZnS and CVD ZnS Electrodes. *J. Electrochem. Soc.* 136: 4, 1989.
- [39] A. Krier, X. L. Huang, and A. Hammiche, Midinfrared: photoluminescence of InAsSb quantum dots grown by liquid phase epitaxy. *Appl. Phys. Lett.* 77: 3791, 2000.
- [40] F. Willig, R. Eichberger, N. S. Sundaresan, B. A. Parkinson: Experimental time scale of Gerischer's distribution curves for electron-transfer reactions at semiconductor electrodes. *J. Am. Chem. Soc.* 112 (7): 2702–2707, 1990.
- [41] J. Schneider and D. Bahnemann: Strong Transient Absorption of Trapped Holes in Anatase and Rutile TiO_2 at High Laser Intensities. *J. Phys. Chem. C* 122: 13979–13985, 2018.
- [42] J. Schneider, K. Nikitin, M. Wark, D. W. Bahnemann, R. Marschall: Improved charge carrier separation in barium tantalate composites investigated by laser flash photolysis. *Phys. Chem. Chem. Phys.* 18: 10719–10726, 2016.

- [43] M. Usman, S. Mendiratta, K. Lu: Semiconductor Metal–Organic Frameworks: Future Low Bandgap. *Adv. Mater.* 29: 1605071, 2017.
- [44] R. Qian, H. Zong, J. Schneider, G. Zhou, T. Zhao, Y. Li, J. Yang, D. W. Bahnemann, J. H. Pan: PVP-assisted laser ablation growth of Ag nanocubes anchored on reduced graphene oxide (rGO) for efficient photocatalytic CO₂ reduction. *Catal. Today* 335: 78-90, 2019.
- [45] M. Lorenc, M. Zroblek, R. Naskrecki, J. Karolczak, J. Kubicki, A. Maciejewski: Artifacts in femtosecond transient absorption spectroscopy. *Appl. Phys. B* 74: 19-27, 2002.
- [46] M. Barroso, A. J. Cowan, S. R. Pendlebury, M. Grätzel, D. R. Klug, J. R. Durrant: The Role of Cobalt Phosphate in Enhancing the Photocatalytic Activity of α -Fe₂O₃ toward Water Oxidation. *J. Am. Chem. Soc.* 133: 14868-14871, 2011.
- [47] I. Grigioni, M. Abdellah, A. Corti, M. V. Dozzi, L. Hammarström, E. Selli: Photoinduced Charge-Transfer Dynamics in WO₃/BiVO₄ Photoanodes Probed through Midinfrared Transient Absorption Spectroscopy. *J. Am. Chem. Soc.* 140: 14042-14045, 2018.
- [48] W. Lin, F. F. Fan, A. J. Bard: High Resolution Photoelectrochemical Etching of n-GaAs with the Scanning Electrochemical and Tunneling Microscope. *J. Electrochem. Soc.* 134: 1038, 1987.
- [49] T. Thundat, L. A. Nagahara, S. M. Lindsay: Scanning tunneling microscopy studies of semiconductor electrochemistry. *Journal of Vacuum Science & Technology A* 8: 539, 1990.
- [50] A. J. Bard, H. D. Abruna, C. E. Chidsey, L. R. Faulkner, S. W. Feldberg, K. Itaya, M. Majda, O. Melroy, R. W. Murray, M. D. Porter, M. P. Soriaga, H. S. White: The Electrode/Electrolyte Interface- A Status Report. *The Journal of Physical Chemistry* 97: 7147-7173, 1993.
- [51] B. Zhang, X. Zhang, X. Xiao, Y. Shen: Photoelectrochemical Water Splitting System: A Study of Interfacial Charge Transfer with Scanning Electrochemical Microscopy. *ACS Appl. Mater. Interfaces* 8: 1606–1614, 2016.
- [52] M. E. Snowden, A. G. Güell, S. C. S. Lai, K. McKelvey, N. Ebejer, M. A. O'Connell, A. W. Colburn, P. R. Unwin: Scanning Electrochemical Cell Microscopy: Theory and Experiment for Quantitative High Resolution Spatially-Resolved Voltammetry and Simultaneous Ion-Conductance Measurements. *Anal. Chem.* 84: 2483–2491, 2012.
- [53] Y. Ma, P. S. Shinde, X. Li, S. Pan: High-Throughput Screening and Surface Interrogation Studies of Au-Modified Hematite Photoanodes by Scanning Electrochemical Microscopy for Solar Water Splitting. *ACS Omega* 4: 17257–17268, 2019.
- [54] X. Zhang, M. Liu, W. Kong, H. Fan: Recent advances in solar cells and photo-electrochemical water splitting by scanning electrochemical microscopy. *Front. Optoelectron.* 11,: 33-347, 2018
- [55] J. Eichhorn, C. Kastl, J. K. Cooper, D. Ziegler, A. M. Schwartzberg, I. D. Sharp, F. M. Toma: Nanoscale imaging of charge carrier transport in water splitting photoanodes. *Nat. Commun.* 9: 2597, 2018.
- [56] F. A. L. Laskowski, S. Z. Oener, M. R. Nellist, A. M. Gordon, D. C. Bain, J. a L. Fehrs, S. W. Boettcher: Nanoscale semiconductor/ catalyst interfaces in photoelectrochemistry. *Nat. Mater.* 19: 69–76, 2020.
- [57] G. Liu, J. Eichhorn, C. Jiang, M. C. Scott, L. H. Hess, J. M. Gregoire, J. A. Haber, I. D. Sharp, F. M. Toma: Interface engineering for light-driven oxidation: Unravelling the passivating and catalytic mechanism in BiVO₄ overlayers. *Sustainable Energy Fuels* 3: 127-135, 2011
- [58] M. R. Nellist, F. A. L. Laskowski, J. Qiu, H. Hajibabaei, K. Sivula, T. W. Hamann, S. W. Boettcher: Atomic force microscopy with nanoelectrode tips for high resolution electrochemical, nanoadhesion and nanoelectrical imaging. *Nanotechnology* 28: 095711, 2017.

Effect of annealing on structure and properties of pulse electroplated Ni-W alloy coating

CHINMAYA KUMAR SARANGI^{1,2}, BIBHU PRASAD SAHU², BARADA KANTA MISHRA³, and RAHUL MITRA²

¹Hydro and Electrometallurgy Department, CSIR-Institute of Minerals and Materials Technology, Bhubaneswar, 751 013, India

²Metallurgical and Materials Engineering Department, Indian Institute of Technology Kharagpur, 721 302, India

³Indian Institute of Technology Goa, 403 401, India

Abstract : The structure and properties of Ni-W alloy coatings, deposited through pulse-plating route from an aqueous sulphate-citrate bath, have been evaluated and compared with those of coatings annealed under vacuum for durations of 2 h, 4 h or 6 h. The effect of annealing on microstructural evolution of the alloy coatings has been examined with emphasis on identification of constituent phases by X-ray diffraction, along with studies of their morphology by scanning and transmission electron microscopy with selected area electron diffraction. Annealing of Ni-W alloy coatings has resulted in the replacement of globular cluster-type appearance by a faceted morphology with the increase in crystallite size and reduction of the micro-strain in the alloy matrix. Both Nanoindentation hardness and elastic modulus of the coatings appear to reach their peak values on annealing for 2 h owing to the formation of NiW and Ni₄W intermetallic phases. However, on annealing for durations ≥ 4 h, the hardness is decreased owing to grain coarsening, whereas the Young's modulus is lowered due to diffusion of Cu from the substrate. The corrosion resistance of the annealed Ni-W alloy coatings, evaluated through potentiodynamic polarization technique, is found to be inferior as compared to that of the as-deposited coatings.

Keywords: Ni-W alloy coatings, Pulse electrodeposition, Annealing, Microhardness, Corrosion resistance

INTRODUCTION

Nanocrystalline Ni-W alloy coatings have emerged as one of the promising and appropriate alternatives to hard-chromium coatings, because of the attractive properties such as hardness, strength, wear resistance, thermal resistance, corrosion resistance, etc [1-3]. In the protective coatings for high temperature applications, nickel and cobalt based alloys are generally preferred, because of their high melting temperatures [4]. Owing to high melting point and thermal stability, tungsten can provide excellent mechanical and anti-corrosion properties, when alloyed with iron-group metals like Ni, Co, or Fe. Higher service life and improved precision can also be achieved while using Ni-W alloy as the tooling material [5]. Materials researchers have put specific focus on the development of Ni-W alloy coatings, which find a wide range of engineering applications due to high hardness and impressive corrosion resistance [6-8].

Pulse electroplating has been identified to be a technologically feasible and economically viable technique for the preparation of nanocrystalline Ni-W alloy coatings [4]. The major advantages of this method, which make it suitable for use in industries, are rapid production, high purity, ability to overcome shape limitations, potential to develop coatings with wide grain size variation, ease of controlling composition, as well as lack of requirement for post-deposition treatment [9].

It has been reported that heat treatment of the Ni-based alloy coatings can lead to an improvement in mechanical and thermal properties along with corrosion resistance [10-12]. The structural changes occurring as a result of heat treatment of the coatings are believed to be responsible for modifying the properties of the coatings. Literature suggests that the hardness of the deposited Ni-W alloys increases with annealing; however, a clear understanding of the hardening mechanism is yet to be demonstrated [13]. Popczyk et al. [14] have reported that heat treatment of the Ni-W alloy coatings can lead to an improvement in the corrosion resistance. Earlier studies indicate that there is a window for improving the mechanical and electrochemical properties of the Ni-W alloy coatings through annealing under controlled conditions. However, systematic studies on the extent of annealing treatment required

for the optimum enhancement in the properties of the Ni-W alloy coatings are found to be missing in the literature and other research reports. Therefore, in this regard, the present work has been focused to study the effect of annealing for different durations on the structure and properties of the Ni-W alloy coatings. The evolution of microstructure and properties has been studied with emphasis on identification of the constituent phases along with the examination of their morphology, besides the evaluation of crystallite size and microstrain in the alloy matrix. Moreover, the results of a comparative study between as-deposited Ni-W alloy and annealed Ni-W alloy coating in terms of the above mentioned microstructural properties, hardness, elastic modulus and corrosion resistance have been reported.

EXPERIMENTAL PROCEDURE

The investigated Ni-22 (at%) W alloy coatings were deposited from a sulphate-citrate bath by pulse current plating technique. The bath composition and operating parameters for electrodeposition of the coatings are presented in Table 1. The initial pH of the electrolytic bath was adjusted to about 8.0 by using dilute sulphuric acid or sodium hydroxide solution. The temperature of the bath was maintained at $\sim 73 \pm 2^\circ\text{C}$ by an automatically controlled hot plate. All the electrodeposition experiments were conducted for a duration of 4 h at a peak current density of 200 mA cm^{-2} and a duty cycle of 25% with T_{on} and T_{off} of 50 ms and 150 ms, respectively using an electrochemical analyzer (Autolab, Netherlands). Copper sheet with a dipping area of $2 \times 3 \text{ cm}^2$ was used as the substrate, and a platinum-coated titanium sheet was used as the anode. Prior to electroplating, the copper substrates were polished, degreased in acetone and rinsed thoroughly in deionised water. The substrates were then activated by immersing in sulphuric acid solution (5vol%) for 30 s followed by washing in deionised water. The as-deposited Ni-W alloy coatings were annealed in a vacuum furnace (Nabertherm make, Germany) at a pressure of 10^{-5} mbar and temperature of 750°C for durations of 2 h, 4 h and 6 h.

Table 1 Electrolytic bath composition and pulse plating parameters used for the deposition of Ni-W alloy coatings.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.05 M
$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	0.10 M
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	0.5 M
NH_4Cl	0.5 M
Temperature of bath	$73 \pm 2^\circ\text{C}$
pH of the bath	8.0
Peak current density	200 mA cm^{-2}
Duty cycle	25% (T_{on} 50 ms; T_{off} 150 ms)
Stirring speed	150 rpm
Time	4 h

The as-deposited and annealed Ni-W alloy coatings were analyzed using X-ray diffraction (XRD) by a diffractometer (Panalytical, Netherland), operated at a voltage of 40 kV and current of 30 mA, using Cu K α radiation of wavelength equal to 0.154 nm. For XRD data acquisition, 2θ was varied from 20° to 80° with respect to the specimen plane at a speed of 2° per min. The average crystallite size (D) and microstrain have been calculated from the XRD peaks using the Williamson-Hall relationship^[15] as follows:

$$B\cos\theta = K\lambda/D + 4\sin\theta\epsilon \quad (1)$$

where B is the integral breadth, θ is the diffraction angle, K is the shape factor (~ 0.9), λ is the X-ray wavelength (0.154 nm), and ϵ is the microstrain. The instrumental broadening has been determined by measuring the full width at half maximum (FWHM) of the peaks in the XRD patterns of annealed nickel. Subsequently, the broadening

due to grain size (B_{actual}) has been calculated using the following relation:

$$B_{\text{actual}} = \sqrt{(B_{\text{obs}}^2 - B_{\text{std}}^2)} \quad (2)$$

where B_{obs} and B_{std} are FWHMs of any reflection from the analyzed sample and annealed nickel sample, respectively.

The surface morphologies of the coatings were examined using a field emission scanning electron microscope (FESEM) (Zeiss SUPRA40 Oberkochen, Germany), and their elemental compositions were evaluated by energy dispersive spectroscopy (EDS). Further, the microstructures of the coatings were examined by using a transmission electron microscope (TEM) (JEM 2100, JEOL Ltd., Tokyo, Japan) being operated at an accelerating voltage of 200 kV. The specimens for TEM studies were prepared through a procedure involving mechanical thinning by polishing first on SiC-coated emery paper, and subsequently using a dimpler (Model 656 Gatan Inc., Pleasanton, CA, USA) to remove material from the side of Cu substrate. The mechanical thinning was followed by argon ion milling with the help of a precision ion polishing system (Model 691, Gatan Inc., Pleasanton, CA, USA) to develop electron transparency.

Nanoindentation of the coatings for the evaluation of hardness, elastic modulus and load-displacement behavior was carried out at 10 positions for each sample using a UMIS nano-indentation system (Fisher-Cripps, Australia) with Berkovich indenter (face angle 65.30°) of tip radius 150 nm. The corrosion behaviour of the coatings was evaluated using a potentiostat/galvanostat (CHI 660E, USA) equipped with a three electrode cell. For carrying out corrosion tests, the as-deposited or annealed coating acted as the working electrode, whereas a platinum wire and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The polarization curves were recorded for investigated coatings at a scan rate of 1 mV s⁻¹ in 3.5 wt% NaCl solution at the ambient temperature.

RESULTS AND DISCUSSION

Phase analysis

The XRD patterns of the as-deposited as well as annealed (2, 4 and 6 h) Ni-W alloy coatings, depicting peaks within the angular range of 20°-80° are shown in Fig. 1(a), whereas their magnified versions with smaller angular range are presented in Fig. 1(b) and (c). In the aforementioned XRD pattern from the as-deposited Ni-W alloy coating (Fig. 1), three diffraction peaks representing {111}, {200}, and {220} of FCC structured Ni are observed. On the other hand, the XRD pattern from the Ni-W alloy coating annealed for 2 h or more reveals additional peaks of intermetallic compounds, Ni₄W and NiW, as shown in Fig. 1. However, the XRD patterns from the Ni-W alloy coatings annealed for 4 h or 6 h exhibit the peaks of NiW and Ni₄W with reduced intensity, as well as an increased preference for <111> orientation of the Ni-W solid solution (Ni_{ss}) alloy grains. Formation of surfaces parallel to densely packed {111} planes is preferred, probably because of their lower surface energy compared to other crystallographic orientations.

According to the binary Ni-W equilibrium phase diagram, Ni₄W and NiW are the stable phases for W contents of 18-19.2 at% (40.7-42.7 wt%) and 49.3-50 at% (75.3-75.8 wt%), respectively [16]. It may be speculated that the enrichment of Cu in the Ni_{ss} matrix during annealing as confirmed by the results of EDS analysis shown in Fig. 3, may have lowered the solubility of W, which in turn may have promoted the formation of Ni₄W and NiW on annealing.

Using Williamson-Hall equation (1), a plot with 4sinθ along the x-axis and Bcosθ along the y-axis for the coatings was drawn, as shown in Fig. 2. After conducting the linear fit to the data, the values of y-intercept and slope have been determined and then using the derived values of y-intercept and slope of the fit, crystallite size and microstrain, respectively for the coatings have been calculated and the results are presented in Table 2. Examination of the data presented in Fig. 2 and Table 2 shows that the average crystallite size of the Ni-W alloy

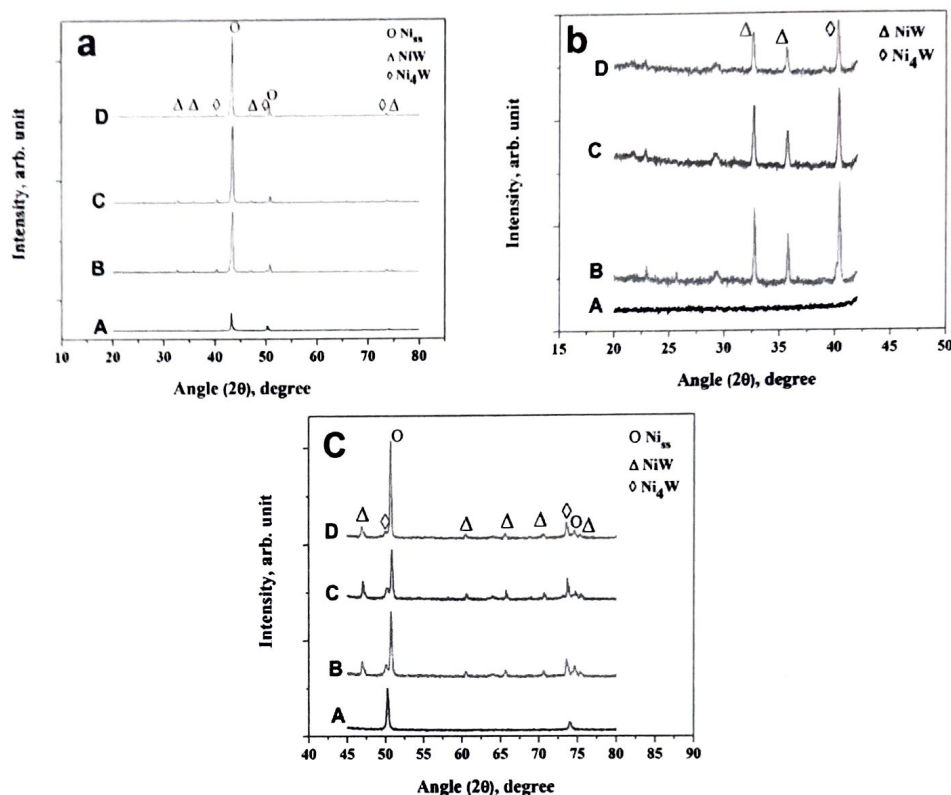


Fig. 1. XRD patterns of the as-deposited and annealed Ni-W alloy coatings, (A) as-deposited, (B) annealed for 2h, (C) annealed for 4h and (D) annealed for 6 h for: (a) the range of angles (2θ) from 20° to 80° ; as well as the magnified views of the peaks within (b) the range of angles (2θ) from 20° to 45° ; and (c) the range of angles (2θ) from 45° to 80° .

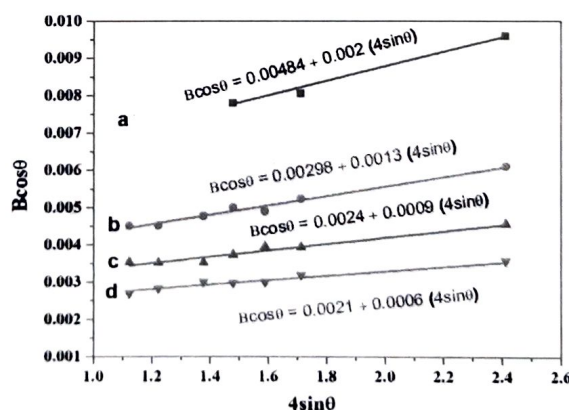


Fig. 2. Plots depicting the variation of average crystallite size and micro-strain with duration of annealing of the investigated Ni-W alloy coatings: (a) as-deposited, (b) annealed for 2 h, (c) annealed for 4 h and (d) annealed for 6 h.

(Ni-rich solid solution, Ni_{ss}) matrix increases with the increase in the duration of annealing as a result of grain growth. The average crystallite size of the Ni_{ss} matrix phase is found to be ~ 28.6 nm, and after annealing for 2 h the crystallite size is observed to increase by $\sim 61.2\%$ to ~ 46.5 nm. Further, the increase in annealing time to 4 h and 6 h results in an increase in the crystallite size by 2 times and 2.3 times, respectively with respect to that observed in the as-deposited coatings. It may be noted that increase in grain size is much sharper for the increase in the duration of annealing up to 4 h, whereas the rate of increase is relatively less significant for annealing duration between 4 h and 6 h. This observation is well-expected as the driving force for coarsening is reduced

after initial rapid coarsening of grain size. In contrast to the trend observed for the Ni_{ss} crystallite size, the micro-strain is found to decrease with the increase in annealing time. Both observations in respect of the crystallite size and micro-strain with the increase in annealing time are consistent with the narrowing of the XRD peaks from the Ni_{ss} , as shown in Fig. 1.

Table 2 Variation of average crystallite size and micro-strain of as-deposited and annealed Ni-W alloy coatings

Sample No.	Duration of annealing (h)	Crystallite size (nm)	Strain (ϵ)
1	0 (as-deposited)	28.6	0.0020
2	2	46.5	0.0013
3	4	57.7	0.0009
4	6	65.8	0.0006

Study of microstructure by scanning electron microscopy

Plan-view

The FESEM micrographs depicting the surface morphologies of as-deposited Ni-W alloy and annealed Ni-W alloy coatings along with average bulk compositions obtained by EDS analysis are shown in Fig.3. Furthermore, the morphology of grains at the surface is depicted at higher magnification in Fig. 4. On qualitative observation, the coatings appear to be dense and well-adhered with the substrate. The concentrations of Ni and W in the as-deposited Ni-W alloy coating are found to be about ~78 at% and ~22 at%, respectively as shown in Fig. 3(a). The compositions of the annealed samples shown in Fig. 3(b)-(d) indicate that Cu has diffused from the substrate to the coating, with its concentration scaling with the duration of annealing. The FESEM image in Fig. 4(a) depicting the surface morphology of as-deposited Ni-W coating at higher magnification shows the presence of globular clusters of Ni_{ss} grains. It is observed that after annealing of the coatings in vacuum, the globular appearance of grains gradually disappears and gets transformed to typically faceted morphology, as shown in Fig. 4(b) and (c). Furthermore, qualitative comparison of Fig. 4(a) through (c) suggests that the grains of Ni_{ss} on the surface have grown in size.

Cross-sectional view

The average thickness of the deposited Ni-W alloy coating samples was determined as ~30 μm by examining their cross-section in the FESEM at low magnification (Fig. 5(a)). Examination of the FESEM images depicting the cross-sectional microstructure of the Ni-W alloy coating annealed for 6 h at different magnifications as shown in Fig. 5(b) and (c), indicates that grain-coarsening has happened primarily at the surface, whereas it is insignificant at sub-surface locations. The coarsening of Ni_{ss} grains along the cross-section may have been inhibited by the formation of Ni_4W and NiW , as evidenced by the results of EDS analysis. Considering the inhibition of grain growth due to the formation of Ni_4W and NiW , it may be inferred that the volume fraction of these intermetallic phases is lower near the surface, where the observed grain size is coarser. The change in the composition of Ni_{ss} due to increase in Cu concentration in course of annealing may have also influenced the grain-coarsening behaviour, which needs to be further investigated. Further study is required to confirm the above-mentioned hypothesis.

Study of microstructure by transmission electron microscopy

Bright-field plan-view TEM micrographs and the corresponding indexed SAED patterns of the as-deposited Ni-W alloy and annealed Ni-W alloy coatings are shown in Fig. 6. The results of TEM studies are in close agreement with those of XRD regarding phase identification and the average grain size. The SAED patterns

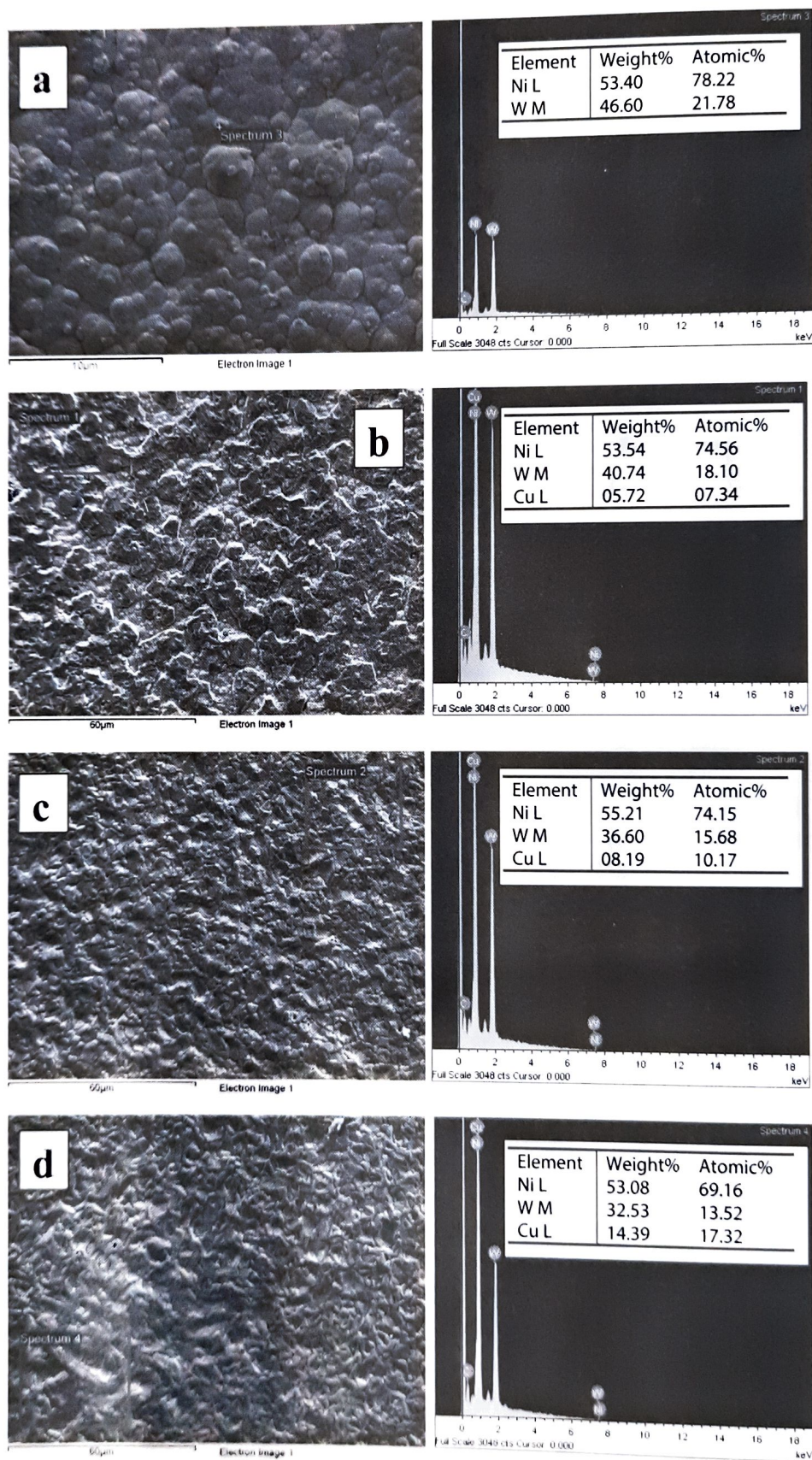


Fig. 3. FESEM micrographs and EDS spectra of Ni-W alloy coatings (a) as-deposited, (b) annealed for 2 h, (c) annealed for 4 h, (d) annealed for 6 h.

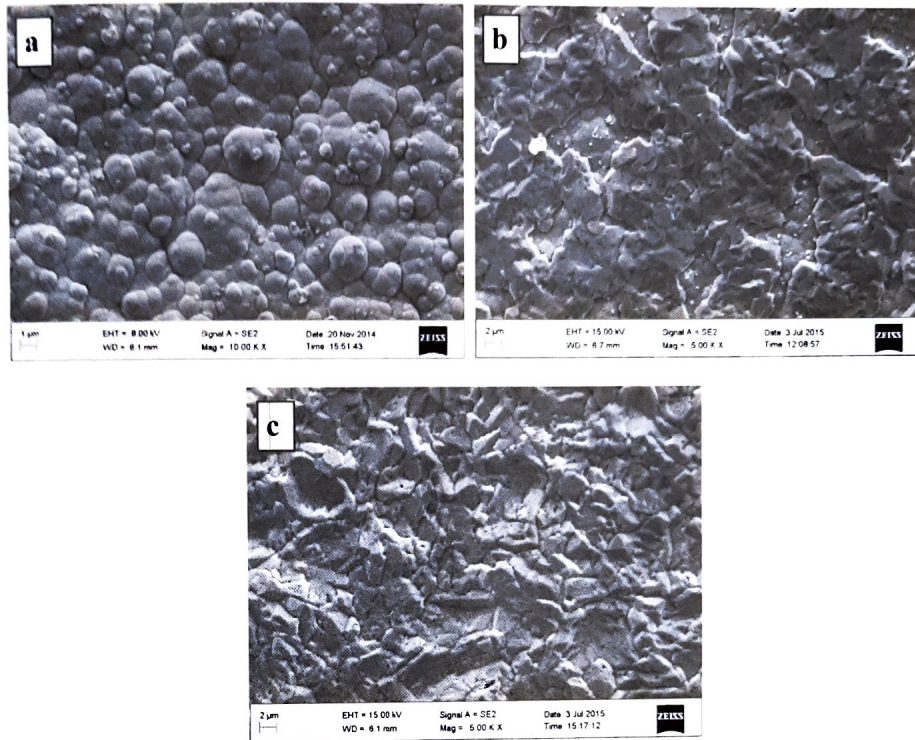


Fig. 4. FESEM images of Ni-W alloy coatings (a) as-deposited, (b) annealed for 2 h, and (c) annealed for 6 h.

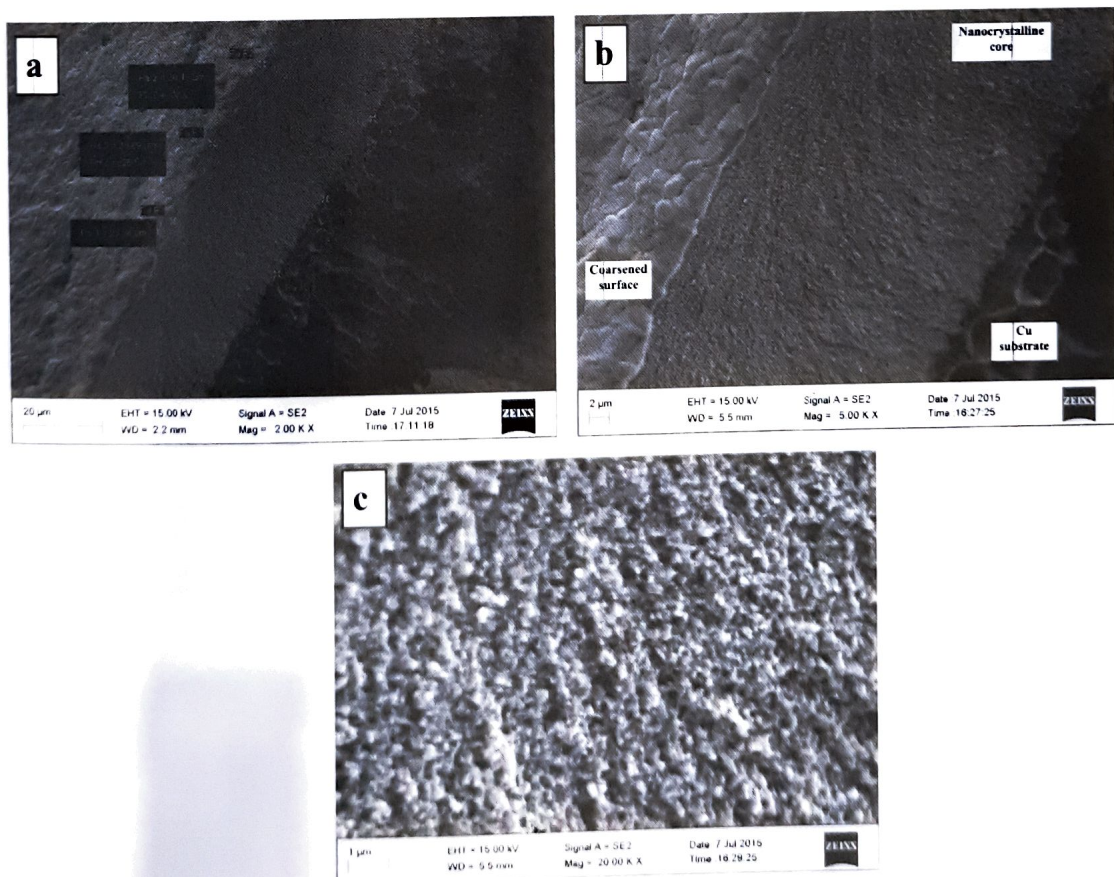


Fig. 5. Cross-sectional FESEM images of the Ni-W alloy coatings: (a) in as deposited condition and after annealing for 6 h at (b) lower magnification, (c) higher magnification.

from the coatings (Figs. 6(b) and (d)) consist of rings representing Ni (111), (200), (220), (311) and (420) planes. Contrary to the results of XRD analysis, the SAED pattern in Fig. 6 (d) does not provide any evidence for the presence of intermetallics, Ni₃W and Ni₄W, which suggests that these phases were not present near the surface. In other words, their formation may have happened at sub-surface locations, where grain growth has not occurred. Such an inference is drawn because the polishing and material removal for TEM sample preparation was carried out from the side of the substrate, such that the prepared thin foil contained the near-surface location of the coating. It is, of course, noteworthy that the rings in the SAED pattern from the annealed Ni-W alloy coating (Fig. 6 (d)) appear discontinuous with spots unlike the continuous ring pattern observed in case of the as-deposited coating (Fig. 6 (b)). Such a difference between the SAED patterns obtained from as-deposited and annealed Ni-W coatings is ascribed to the presence of coarser grains in the latter sample. The inference is drawn regarding grain coarsening from the results of TEM studies qualitatively in agreement with the results of grain size assessment by XRD analysis (Table 2). The absence or lower volume fraction of the intermetallic phases, Ni₃W and Ni₄W may be considered to have promoted unhindered grain coarsening of the Ni_{ss} phase near the surface, as shown in Fig. 5.

Nano-indentation hardness and Young's modulus

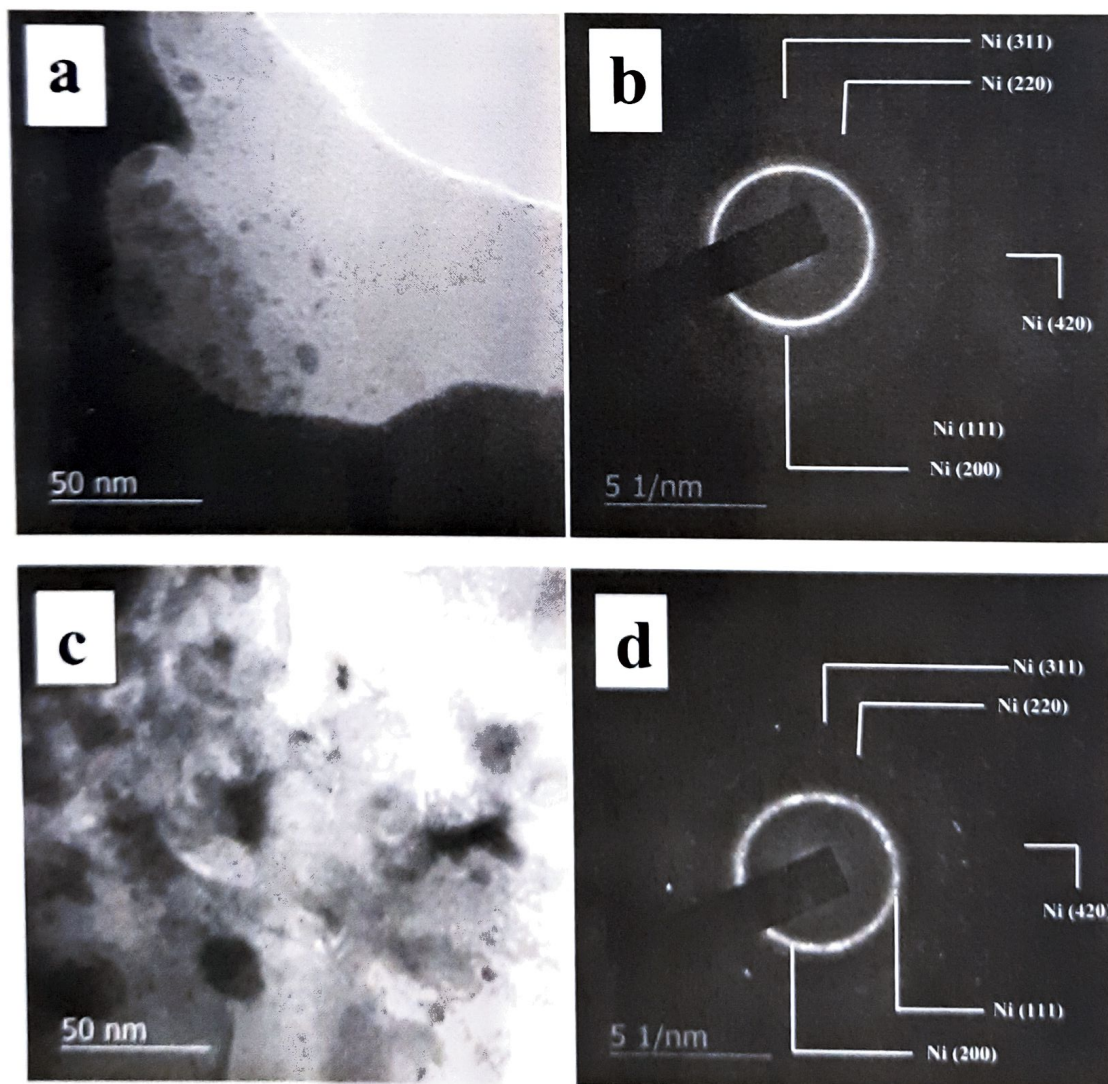


Fig. 6. TEM study of the Ni-W alloy coatings: (a) TEM image and (b) SAED pattern of as-deposited coating; (c) TEM image and (d) SAED pattern of coating annealed for 6 h.

The plots of load against depth obtained from the nanoindentation tests carried out at a load of 10 mN are shown in Fig. 7(a). The as-deposited Ni-W alloy sample was found to exhibit a penetration depth of 0.54 μm , which is higher than that observed for the Ni-W alloy coatings annealed for 2 h and 4 h and equivalent to that noticed for the coating annealed for 6 h. Under similar load application, the average penetration depth ($\sim 0.3 \mu\text{m}$) is found to be the least, which provides a qualitative indication of the hardness being the highest in case of the Ni-W alloy coating subjected to annealing for 2 h. Lower depth of penetration along with higher hardness of the Ni-W alloy coating annealed for 2 h compared to that recorded for the as-deposited condition may be attributed to the precipitation of the intermetallic compounds such as NiW and Ni_4W as well as limited coarsening of the Ni_{35} grains in the matrix of the Ni-W alloy at the sub-surface locations as a result of annealing.

Plots depicting the variation of hardness and elastic modulus of the Ni-W alloy coatings as a function of the annealing duration are shown in Figs. 7(b) and (c), respectively. As shown in these figures, after annealing for 2 h, the hardness of the annealed coatings increases by $\sim 22\%$ to a maximum value of $\sim 8.3 \text{ GPa}$ (Fig. 7(b)), whereas with annealing for longer period of time beyond 2 h for 4 h and 6 h, the hardness of the coating has decreased by $\sim 5.4\%$ and $\sim 28.4\%$, respectively. A similar trend in hardness increment was reported by Hou et al. [5] and according to them, the precipitation of NiW and Ni_4W intermetallic phases contribute to such enhancement in the hardness of the coating. Furthermore, they have stated that excessive annealing at 700°C tends to decrease the hardness of Ni-W alloy coating due to grain coarsening. On the other hands, Hayata et al. have reported an increase in hardness of the Ni-40.7W alloy from 15 kN/mm^2 to 22 kN/mm^2 after annealing temperatures in the range of $\sim 450\text{--}550^\circ\text{C}$ as a consequence of precipitation of Ni_4W and NiW phases in the alloy matrix [17]. A similar observation has been also reported in case of the Ni-Mo-P coatings [18], which have exhibited a very sharp increase in hardness from 309 Hv to 1041 Hv as a result of the formation of Ni_3P and NiMo phases in the alloy matrix on annealing at 600°C .

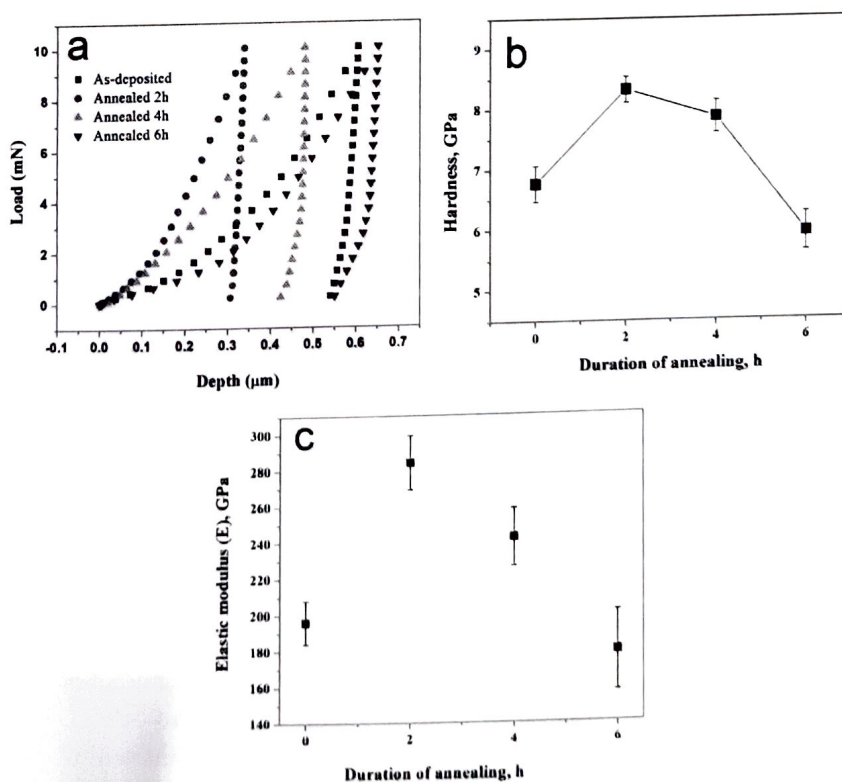


Fig. 7. The results of nanoindentation experiments on as-deposited and annealed Ni-W alloy coatings: Plots depicting (a) variation of load with depth, as well as variation of (b) hardness and (c) Young's modulus with duration of annealing.

After annealing the Ni-W alloy coating for 2 h, Young's modulus is found to increase by ~44.8% to 284 GPa (Fig. 7(c)). Such an increase in Young's modulus of the Ni-W alloy coating on annealing may be attributed to the formation of intermetallic phases, NiW and Ni₄W in the alloy matrix. These intermetallic phases are found to possess higher Young's modulus compared to that of pure Ni or Ni_{ss} matrix, because of their strong directional bonding. However, annealing for a longer time of 4 h or 6 h has resulted in a decrease in Young's modulus by ~14.8% or ~36.9%, respectively. The decrease in Young's modulus as a consequence of the increase in the duration of annealing may be attributed to the enrichment of the Ni-W alloy matrix with Cu during annealing, with the amount of NiW and Ni₄W remaining more or less unchanged. As Cu has a lower melting point as well as Young's modulus compared to that of Ni and W, its enrichment in the Ni_{ss} matrix is expected to reduce both these properties.

Corrosion resistance of the coatings

The potentiodynamic polarization curves of the as-deposited and annealed Ni-W alloy coatings obtained in 3.5 wt% NaCl solution are presented in Fig. 8. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) have been calculated from the intersection of the cathodic and anodic Tafel curves using the Tafel extrapolation method, and are summarized in Table 3. The results clearly reveal that among the investigated Ni-W alloy coatings, the as-deposited samples show the highest corrosion resistance. From the results in Table 3, it can be observed that with the increase in the duration of annealing of the Ni-W alloy coating, both corrosion potential and polarization resistance decrease, while the corrosion current density and corrosion rate of the composite coating increase. From the results in Table 3, it is noticed that the polarization resistance (R_p) has decreased by 23.7% on annealing for 2 h, whereas it has decreased more drastically, i.e. by 67.6% and 71% on annealing for 4 h and 6 h, respectively. Therefore, it may be inferred that the corrosion resistance is worsened more severely after annealing for durations ≥ 4 h compared to that after 2 h.

Table 3 Corrosion potential (E_{corr}) and corrosion current density (i_{corr}) for as-deposited and annealed Ni-W alloy coatings

Ni-W alloy coating type	E_{corr} (vs. SCE), V	Error E_{corr} (vs. SCE), V	I_{corr} (A cm^{-2}) ($\times 10^{-5}$)	Polarization resistance, R_p (ohm)	Error R_p (ohm)	Corrosion rate (mil year^{-1})
As-deposited	-0.534	± 0.012	3.545	1230	± 12	7.664
Annealed 2h	-0.547	± 0.010	6.208	938	± 15	12.461
Annealed 4h	-0.576	± 0.017	12.41	398	± 13	24.282
Annealed 6h	-0.580	± 0.011	15.09	357	± 09	28.753

The significant decrease in corrosion resistance of the annealed Ni-W alloy coatings may be attributed to the formation of the intermetallic compounds such as Ni₄W and NiW, such that their interfaces with the matrix act as cathodic regions with respect to the alloy matrix grains, leading to galvanic corrosion of the coating. Furthermore, the coarsening of grain size caused by annealing leads to a significant decrease in the net grain boundary area. As the grain boundaries are anodic with respect to grain interior, a decrease in the grain boundary area with the increase in grain size is also expected to decrease the number of corrosion micro-cells. Due to less number of corrosion micro-cells formed in the Ni-W alloy, localized corrosion is also promoted. Considering that grain coarsening is more significant, i.e. ≥ 2 times on annealing for durations ≥ 4 h, it is intuitive that the corrosion resistance will also be worsened more significantly.

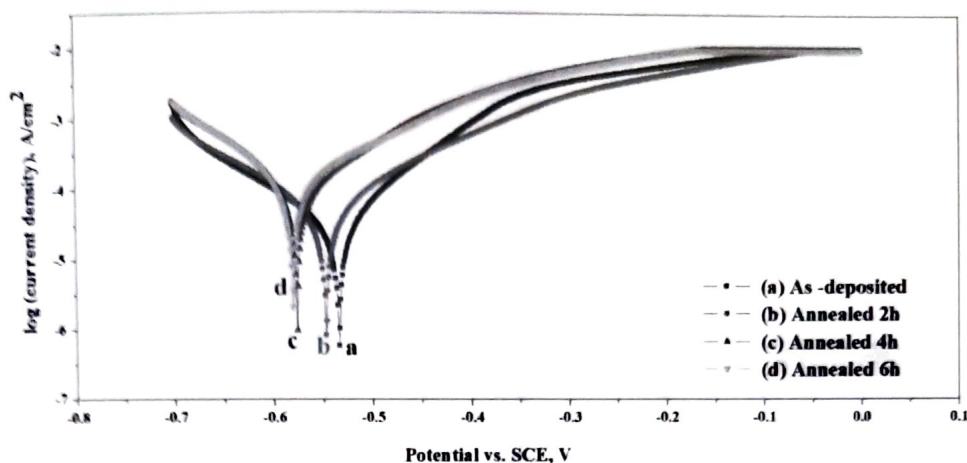


Fig. 8. Potentiodynamic polarization curves obtained for the as-deposited and annealed Ni-W alloy coatings

Based on the results of the present study the Ni-W alloy coatings annealed for 2 h have exhibited the highest hardness and Young's modulus with a limited decrease in polarization resistance, and therefore these coatings appear to be preferred for protective applications, if corrosion inhibition is not the most significant requirement. However, the as-deposited Ni-W alloy coatings appear to be more suitable for use, if corrosion resistance is the primary requirement.

CONCLUSIONS

The structure-property relationship of the as-deposited and annealed Ni-W alloy coatings deposited through pulse electrodeposition technique has been investigated. Annealing of the Ni-W alloy coatings results in an increase of the crystallite size and consequently leads to significant grain growth at the surface. Furthermore, a preferred orientation of $\langle 111 \rangle$ is observed in the Ni-W with the increase in the duration of annealing. The FESEM images of cross-sections have indicated the occurrence of substantial grain coarsening at the surface of the coating, keeping nanocrystalline structure unaltered in the core.

The hardness and Young's modulus of the Ni-W alloy coatings have increased to maximum values after annealing for 2 h as a result of formation of Ni_4W and NiW intermetallic phases. However, on annealing for durations ≥ 4 h, the hardness has decreased due to grain coarsening, whereas the Young's modulus has been lowered due to diffusion of Cu from the substrate.

The corrosion rate of the coating is increased on annealing due to the occurrence of more localized corrosion owing to the reduction of the grain boundary area, with the increase in the interfacial area with the formation of NiW and Ni_4W phases. The present study has shown that the use of annealed Ni-W alloy coatings can be a good option for specific applications requiring high hardness and elastic modulus. However, the use of annealed Ni-W alloy coatings may not be an ideal choice for the applications involving protection against corrosion.

ACKNOWLEDGMENT

This work was financially supported by Ministry of Earth Sciences (MoES), India.

REFERENCES

- [1] M. Zemanova, M. Krivosudska, M. Chovancova, V. Jorik: Pulse electrodeposition and corrosion properties of Ni-W alloy coatings. *J. Appl. Electrochem.* **41**: 1077–1085, 2011. <https://doi.org/10.1007/s10800-011-0331-y>.
- [2] L. Anicai: Ni-W alloys coatings as ecological alternative for chromium plating – Evaluation of corrosion behaviour. *Corros. Rev.* **25**: 607–620, 2007. <https://doi.org/10.1515/CORRREV.2007.25.5-6.607>.

- [3] H. Alimadadi, M. Ahmadi, M. Aliofkhaezai, S.R. Younesi: Corrosion properties of electrodeposited nanocrystalline and amorphous patterned Ni-W alloy. *Mater.Des.* 30: 1356–1361, 2009. <https://doi.org/10.1016/j.matdes.2008.06.036>.
- [4] M. Donten, H. Cesiulis, Z. Stojek: Electrodeposition and properties of Ni-W, Fe-W and Fe-Ni-W amorphous alloys. A comparative study. *Electrochim. Acta* 45: 3389–3396, 2000. [https://doi.org/10.1016/S0013-4686\(00\)00437-0](https://doi.org/10.1016/S0013-4686(00)00437-0).
- [5] K.H. Hou, Y.F. Chang, S.M. Chang, C.H. Chang: The heat treatment effect on the structure and mechanical properties of electrodeposited nano grain size Ni-W alloy coatings. *Thin Solid Films* 518: 7535–7540, 2010. <https://doi.org/10.1016/j.tsf.2010.05.041>.
- [6] Q. Feng, T. Li, H. Yue, K. Qi, F. Bai, J. Jin: Preparation and characterization of nickel nano- Al_2O_3 composite coatings by sediment co-deposition. *Appl. Surf. Sci.* 254: 2262–2268, 2008. <https://doi.org/10.1016/j.apsusc.2007.09.014>.
- [7] D.K. Singh and V.B. Singh: Electrodeposition and characterization of Ni-TiC composite using N-methylformamide bath. *Mater. Sci. Eng. A* 532: 493–499, 2012. <https://doi.org/10.1016/j.msea.2011.10.115>.
- [8] B.P. Sahu, C.K. Sarangi, R. Mitra: Effect of Zr content on structure property relations of Ni-Zr alloy thin films with mixed nanocrystalline and amorphous structure. *Thin Solid Films* 660: 31–45, 2018. <https://doi.org/10.1016/j.tsf.2018.05.050>.
- [9] I. Gurrappa, L. Binder: Electrodeposition of nanostructured coatings and their characterization—A review. *Sci. Technol. Adv. Mater.* 9: 043001 (11pp), 2008. <https://doi.org/10.1088/1468-6996/9/4/043001>.
- [10] K. Wykpiś, M. Popczyk, J. Niedbala, A. Budniok, E. Lagiewka, B. Bierska-Piech: Influence of thermal treatment on the corrosion resistance of electrolytic Zn-Ni coatings. *Materials Science-Poland* 29: 177–183, 2011. <https://doi.org/10.2478/s13536-011-0028-2>.
- [11] M. Popczyk, B. Losiewicz, E. Lagiewka, A. Budniok: Influence of thermal treatment on the electrochemical properties of Ni+Mo composite coatings in an alkaline solutions. *Solid State Phenomena* 228: 231–236, 2015. <https://doi.org/10.4028/www.scientific.net/SSP.228.231>.
- [12] K. Wykpiś, M. Popczyk, J. Niedbala, B. Bierska-Piech, A. Budniok, E. Lagiewka: Influence of thermal treatment on the corrosion resistance of electrolytic Zn-Ni+Ni composite coatings. *Adv. Compos. Mater.* 24: 431–438, 2015. <https://doi.org/10.1080/09243046.2014.901471>.
- [13] A.J. Detor, C.A. Schuh: Microstructural evolution during the heat treatment of nanocrystalline alloys. *J. Mater. Res.* 22: 3233–3248, 2007. <https://doi.org/10.1557/JMR.2007.0403>.
- [14] M. Popczyk, J. Kubisztal, A.S. Swinarew, Z. Waskiewicz, A. Stanula, B. Knechtle: Corrosion resistance of heat-treated Ni-W alloy coatings. *Materials* 13: 1172–1183, 2020. [doi:10.3390/ma13051172](https://doi.org/10.3390/ma13051172).
- [15] V.D. Mote, Y. Purushotham, B.N. Dole, (2012) Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. *J.Theor. Appl. Phys.* 6: 6, <https://doi.org/10.1186/2251-7235-6-6>.
- [16] M. Hansen: Constitution of binary alloys, McGraw-Hill Book Co., New York, 1075, 1958.
- [17] S. Hayata, S. Oue, H. Nakano, T. Takahashi: Effect of annealing on the structure and hardness of electrodeposited Ni-W alloys. *ISIJ International* 55: 1083–1090, 2015. <http://dx.doi.org/10.2355/isijinternational.55.1083>
- [18] R.L. Melo, P.N.S. Casciano, A.N. Correia, P. de Lima-Neto: Characterisation of electrodeposited and heat-treated Ni-Mo-P coatings. *J. Braz. Chem. Soc.* 23: 328–334, 2012. <http://dx.doi.org/10.1590/S0103-50532012000200020>.

Vacuum furnaces for metallurgical processing

V VASUDEVA RAO¹ and V RAVINDRA^{2*}

¹ Cryogenic Engineering Centre, IIT Kharagpur

² School of Energy Science & Engineering, IIT Kharagpur

Abstract: Large scale vacuum furnaces are becoming crucial in metallurgical processes like melting, casting, heat treatment, degassing, annealing and brazing. The vacuum conditions help in reducing contamination (like oxidation) and improve the micro-structure to get favourable metallurgical properties for industrial applications. The vacuum also reduces the melting and boiling points of metals and alloys, thereby reducing the electrical power requirement in high temperature furnaces for clean metallurgical processing. The present paper describes the design criteria of vacuum metallurgical furnaces involving vacuum equipment, heating elements and process instrumentation.

Keywords: Vacuum furnace, Pumps, Hot zone, heating elements, thermocouples, safety interlocks.

INTRODUCTION

Vacuum furnaces are finding increasing application in the metallurgical processing of high temperature materials, where pick up of Oxygen and Nitrogen during melting, casting and subsequent heat treatment is minimum^[1]. The vacuum environment is a pure protective atmosphere than any inert gas. For most of the metallurgical processes, such as sintering, brazing, annealing, and melting & casting, a vacuum of the order of 1×10^{-5} Torr is adequate^[2]. Hence, the vacuum system consists of a combination of a mechanical vane pump/piston pump and oil diffusion pump. In case of furnaces which involve heavy degassing, a roots pump (increasing the effective pumping speed of roots-rotary combination) is essential for maintaining the required backing pressure of the diffusion pump for its efficiency.

The pumping system includes other sub-assemblies such as chevron baffles, valves and pipe lines.

The various types of valves used in the pumping line are angle valves, ball valves, butterfly valves and gate valves. Gate valves are the best suited for vacuum pumping line, as they offer minimum impedance to gas flow. For high vacuum line, angle valves fabricated out of stainless steel are used. The pipelines in the high vacuum side (near the furnace chamber) should be designed to have high flow conductance (C), so that the effective pumping speed (S_{eff}) of the HV pump at the chamber is sufficient^[3]. S_{eff} can be estimated from the manufacturer's specified maximum speed (S_{max}) and the conductance (C) by the following equation:

$$\frac{1}{S_{eff}} = \frac{1}{S_{max}} + \frac{1}{C}$$

The throughput, (Q) representing the amount of pumped gases from the furnace chamber at any pressure (P) is given by $Q = P \cdot S_{eff}$.

CLASSIFICATION OF VACUUM FURNACES

Vacuum furnaces are broadly classified into two types, i.e cold wall and hot wall types

Cold wall type: The vacuum chamber is water cooled and kept at room temperature. The job is kept in a hot zone (resistance heating/induction heating) supported by thermally insulating structures. Here the size of the hot zone is small and energy input is less. But degassing from the walls of the vacuum shell remains as a problem to be solved.

Hot wall type: The vacuum chamber/muffle is externally heated (by resistive heating) and job located inside receives heat mainly by radiation. Degassing/water vapour problems are absent. It can handle large quantities of

*Corresponding Author, Email :vvr Rao@cryo.iitkgp.ac.in

jobs to be processed. However, these are not popular, as they require special vacuum seals which can withstand high chamber temperature and thermal insulation outside to reduce electrical heating power requirement and reduce room heating. Hence the rest of the paper deals with cold wall type furnace.

DESIGN OF VACUUM CHAMBER CONSIDERATIONS FOR COLD WALL TYPE FURNACE

Fig 1 shows the schematic of a typical cold wall type vacuum furnace for high quality brazing application. It consists of a double walled cylindrical chamber, matching diffusion/rotary vacuum pumping system, hot zone with heating elements and shields, several control valves and sensors (for pressure and temperature measurement).

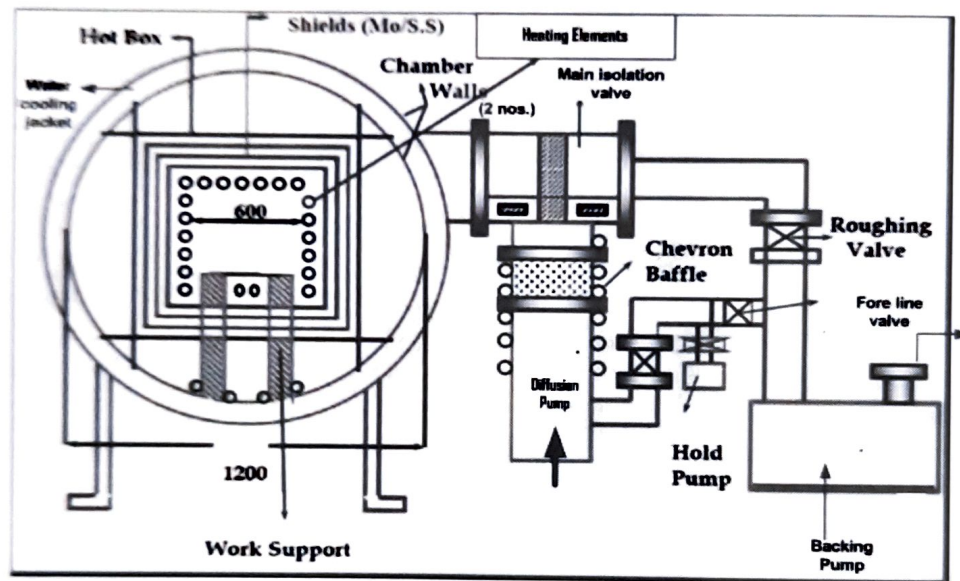


Fig 1: Schematic of typical double walled vacuum brazing furnace (dimensions in mm)

For the fabrication of chamber, either hot rolled mild steel or stainless steels of grade 304, 304L and 316 are used. The chamber should not collapse under vacuum. The thickness of the chamber should be optimised to stand the pressure difference (1 Kg/cm^2 + cooling water pressure in the outer jacket) and not to increase the mass and out gassing rate. Further it should be able to prevent leakages from outside atmosphere, when it is pumped down to a low pressure and to permit the material to be processed without any damage to the chamber as well as to the product. However, thinner sheets (to create lower weight) can also be used by reinforcing the strength of the chamber by welding stiffeners. For vacuum applications, argon arc welding is preferred as the contamination from flux is totally avoided. If complete argon arc welding is not possible, we can weld few tags and then remaining by brazing with compatible metals/flux.

It is essential to have good surface finish in all the grooves meant for 'O' rings, Wilson seals for rotating devices and door seals. Regarding shape, cylindrical and rectangular chambers are very often used. The best method of cylindrical chamber fabrication is from a sheet cylindrically rolled up and dished heads on both ends welded throughout. Although this type of construction offers good mechanical strength, some designers select a rectangular cross section for efficient space utilization and use of low capacity vacuum pumps. However, rectangular chambers have to be designed for higher stresses and obviously require higher shell thickness.

With respect to orientation/operation, the furnace chambers are classified as:

- Vertical type, bottom loaded for heavy jobs loaded from bottom opening
- Vertical type, top loaded where top dished end can be lifted by an over head hoist and the job can be loaded by a crane.

- iii. Horizontal type, front loaded (by opening the front door with suitable seals and clamps) for long light weight components/flat pieces etc.

For the purpose of external water cooling, most of the manufacturers prefer double walled configuration as the cooling efficiency is maximum and so the furnace can be designed for very high temperatures (1400°C). The basic disadvantage in this design is the repairing of any water leak developed in the inner vacuum chamber. This is dangerous, as one cc of water leaking in a vacuum chamber at 10^{-5} Torr produces nearly 108 litres (i.e. 100 million litres) of vapour, contributing heavy unwanted load on high vacuum pumps. The contamination due to water vapour and other species can be monitored using a residual gas analyser (RGA) connected with a valve to the vacuum furnace chamber.

HOT ZONE FOR COLD WALLED FURNACES

The primary criterion for the hot zone of vacuum furnace (See Fig. 1) is that the entire volume of the work piece should experience the same temperature. The important parameters on which the thermal uniformity of the hot zone depends are size, shape and location of the heating elements, rate of heating, the type of insulation/shields used etc. In general, the hot zone of the furnace consists of suitable heating elements, thermal insulation/radiation shields to conserve the heat and ceramics for electrical/thermal insulation.

Heating Elements: Kanthal is not recommended for temperatures above 900°C in a vacuum, as its electrical characteristics change in course of time due to chromium losses. Molybdenum provides the high power density required for vacuum furnaces. However above 1400°C, the discharge voltage is 40V, and so the cross-sectional area of the rod/strip has to be increased which in turn imposes constraints on the formability. Hence, for operations above 1400°C molybdenum is not preferred. Besides, after a few heats, grain growth occurs which will be sufficient to cause the material to become very brittle, thereby seriously limiting its ability to withstand any thermal shock due to which frequent replacement is required.

For temperatures between 1400-1800°C, tungsten/tantalum is preferred due to its capability to withstand thermal shock. However, fabrication difficulties and higher initial costs are significant points to be considered. With the availability of high-quality graphite, graphite elements have been widely used up to 2000°C. The advantages of graphite heating elements are Low initial cost, no change in resistance at high temperatures, high hot strength, ability to withstand reasonable mechanical shocks and accidental high-temperature air breaks and ease of fabrication of the hot zone due to its availability in the forms of thin sheets, strips and cloth. However, the user has to ensure that the heating elements do not come in contact with the job, as carbon can diffuse into base metal interstitially. If carbon contamination is not tolerable even in ppm level, these elements are not recommended.

Depending on the uniformity of temperature required the heating elements are located on either on two sides, four sides or six sides. For zone trimming, the heating elements are located on all six sides. However, power coupling is adjusted depending on the size, shape and uniformity of temperature required, generally, this configuration is followed in brazing furnaces.

Insulation/Shields: The efficiency of the furnace depends on the way in which the heat is conserved. The main mode of heat loss in any furnace is through radiation and hence designing radiation shields/insulation plays an important role in the overall design of the furnace. The essential requirement is the use of highly polished metallic sheets (with low emissivity) as shields. Depending on the operating temperature and the shield materials, the number of shields needed may vary. The common materials widely used for shields are stainless steel, molybdenum and tantalum. Of these molybdenum and tantalum have very low emissivities in comparison to stainless steel and hence minimize heat losses. Thus, for high temperature applications above 800°C, four polished stainless steel sheets are used. For temperatures up to 1600°C, six shields, consisting of a combination of SS + Mo, are used. Graphite felt can also be used as the insulating material in place of shields where carbon contamination is not critical.

Induction heating: Induction heating is characterised by excellent control over alloy composition because of the stirring action generated by eddy currents. Hence it is preferred for alloy melting and refining processes. Induction stirring homogenises the melt as well as brings the reactants to the melt vacuum interface so that the reactions can proceed rapidly. Induction is also used for applications like sintering, brazing, annealing etc, where temperature accuracy on the component need not be so accurate. With the development of medium frequency generators using thyristor techniques, it has become possible to design vacuum furnaces having induction coils located inside the cold walled furnace. The frequency of these generators is in the range of 0.5 to 10 KHz. The induction coils are fabricated out of conventional copper tubes which are water cooled using softened water. If needed, magnetic shunts can be used to prevent induction leakage.

PROCESS INSTRUMENTATION FOR VACUUM FURNACES

Today, microprocessor based temperature programmers/controllers, wherein it is possible to preset heating rates, holding time, cooling rates etc., are available. Temperature Recorder/Over temperature protection devices are used when multiple thermocouples are used for recording the temperature at different locations of the job. Indicating lights corresponding to different on conditions display the status of the furnace operation. In addition, alarms and fault indication lights are also to be provided. It is advisable to keep a helium- Leak detector as an essential accessory for trouble shooting and leak rate measurement.

Safety interlocks linking furnace operation with water flow, overheating and valve closing are essential to ensure that proper sequential operations are followed. This helps in increasing the life and preventing the frequent breakdown of the furnace and its subsystems.

Thermocouples for temperature measurement in vacuum furnaces are to be chosen on the basis of (a) useful temperature range, (b) sensitivity, and (c) speed of response. Metals and alloys with high vapor pressures should be avoided where elevated temperatures and bake-out are scheduled. The range of emfs produced by most conventional couples in use is up to about $50\mu\text{V}/^\circ\text{C}$. The speed of response is largely determined by the size of wire used for the two metals, and is greater with finer wires than with larger sizes. Platinum and platinum-rhodium alloy couples are expensive but can be used at temperature up to 1500°C in air. Chromel-Alumel thermocouples are widely used in industrial and laboratory equipment because of their uniformity, corrosion resistance, sensitivity, and relatively low cost (compared to platinum). Chromel-Alumel thermocouples can be used between -200 and $+1260^\circ\text{C}$ in the air or non-reducing environments. Copper-Constantan junctions can be used in the range -260 to $+350^\circ\text{C}$, the upper value being set by the rapid oxidation of copper at higher temperatures.

HEAT TRANSFER IN VACUUM FURNACE SYSTEMS

Above approximately 10 Torr, the heat transfer through gas inside a relatively small chamber is dominated by convection (bulk motion of gas). Between 1 to 10^{-3} torr the heat transfer is through gas conduction which is a linear function of pressure (hence applied in thermal conductivity gauges). In high vacuum conditions (Below 10^{-4} Torr) the heat transfer is mainly due to radiation and to some extent by solid conduction through support structures. It is to be mentioned here that if two solid pieces are in just apparent contact in a vacuum chamber the heat transfer is very poor, as the real area of contact between two rigid bodies is usually only 0.1% of the apparent area. Heat is transferred only through a few touching high points forces must be used. Even then, the heat transfer by conduction will be limited to the small areas of contact created near the clamping bolts.

In view of the above facts, we can calculate the temperature rise of the job in a vacuum furnace due to resistive heating from surrounding heating elements, based on radiation formula.

$$Q_{12} = \delta_{12} A_1 (T_1^4 - T_2^4)$$

$$\text{where } \delta_{12} = C_b / (1/E_1 + A_1/A_2 (1/E_2 - 1))$$

where C_b = radiation coefficient of the black body i.e. 5.7×10^{-11} KW/(m^2T^4)

E_1, E_2 = emissivities of 1st and 2nd shields.

A_1, A_2 = Areas of the 1st and 2nd shields

T_1, T_2 = Temperatures of the 1st and 2nd shields.

As the radiation between two surfaces is proportional to the difference in fourth power of temperature, the heat flux in the initial period to the job from a heating element (reached fast to the equilibrium, say 800°C, due to resistive heating) is very high. Hence if we want more or less linear slow increase in job temperature, it is very important to raise the temperature of the heating elements in steps and allow the job to reach that set limit. For heating in several steps using suitable temperature controllers, we can apply radiation formula piecewise taking the necessary temperature limits. Once heat flux is known, the temperature rise can be calculated using the physical properties of the job namely specific heat (more or less a constant value in high temperature range) and mass. For calculating heat flux due to support solid structures, one can use fourier equation as given below, However, in high temperature region for most of the metals thermal conductivity does not change much and can be taken as constant.

$$Q = A/L K(T)dT$$

CONCLUSIONS

The importance of using vacuum environment in large vacuum furnaces is increasing to process metals and alloys at high temperatures. The technical details are explained in this paper, highlighting vacuum and heat transfer aspects.

ACKNOWLEDGMENTS

The authors would like to acknowledge Mr P Subba Rao for his help in preparing the manuscript.

REFERENCES

- [1] Vacuum metallurgy by A. Chowdhury, Publisher: ASM International, 1990.
- [2] Vacuum technology: practical heat treating and brazing by Roger Fabian, ASM international, 1993
- [3] Vacuum science and technology – by VV Rao, TB Ghosh and KL Chopra, Allied Publishers, 1998

Preparation of Manuscripts

1. Manuscripts should be sent in MS Word and pdf format.
2. Text should be 12 pt Times New Roman, double-spaced, left justified, A4 sized paper with wide margin.
3. All pages should be numbered consecutively, beginning with page 1, the title page.
4. Tables and figures should be numbered serially. Figures should have legends if applicable.
5. Tables and figures will be placed near their first mention in the text; all tables and figures must be referred to in the manuscript.
6. The following information must be included:
 - ❖ Title of the article;
 - ❖ Name(s) and initial(s) of author(s)
 - ❖ Affiliation(s) of author(s);
 - ❖ Name, address, telephone, mobile number and e-mail address of the corresponding author.
 - ❖ **Abstract:** Each article should include a brief abstract of 250 words, that should highlight the objectives, methods, results, and conclusions of the paper.
 - ❖ **Keywords:** To identify the subjects under which the article may be indexed, 6-10 key words should be provided.
 - ❖ **References:** In the text, references to the literature should be presented within square bracket indicating the reference number [1]
 - ❖ **Paper:**

[1] J. Singh, A. Kumar: Investigation of structural, morphological and electrochemical properties of mesoporous $\text{La}_2\text{CuCoO}_6$ rods fabricated by facile hydrothermal route. *Int. J. Miner. Metall. Mater.* 27: 987–995, 2020
 - ❖ **Book:**

[2] J.D. Verhoeven: Fundamentals of physical metallurgy, 1st Edition, New York: Wiley, New York, pp. 55-61, 1975
 - ❖ **Online document**

[3] Cory Mitchell: Fractal Indicator Definition and Applications. Technical analysis basic education. Available via <https://www.investopedia.com/terms/f/fractal.asp>, Retrieved 3 August 2020
 - ❖ **Illustrations :** These include photographs, drawings and line art includes graphs, flowcharts, diagrams etc which can be reproduced without losing any clarity. Figure legends or captions should follow the order in which they appear in the manuscript, be numbered with Arabic numerals and should not contain a text repeated. The preferred file formats for images and line art are TIF/TIFF and JPG. For good image quality, scanned black & white photographs should be provided as 300 ppi TIFF files and line art should be provided as 600 ppi TIFF files.
 - ❖ **Color Figures :** The authors should accept the obligation of bearing the expenses of colour images in the printed version of the journal while no charge is required for their appearance in the electronic version of the journal. Colour illustrations should be provided as scanned TIFF files at a minimum of 300 ppi with a 24-bit colour depth.
 - ❖ **Mathematical Equations :** Mathematical equations, suitably numbered, should be inserted in the text through "Equation editor" of MS word as per the example

$$P(e) = \frac{1}{2} \left[1 - \exp\left(-\frac{K}{2\sqrt{2}}\right) \right] \dots\dots\dots(\text{Eq 1})$$

- ❖ Symbols, Abbreviations, Units, etc.: It is mandatory to define the symbols and acronyms at first mention within the text and also in titles and abstracts. The authors are requested to follow internationally accepted rules for nomenclature, abbreviations, symbols and units.
- ❖ **Computer Code:** Pseudo algorithms, as presented below, with appropriate reference should be submitted.
 - ❖ **Title** : To compute power spectral density and corresponding frequency
 - Input** : Time domain data X(t)
 - Output** : P
 - Read the signal X(t)
 - Crop the signal and get the length N
 - Supply sampling frequency, f_s
 - Do fast Fourier transformation of the signal

$$X_k = \text{fft}(X(1:N), f_s);$$
 - Compute power spectral density and corresponding frequency by

$$P = X_k \cdot \text{conj}(X_k) / N;$$

$$f = \text{fs} * (1:N) / N;$$

NML PUBLICATIONS

CSIR-National Metallurgical Laboratory (NML) has recently published the following Scientific & Technical books. The year of publication and the price fixed has been shown in the parenthesis respectively. The request for procurement of publication is to be made to the Director, CSIR-National Metallurgical Laboratory, Jamshedpur - 831 007, India (e-mail : director@nmlindia.org) along with the Bank Draft in Favour of Director, NML Jamshedpur, payable at State Bank of India, NML Branch (Code No. 3329) Jamshedpur, India.

1. Electronic Waste (Eds. R. Singh, A. Das, K.K. Bhattacharyya and N.G. Goswami)	(2010)	(Rs. 950/-, US \$100)
2. Remaining Life Assessment of Aged Components in Thermal Power Plants and Petrochemical Industries (Eds. A.K. Ray, S. Chaudhuri, N.G. Goswami and R.N. Ghosh)	(2008)	(Rs. 950/-, US \$100)
3. Agglomeration and Characterization of Iron Bearing Raw Materials (Eds. D. Bandyopadhyay, M.C. Goswami, N.G. Goswami and G.K. Mandal)	(2008)	(Rs. 800/-, US \$100)
4. Extraction of Non-ferrous Metals and their Recycling (Eds. R.K. Jana, Abhilash and N.G. Goswami)	(2008)	(Rs. 800/-, US \$100)
5. Proceedings of the National Workshop on Coal Processing in Hindi (Eds. : R. Singh, R.P. Bhagat, (Eds. : R. Singh, R.P. Bhagat, Avimanyu Das, K.K. Bhattacharyya, P.N. Mishra and N.G. Goswami)	(2007)	(Rs. 700/-, US \$90)
6. Processing of Iron ore (Eds. R. Singh, Avimanyu Das and N.G. Goswami)	(2007)	(Rs. 800/-, US \$100)
7. Special Metal Casting and Forming Processes (Eds. K.L. Sahoo, G.K. Mandal, N.G. Goswami and Sukomal Ghosh)	(2007)	(Rs. 800/-, US \$100)
8. Advanced Gravity Separation (Eds. : R. Singh, A. Das and N.G. Goswami)	(2007)	(Rs. 600/-, US\$ 70)
9. Synergy of R&D and Marketing (Eds. : P.N. Chaudhury, N.V. Satyanarayana, A.Seshu Kumar & N.G. Goswami)	(2003)	(Rs. 800/-, US\$ 100)
10. Metallurgy in India - A retrospective (Eds. : P. Ramachandra Rao and N.G. Goswami)	(2001)	(Rs. 1500/-, US\$110)
11. Recent Trends in Structural Integrity Assessment (Eds. : V.R. Ranaganath, S. Tarafder and Aruna Bahadur)	(2001)	(Rs. 850/-, US\$ 100)
12. Processing of Fines (Eds. : P. Bhattacharyya, R. Singh & N.G. Goswami)	(2000)	(Rs. 1200/-, US\$ 115)
13. Non Ferrous Metals and Materials (Eds. : D.M. Chakrabarti, R.K. Jana, V. Kumar B.D. Pandey & N.G. Goswami)	(2000)	(Rs. 700/-, US\$ 100)
14. Non Ferrous Extractive Metallurgy in the New Millennium (Eds. : P. Ramachandra Rao, Rakesh Kumar, S. Srikanth & N.G. Goswami)	(1999)	(Rs. 1200/-, US\$ 115)
15. Environmental & Waste Management in Iron & Steel Industries (Eds. : A. Bandyopadhyay, N.G. Goswami & P. Ramachandra Rao)	(1999)	(Rs. 800/-, US\$ 100)
16. Fly Ash Utilisation for Value Added Products (Eds. : B. Chatterjee, K.K. Singh & N.G. Goswami)	(1999)	(Rs. 600/-, US\$ 80)
17. Materials Characterization Techniques — Principles and Applications (Eds. : G. Sridhar, S. Ghosh Chowdhury & N.G. Goswami)	(1999)	(Rs. 1000/-, US\$ 110)
18. Environmental & Waste Management in Non-Ferrous Industries (Eds. : A. Bandyopadhyay, N.G. Goswami & P. Ramachandra Rao)	(1998)	(Rs. 700/-, US\$ 100)
19. Modern Methods of Chemical Analysis for Minerals, Metals Refractory Materials & Environmental Pollutants (Eds. : S.C. Srivastava, K.K. Padhi, L.P. Pandey & N.G. Goswami)	(1998)	(Rs. 300/-, US\$ 30)
20. Composite Materials (Eds. : R.R. Bhat, S. Ghosh & C.S.S. Krishna Rao)	(1998)	(Rs. 500/-, US\$ 70)
21. Nondestructive Evaluation of Materials (Eds. : A. Mitra, N. Parida, D.K. Bhattacharya & N.G. Goswami)	(1997)	(Rs. 800/-, US\$ 100)
22. Ferro-Alloys Industries in the Liberalised Economy (Eds. : A.K. Vaish, S.D. Singh, N.G. Goswami & P. Ramachandra Rao)	(1997)	(Rs. 600/-, US\$ 80)
23. Processing of Fines (Eds. : P. Bhattacharyya, R. Singh, K.V. Rao and N.G. Goswami)	(1997)	(Rs. 1000/-, US\$ 110)
24. Failure Analysis (Eds. : S.R. Singh, N. Parida, D.K. Bhattacharya & N.G. Goswami)	(1997)	(Rs. 800/-, US\$ 100)
25. Computer Applications in Materials & Metallurgical Engineering (Eds. : R.N. Ghosh, S. Tarafder & N.G. Goswami)	(1996)	(Rs. 700/-, US\$ 100)
26. Transport Phenomena in Metallurgical Processes (Eds. : S. Prakash & P. Ramachandra Rao)	(1996)	(Rs. 850/-, US\$ 100)
27. Environmental & Waste Management in Metallurgical Industries (Eds. : A. Bandyopadhyay, N.G. Goswami & P. Ramachandra Rao)	(1996)	(Rs. 700/-, US\$ 100)
28. Modern Methods of Chemical Analysis for Minerals, Metals, Refractory Materials & Ferro-alloys (Eds. : S.C. Srivastava, L.P. Pandey & N.G. Goswami)	(1996)	(Rs. 650/-, US\$ 70)
29. Boiler Corrosion (Eds. : I. Chatteraj, I. Singh, S.K. Narang, D.D.N. Singh & N.G. Goswami)	(1995)	(Rs. 500/-, US\$ 70)
30. Alternative Charge Materials for Electric Arc & Induction Furnaces (Eds. : K.N. Gupta, K.K. Mishra, K.K. Singh, A.K. Vaish, S.D. Singh, A. Bandyopadhyay & N.G. Goswami)	(1994)	(Rs. 500/-, US\$ 70)

ISSN 0974-1267 (Online)

ISSN 0972-4257 (Print)



Published by

CSIR-National Metallurgical Laboratory

Jamshedpur - 831007, Jharkhand, India

www.nmlindia.org