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Micro-Raman Spectroscopic Studies for Evaluation of Self-Healing Property of Corrosion Protection Coatings on Al and Mg alloys

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ABSTRACT

Aluminum and Magnesium alloys have wide range of applications in aerospace and automobile industries due to their high strength-to-weight ratio. However, during their service, components made from these materials get corroded. Paints are generally used to render barrier type protection to the surfaces. Hexavalent chromium-based conversion coatings/primers are commonly applied prior to paint deposition. Due to their carcinogenic effect, chromate conversion coatings have been globally banned and hence, researchers are seriously developing chrome-free, self-healing conversion coatings. Sol-gel derived coatings are being evaluated, since they possess the necessary qualities to be a potential replacement to Cr^{6+}-based coatings. In this context, cationic inhibitor loaded nanoclays were dispersed into an organic-inorganic hybrid silica sol-gel matrix. Coatings were deposited onto aluminum alloy A356.0 and magnesium alloy AZ91 using dip coating technique and thermal cured at 130^{o}C. An artificial scribe was made on the coated substrate and immersed into 3.5 % NaCl solution for

120 h. Micro-Raman spectroscopic studies were carried out on these samples to study the localized self-healing property of the coatings. The results obtained from micro-Raman studies

could confirm the inhibitor release on the scribed area and formation of a passive layer could be observed, thereby confirming self-healing effect. Nanoclay based sol coated substrates were found to be very promising for long term corrosion protection.

Keywords: Self-healing, Nanoclay, Al and Mg alloys, Micro-Raman spectroscopy

INTRODUCTION

Aluminium and magnesium alloys, owing to their low density and high specific strength of about 1/3 and 1/4 that of steel respectively, are being extensively used in automotive and aerospace industries [1]. This can significantly decrease the weight of automobiles without sacrificing structural strength. However, during their exposure to atmospheric conditions under various applications, they are prone to corrosion due to properties such as poor corrosion resistance, high oxidation potential, etc. This affects on overall economy of the applications.

Various approaches have been tried till date to reduce or prevent the influence of corrosion; one of the most popular is use of hexavalent chromium-based conversion coatings. However, due to carcinogenic effect of aforementioned coatings, they have been banned globally [2,3]. Hence, researchers have invented several other ways to develop chrome free self-healing coatings which will provide prolonged corrosion protection [4-6]. One of the most promising ways to provide corrosion protection is sol-gel process due to its major advantages such as crack-free thick coatings with controlled composition and morphology can be obtained at low curing temperatures. Sol-gel process provides an appropriate route to combine inorganic and organic components as a homogeneous hybrid by which organic and inorganic components can be chemically linked or just physically blended. An important factor which enhances compatibility in hybrid materials is the formation of covalent bond between organic polymers and inorganic components [7]

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Sol-gel coatings can be applied to metal substrates by simple techniques such as dip coating, spray coating and spin coating. However, even if a small defect in the coating is present or developed during service, the corrosive medium is easily able to reach the metal surface, which enhances the corrosion rate. Therefore, development of coatings with an ability to provide prolonged barrier protection and active corrosion protection (self-healing ability) at the corroded site is the need of the hour. In this context, generally two approaches have been employed; either introducing the corrosion inhibiting material directly into the coating matrix [8,9] or encapsulating it in micro/nanocontainers, such as carbon nanotubes, nanoporous metal oxide particles, polymeric capsules to facilitate their controlled release [4,10]. However, direct introduction of the inhibitor in the coating causes its degradation and deactivation of inhibitor [11,12]. As an alternative, encapsulating inhibiting material into nanocontainers for controlled release is considered to be an effective strategy for achieving corrosion protection with good

barrier properties and self-healing ability. However, for large scale application of nanocontainer based self-healing coatings on the substrate, there are limitations with respect to costs. Hence, cost effective alternatives for these nanocontainers could be the use of naturally available clays. Naturally occurring organic clay minerals such as halloysite and montmorillonite have

advantages such as being non-toxic, cheap, easily available and eco-friendly. Past investigations have revealed that, 1–5 wt % addition of clays into coating formulations enhance

the anticorrosive, barrier, thermal and mechanical properties[13,15,16]. Halloysite nanoclays are double layered aluminosilicate with concentric tubular structure, chemically similar to kaolin. They have concentric positively and negatively charged inner and outer layers of Al_2O_3 and SiO_2, respectively. Moreover, they have the capacity to entrap wide range of active materials such as drug particles, catalysts, inhibitors, marine biocides, etc. within the lumen and void spaces in the multilayered aluminosilicate structure [13]. The use of HNTs as nanocontainers for the encapsulation of cationic inhibitors like Ce^{3+}, Zr^{4+} as self-healing corrosion protection was first time reported in our earlier studies [14-16]. In the event of damage occurring in the coating, Ce^{3+} and Zr^{4+}, are released from the lumen of HNTs, when they simultaneously act as catalysts for polymerization of epoxy groups present in the sol matrix in addition to forming passive layers of their corresponding oxides, thereby providing a self-healing effect.

Self-healing mechanism is a localized phenomenon, which occurs in presence of self-healing material, i.e., monomers/corrosion inhibitors and only during the onset of damage to the coating, which exposes the substrate to corrosive medium. Mostly, self-healing ability of coatings can be evaluated by localized electrochemical tests such as scanning vibrating electrode technique (SVET), scanning electrochemical microscopy (SECM), scanning Kelvin probe (SKP) etc. To the best of our knowledge, micro-Raman spectroscopy for evaluating the self-healing property has not been commonly employed. However, for the first time, the mechanism of self-healing action was confirmed by micro-Raman spectroscopic analysis in our previous studies on pure aluminum [16].

Hence, the objective of the present investigation is to study the mechanism of self-healing ability of coatings with inhibitor loaded HNTs dispersed in hybrid organic-inorganic matrix sol using micro-Raman analysis on aluminum alloy A356.0 and magnesium alloy AZ91D.

EXPERIMENTAL PROCEDURE

MATERIALS

3-Glycidoxypropyltrimethoxysilane (GPTMS, Gelest Inc., USA, 98%) and Tetraethoxysilane (TEOS, Gelest Inc., 98%) were used as starting materials for synthesis of the matrix (MAT) sol with HCl as catalyst. Halloysite nanotubes, naturally available clay obtained from Sigma Aldrich, USA was used as nanocontainer for loading of corrosion inhibitors. Cerium nitrate hexahydrate (Loba Chemie, India, 99.9%) and zirconium n-propoxide (Gelest Inc., USA, 70% in propanol)

were used as corrosion inhibitors and catalyst, respectively. Methacrylic acid (MAA, ABCR GmbH & Co. KG, Germany, 99% stabilized with 100–250 ppm hydroquinone or 4-methoxy phenol), an acrylic monomer also loaded inside HNTs. Urea, formaldehyde, and resorcinol

procured from Fisher Scientific, India, were used for synthesis of polymeric microcapsules for capping the ends of the loaded nanotubes.

Pure aluminum, aluminum alloy A356.0 and magnesium alloy AZ91D substrates were in sizes of 100 mm x 100 mm x 1 mm, 100 mm x 100 mm x 3 mm and 25 mm x 20 mm x 5 mm, respectively. The composition of the substrates in wt % were found to be 99.5% Al for pure aluminum, Si-16.0, Mg-0.3, Ti-0.3, Fe-0.2, Sn-0.44, Pb-0.15 and the rest Al. for A356.0 and Mg-89.46, Al-9.14, Si-0.13, Zn-0.86, Mn-0.30, Cu-0.09, Fe-0.01 and Ni-0.01 for AZ91D. Both Al and Mg alloy substrates were polished with 1000 grit emery sheet followed by repeated degreasing with acetone for 30 min and finally drying in air.

SOL SYNTHESIS AND COATING DEPOSITION

Halloysite nanotubes were etched as per procedure described in [14-16], followed by washing with deionized water and drying in order to get enlarged lumen diameter to incorporate more amount of inhibitors. Ce^{3+} and Zr^{4+} were taken in molar ratio of 1:32 and loaded into the enlarged lumen of HNTs in vacuum desiccator. The hybrid organic-inorganic matrix sol was prepared by hydrolysis of GPTMS and TEOS in molar ratio of 3:5:1 with HCl as catalyst as reported in our earlier studies [14-16]. The polymeric microcapsules which were used as capping agents to stopper the ends of the HNTs were synthesized using the method reported by White et al. [17,18] and processed using the method reported in [19]. The self-healing (SH) sol comprises 2 wt% inhibitor loaded halloysite nanotubes stoppered with polymeric microcapsules dispersed in hybrid matrix sol. The polymeric microcapsules acted as a capping agent for the halloysite nanotubes.

Coatings were generated on pure Al, Al and Mg alloys using dip coating technique at withdrawal speed of 1 mm/s followed by curing at 130° C for 1 h in hot air oven.

CHARACTERIZATION:

Micro-Raman spectroscopic analysis was carried out for uncoated and SH sol coated pure aluminum, A356.0 and AZ91D substrates, in the scribed region, after immersion in 3.5 wt % NaCl for 120 h. The data was obtained using Horiba Jobin Yvon- LABRAM HR-800 Raman spectrometer with Ar ion laser of 514 nm as the light source over the scan range of 100-2000 cm^{-1}.

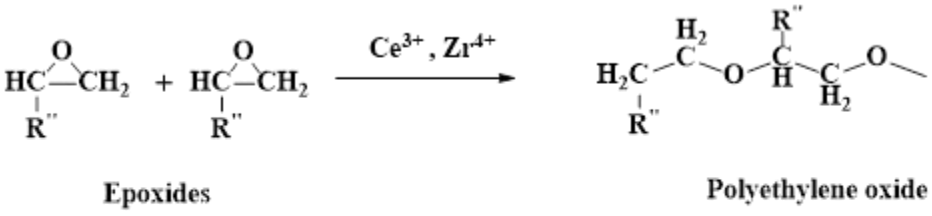
RESULTS AND DISCUSSION

MICRO-RAMAN SPECTROSCOPIC ANALYSIS:

Pure aluminum:

Micro-Raman spectroscopic studies were initially carried out on pure aluminum substrates, for confirming of mechanism of self-healing action. These studies were further extended on to aluminum alloy A356.0 and magnesium alloy AZ91D. Micro-Raman spectra were recorded for all the substrates in the scribed region after exposure to 3.5 wt % NaCl solution for 120 h

The micro-Raman spectrum of bare aluminum substrate after immersion (not shown here) has exhibited only one broad peak at 860 cm^{-1}, that corresponds to alumina. This indicated the formation of corrosion product (alumina) on exposure to the corrosive medium. The spectrum for the SH-coated substrate after immersion as depicted in Fig. 1, showed peaks at 235 cm^{-1} corresponding to zirconia [20], and at 480 cm^{-1} corresponding to ceria. A sharp, highly intense peak at 1440 cm^{-1}, was observed which corresponds to δ (CH2) stretching frequency of polyethylene oxide (PEO). The presence of the peaks clearly indicated the formation of polymer (as per eqn 1) and respective oxides of the cerium and zirconium (i.e., ceria and zirconia) in the scribed area. This confirmed that the inhibitors have got released into the scratch from the surrounding area to self-heal the damage (scribe) by (a) polymerization of epoxy group in the matrix to form a thick layer and (b) by formation of a passive CeO_2 and ZrO_2 layers.



Eqn (1)

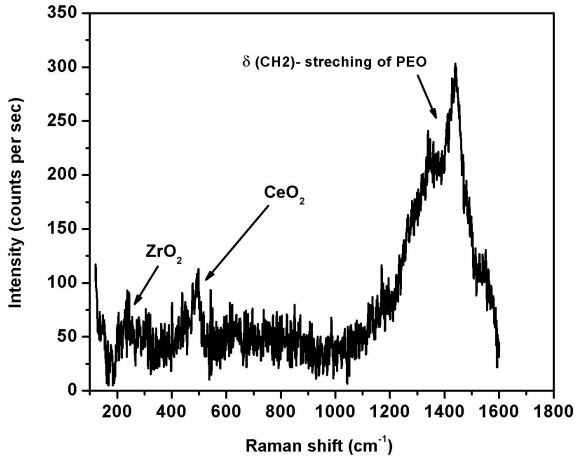


Figure 1: Micro-Raman spectrum of SH coated pure aluminum, in the scratch region after exposure to corrosive medium for 120 h

Aluminum alloy A356.0:

The uncoated A356.0 alloy substrate, after exposure to corrosive medium has not shown any prominent crystalline peaks in the scribed area. The micro-Raman spectrum for SH coated A356.0 after immersion as given in Fig. 2, has shown a sharp, highly intense peak at 521 cm^{-1} corresponding to crystalline silicon belonging to alloying element Si in A356.0 alloy, and peaks at 232 cm^{-1} and 294 cm^{-1} correspond to zirconia [20]. Peaks corresponding for ceria and PEO were not seen in this spectrum due to the domination of crystalline silicon present in this alloy. This indicated that Zr^{4+} has got released into the scratch from locations in the vicinity of the scratch to self-heal the damage by formation of passive ZrO_2 layer.

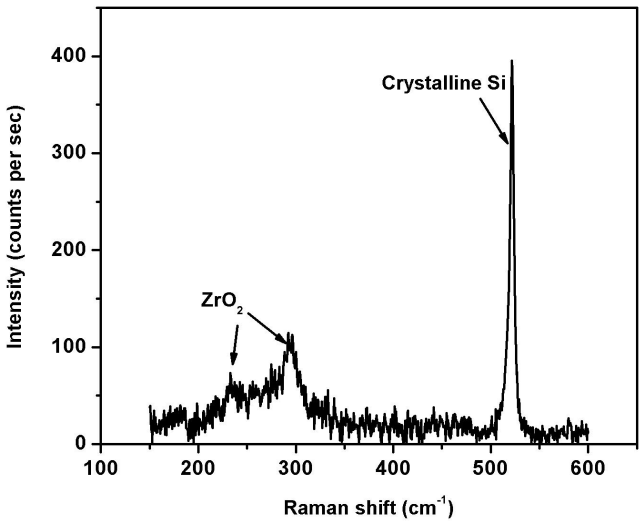


Figure 2: Micro-Raman spectrum of SH coated A356.0 substrate in the scribed area, after exposure to 3. 5 wt % NaCl for 120 h

Magnesium alloy AZ91D:

The micro-Raman spectrum for the SH sol coated AZ91D substrate after 120 h exposure to 3.5% NaCl is shown in Fig. 3. Peaks at 254 cm^{-1} and 554 cm^{-1} were observed, which corresponded to zirconia [20] phase, indicating the release of Zr^{4+} in to the scribed area and showing self-healing ability forming passive layer of ZrO_2. In this case, there were no other prominent peaks observed for other alloying elements.

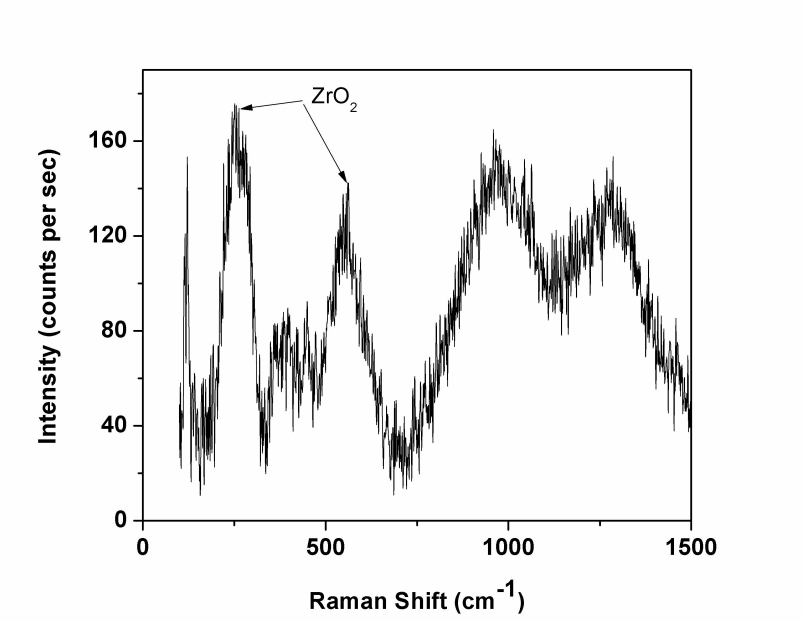


Figure 3: Micro-Raman spectrum of SH coated AZ91D substrate in the scribed area, after exposure to 3. 5 wt % NaCl for 120 h.

CONCLUSIONS

- For the first time in literature, micro-Raman spectroscopy analysis was used to confirm the self-healing mechanism in addition to conventional localized electrochemical tests.

- In case of pure aluminum, a) the release of cationic inhibitors into the scratch region; b) their catalytic behavior for polymerization of the monomers and c) inhibitor behavior in forming the passive layers of ceria and zirconia was clearly indicated by micro-Raman spectroscopic analysis, thereby confirming the self-healing activity

- In case of A356.0 and AZ91D alloys, the formation of passive layer of zirconia has been observed

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