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Electrochemical characterization of nano zinc ferrite coating on carbon steel by pulsed laser deposition

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ABSTRACT

The structural materials in water-cooled nuclear power reactors are mainly iron and nickel based alloys. Continuous operation of these nuclear reactors at high temperature and high pressure aqueous environment leads to the formation of various oxides due to corrosion of the structural materials. Since the corrosion process is mainly interfacial and electrochemical in nature, the interfaces formed between the alloys/oxide and oxide/solution plays a crucial role in deciding the overall corrosion resistance of the structural materials. In this context, efforts are being made to modify the size of the oxide particles (surface morphology) to nano size and/or change the composition of the oxides by the addition of an external metal ion (Metal Ion Passivation) both of which are likely to improve the adherence and protectiveness of the interfacial film. In this paper, attempts were made to form an additional nano zinc ferrite ($ZnFe_2O_4$) coating by pulsed laser deposition technique on the magnetite (Fe_3O_4) layer formed on carbon steel for improving the corrosion resistance of the base metal. The $ZnFe_2O_4$ was synthesized by co-precipitation method and its phase purity was confirmed by Raman Spectroscopy and X-Ray Diffraction studies. 10 mm diameter ferrite targets were prepared and a thin film of $ZnFe_2O_4$ was deposited on the Fe_3O_4 coated carbon steel specimens using pulsed laser deposition technique. Characterization of this deposited ferrite film was carried out by Raman spectroscopy, X-Ray Diffraction, X-ray Photoelectron Spectroscopy and Secondary Electron Microscopy. The semiconductor properties of these oxides were investigated by Mott-Schottky plots. The mechanism of corrosion resistance/improvement in the deposited layer was studied by electrochemical techniques and the results are presented in detail in this paper.

1. Introduction

Carbon Steel (CS) is one of the alloys used as out of core structural material in the primary heat transport (PHT) system of Indian Pressurized Heavy Water Reactors (PHWRs). During the operation of water-cooled nuclear reactors, corrosion products are generated due to the interaction of high temperature coolant with the structural materials of the PHT system. Some of these corrosion products are carried to the reactor core with coolant where they get neutron activated and thereby become activated corrosion products. Subsequently, they get redispersed to out of core locations where the oxide present over the surfaces acts as the host lattice for the incorporation of activated corrosion products. Some of these nuclides are long lived and are of concern in the activity transport process which results in the radiation field build-up in the reactor coolant circuit. Apart from going for better corrosion resistant materials, efforts are also being made to apply a kind of adherent coating on the existing alloy surfaces, to modify the size of the oxide particles (surface morphology) to nano-size and/or change the composition of the oxides by the addition of an external metal ion (Metal Ion Passivation, MIP) all of which are likely to improve the adherence and protectiveness of the interfacial film. Several methods like sol–gel [1], metal ion implantation [2] and physical vapor deposition [3] are used for developing coatings on alloys. In PHWRs, though the corrosion rate of carbon steel is reduced by forming a passive magnetite (Fe_3O_4) layer, the radioactivity transport problems necessitate further reduction in the metal ion release. Though the role of MIP in reducing corrosion is not very clear, in boiling water reactors it was observed that the addition of zinc ion (Zn^{2+}) at ppb level reduced the release of corrosion products into the coolant by modifying the oxide layer over the structural materials [4]. Reduction in corrosion product release of carbon steel was observed due to magnesium ion passivation in simulated

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PHWR - PHT coolant conditions [5]. To further minimize the corrosion rates of these structural materials, these surface oxides could be made into nano-size which would also improve the adherence and protectiveness of the interfacial film. Nano-materials are unique because of their smaller size and hence a higher surface-to-volume ratio. The use of nano-particles for anticorrosion coatings has achieved significant attention and importance [6]. Several researchers have shown nano-particles to perform better and qualify them as a better alternative for anticorrosion coatings in composites and polymers [7–8]. Various methods such as co-precipitation [9], pulsed laser deposition (PLD) [10–12], electrodeposition [13], spin-coating [14], sol–gel [15–16], spray pyrolysis [17] and chemical vapor deposition [18] have been already employed to prepare nanostructured thin films and nanoparticles. In this paper, attempts were made to form an additional nano zinc ferrite ($ZnFe_2O_4$) coating on Fe_3O_4 by PLD technique and its effectiveness for further improvement of the corrosion resistance of carbon steel has been tested. The oxides formed were characterized by Raman spectroscopy, X-Ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) measurements. Mott–Schottky method has been widely used to study and characterize the semiconducting properties of the passive films on iron alloys [19–20]. The oxides formed are semiconducting in nature; hence Mott-Schottky analysis was carried out in aqueous electrolyte with pH of 10.3, increase in pH was achieved by Lithium Hydroxide (LiOH), to understand the electronic properties of these oxides. The corrosion resistance and the stability of these oxides in LiOH medium were studied by electrochemical methods such as Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Anodic Polarization (PDAP).

2. Experimental procedure

2.1. Formation of Fe_3O_4 on carbon steel

The carbon steel specimens of size 1 cm × 1 cm (composition in weight %: C-0.16, Mn-0.85, Si-0.35, Cr < 0.3, Ni < 0.14 and balance iron) were polished with different grades of silicon carbide (SiC) papers ranging from 80 to 1200 grit. The specimens were further polished up to 1 μm to have a smooth diamond mirror finish. Then, they were washed with distilled water, degreased with acetone, dried in air and immediately exposed to LiOH medium containing 1.5 ppm of Li^+ ion with pH 10.3 and conductivity 43 μS/cm and a thin Fe_3O_4 coating was developed on carbon steel specimen in a pre-conditioned autoclave by keeping the specimen for 96 h at 250 °C. The autoclave solution was deaerated by purging Argon gas before heating and 0.3 ml of Hydrazine was added in 500 ml LiOH solution to scavenge the remaining Oxygen.

All the solutions were prepared using analytical grade chemicals. The LiOH solution was prepared by passing suitable amounts of Lithium Carbonate ($LiCO_3$) solution through regenerated anion (OH^-) resin column with an optimized flow rate of 15 mL/min to achieve complete conversion to LiOH. Fresh LiOH was prepared for each electrochemical experiment and the pH was in the range 10.2–10.4 and conductivity was in the range 40–47 μS/cm.

2.2. Synthesis and deposition of $ZnFe_2O_4$ on carbon steel

2.2.1. Synthesis of $ZnFe_2O_4$ powder

Zinc (II) Sulphate ($ZnSO_4 \cdot 7H_2O$) and Ammonium Iron (II) Sulphate ($NH_4Fe\ (SO_4)_2$) were used as starting chemicals. Synthesis was carried out in open atmosphere, in a beaker. The stoichiometric amounts of salts were dissolved in 500 ml double distilled water. NaOH was added to the above solution by continuously stirring and the precipitate started forming till the pH reached 10.5. The precipitate was allowed to settle and then it was washed till the pH attained ~8.0. Then, the precipitate was kept in an oven at 110 °C till all the water evaporated to form a hard solid mass. This hard solid mass was crushed to powder using mortar and pestle and then transferred to a crucible. This powder was heated in a furnace at 650 °C for 6 h. The weight of the powder was taken. The formation of stoichiometric $ZnFe_2O_4$ in the powder was confirmed by Raman spectroscopy and powder XRD.

2.2.2. Pulsed laser deposition of $ZnFe_2O_4$

PLD technique was used to deposit $ZnFe_2O_4$ on Fe_3O_4 coated carbon steel. The $ZnFe_2O_4$ powder was compacted into a 10 mm diameter circular pellet of 3 mm thickness by applying a pressure of 3.18×10^8 Pascal and then sintered at 1000 °C for 24 h and cooled to room temperature to obtain the target required for deposition. The experimental density of sintered target was calculated to be 4.14 g/cm^3 against the theoretical density of 5.1 g/cm^3. The achieved density was ~80% of theoretical value required for the PLD target preparation. Thin film of $ZnFe_2O_4$ was deposited by using ND-YAG laser (M/S Quanta System, Italy) operating at 1064 nm with pulse width and energy of 5 ns and 500 mJ respectively. The beam was focused to 2 mm on a rotating target. The substrate was kept at a distance 5 cm from the rotating target. The substrate temperature was 400 °C and the oxygen pressure was 2 Pascal. 18,000 laser shots were given and the deposited ferrite film thickness was 0.464 μm as measured by stylus profilometer. Since Fe_3O_4 and $ZnFe_2O_4$ have common spinel structure with almost similar lattice parameters, $ZnFe_2O_4$ coating formed over Fe_3O_4 film was found to be adherent and smooth. The deposited film was characterized by Raman, XRD, XPS and SEM.

2.3. Characterization of deposited oxide

2.3.1. Laser Raman spectroscopic analysis

Raman spectra were recorded on the sample using HORIBA Jobin Yvon HR 800 spectrometer, France with 514.5 nm Ar^+ ion laser from 100 to 1500 cm^{-1}. Laser power was optimized to 0.5 mW on the sample surface and acquisition was carried out for 30 s using a 100× objective lens and 1800 grooves/mm grating.

2.3.2. X-ray diffraction analysis

XRD studies were carried out using STOE diffractometer in the Bragg-Brentano geometry on these films with Cu k_α as the incident radiation ($\lambda = 1.54056$ Å) in the range of $2\theta = 10$–90 with a step size of 0.05°. The crystallite size of oxides was determined from the Scherrer formula given by Eq. (2),

$$L = K\lambda/\beta\cos\theta \tag{2}$$

where L is the average particle size, K is the Scherrer constant related to the shape and index (*hkl*) of crystals [21], λ is the wavelength of incident radiation and β is obtained from the Warren and Biscoe equation given by Eq. (3) [22],

$$\beta^2 = B^2 - b^2 \tag{3}$$

where B and b are the full width at half maxima (FWHM) for the sample under investigation and a standard sample respectively.

2.3.3. Scanning electron microscopic analysis

The surface morphology and the elemental composition of the oxide sample were characterized by FE-SEM (Helios Nanolab 600i) operating at 20 keV electron beam energy. Energy Dispersive X-ray Spectroscopy (EDAX) analysis of the samples was carried out using 20 keV beam energy and the microscope was fitted with an X-max 80 mm^2 EDAX detector from Oxford Instruments.

2.3.4. X-ray photoelectron spectroscopic analysis

Oxidation states of Fe and Zn in coatings were identified with the help of XPS technique (Model VG ESCALAB MK 200×, UK). Al k_α X-ray (energy 1486.6 eV) source was used for photoemission and the spectra were collected by a 150 mm hemispherical analyzer at 20 eV pass