Available online <u>www.jocpr.com</u>

Journal of Chemical and Pharmaceutical Research, 2012, 4(1):440-449



Research Article

ISSN : 0975-7384 CODEN(USA) : JCPRC5

Electrodeposition of Zn–Graphite nanoparticles composite and their characterization

H. B. Muralidhara^{1,*}, Y. Arthoba Nayaka², J. Balasubramanyam¹, K. Yogesh Kumar¹, H. Hanumanthappa¹, M.S. Veena¹

¹Centre for Nanosciences, K.S. Institute of Technology, Visvesvaraya Technological University, Bangalore, India ²Department of PG Studies and Research in Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, India

ABSTRACT

The Zn–Graphite nanoparticles (Zn-Gnps) composite nano-coatings were prepared by electrochemical deposition method and pure Zn coating was also prepared as a comparison. Salt-spray test and electrochemical measurements indicated nanocrystalline Zn-Gnps composite coatings have better corrosion resistance than the zinc coatings deposited from a simple acid zincate bath. The surface morphology of the zinc deposits were studied by scanning electron microscopy (SEM). The preferred orientation and average size of the Zn-Gnps coatings were studied by X-ray diffraction analysis. The experimental results indicated that the addition of Gnps into an electrolytic bath leads to a nanocrystalline deposition with the grain-sizes varying from 20-26 nm.

Key words: Composite coating, Corrosion, Electrochemical method, Graphite nanoparticles.

INTRODUCTION

Composite coatings consist of a metal or metal alloy matrix containing a dispersed phase of non-metallic particles. Such coatings have been developed for improved material properties with regard to corrosion stability, wear resistance, friction protection, self-lubrication, high temperature stability, electrical contacts and improved catalytic activity.

The metals providing the matrix are mainly nickel, cobalt, copper, silver, zinc or gold. The list of particles embedded into the metal matrix ranges from carbides (e.g. SiC, WC, TiC), oxides (e.g. Al_2O_3 , TiO₂) to lubricants (e.g. MoS₂, graphite, hexagonal BN) and polymer particles such as PTFE [1-6].

Among the various nanocompounds Gnps have attracted especially close attention. Gnps, with sp² hybridization, has got good electrical conductivity and low coefficient of friction, high wear resistance and superior lubricating property.

Composite coatings based on Zn are finding increased interest in surface technology and corrosion protection. Potential fields of application are improved corrosion and wear resistance of Zn composite layers with extended life time [7-11].

H. B. Muralidhara et al

A large number of techniques such as sol-gel, CVD, sputtering, self-assembled monolayers, liquid phase deposition, atomic layer deposition etc have been utilized for the fabrication of composite films. The development of new low-cost processes, which are of environmental interest, for the deposition of such films is of considerable interest. Electrodeposition technique using aqueous solutions provide an attractive approach to meeting these needs [12-16].

The composite coating could be used on steel components as a substitute for pure Zn coating to enhance their service life by controlling or preventing the formation of white zinc rust. Zn-Gnps composite coatings are economically viable than other composite coatings [17, 18]. In the present paper Gnps, embedded in a Zn matrix, are generated by electrochemical technique have been selected. Corrosion behavior of pure Zn coating and nano composite coating was studied.

EXPERIMENTAL SECTION

Electrochemical generation of graphite nanoparticles

Gnps were electrochemically generated by anodic stripping of graphite electrode in 2M sulphuric acid using a dc current of 0.25 A in an single compartment cell. The obtained analyte containing Gnps were centrifuge at 4000 rpm for 20 min. The Gnps settled at the bottom were washed with distilled water and acetone. These Gnps were heated to 750°C in a digitally controlled furnace for 4 h. The perfect single crystalline Gnps with about 15 nm diameter and 200 nm length have been synthesized. Fig.1 and 2 shows the X-ray diffraction pattern and SEM image of electrochemically synthesized Gnps.



Fig. 1. X-Ray diffraction pattern of electrochemically synthesized Gnps



Fig. 2. SEM photomicrograph of electrochemically synthesized Gnps

H. B. Muralidhara et al

Plating process

Functional zinc composite coatings on sheet steel have been electroplated from a low acidic zinc electrolyte of conventional composition 200 g/l ZnSO₄.6H₂O, 40 g/l Na₂SO₄, 40 g/l H₃BO₃, 4 g/l Gnps and 2 g/l Cetyl trimethyl ammonium bromide (CTAB) as cationic surfactant. CTAB improves the hydrophilic ability of the Gnps. The bath solution was continuously agitated using mechanical stirrer with 1000 rpm. The experimental parameters essential for a homogeneous particle incorporation into the zinc matrix were determined and optimized.

Analytical reagents and distilled water was used to prepare the plating bath solution. The cathode was mild steel and anode was pure zinc (99.99%). The mild steel prior to the plating experiments, was polished mechanically, degreased with vapours of trichloroethylene in degreasing plant and finally washed with distilled water and dried. The anode was activated each time by dipping in 10% HCl for few seconds and was washed with distilled water. The bath temperature was held at 298 K and pH of the bath solution was 3. The cathodic current density was controlled at 3 Adm⁻² using digital dc power supply.

Scanning Electron Microscope Analysis

The surface morphology of the deposit was recorded by using a scanning electron microscope, (JSM-5500 LV, SEM, JEOL, JAPAN). SEM images of the coated specimens before and after corrosion tests in 3.5 wt.% NaCl solution were used to assess their corrosion performance.

Weight-loss measurements

The corrosion behavior of Zn coated samples with and without Gnps were studied by weight-loss measurements at 298 K [13]. The exposed area of the specimen was 3×4 cm². The coating thickness was in the range of 15-20 μ m. The corrosive medium was 3.5 wt.% NaCl. The coated samples were immersed in NaCl solution and the plates were weighed periodically for every 24 h in 15 days. The loss in weight so obtained was used to determine the corrosion velocity.

Electrochemical measurements

The effect of composite coating on corrosion resistance of the zinc deposits was studied in 3.5 wt.% NaCl solution by galvanostatic polarization method. A three compartment cell was used for the polarization study. The coated steel specimens of Zn and Zn-Gnps were used as the working electrode (WE) and masked with lacquer to expose 1 cm² area. A platinum foil of 0.5 cm² was used as the counter electrode (CE) with saturated calomel as reference electrode (RE). The working electrode was kept it in the 3.5 wt.% NaCl electrolyte for 20 min to establish a stable rest potential. The WE was polarized from the rest potential (OCP) against SCE. The cathodic polarisation was carried out for both pure Zn and Zn-Gnps composite coatings.

Open circuit potential (OCP) measurements

The variation of OCP of steel samples with and without Gnps were measured as a function of exposure time at 298 K. The exposed area of the specimen was 3×4 cm². The coating thickness was in the range of 15-20 μ m. The corrosive medium was 3.5 wt.% NaCl. The corrosion potentials were measured in every 30 min interval for a period of 15 h.

Salt spray tests

Salt spray test as per ASTM B 117 was carried out in a salt spray chamber [12]. The steel samples of 5×5 cm² area were taken for this study. The deposited plates were subjected to a continuous spray of 5 wt.% sodium chloride vapours. The specimens were observed visually for an interval of every 24 h and the duration of the time for the formation of the white rust was noted.

X-ray diffraction analysis

Powder X-ray diffraction (Philips TW 3710) study was carried out using nickel-filtered Cu- K_{α} radiation to determine the lattice parameter, crystallographic texture and approximate average grain size of the deposit. The grain-sizes of the coating were measured through the Scherrer's equation [13].

Surface morphology results

RESULTS AND DISCUSSION

The surface morphology of the nano structured film is studied by scanning electron micrograph images. From these images various shapes and sizes of the particles are observed. Fig. 3(a) is the SEM photomicrograph of the pure Zn

deposit shows coarse-grained deposit having irregular crystal size. SEM photomicrograph of deposit obtained from the Zn-Gnps shows perfect crystal growth, uniform arrangement of crystals, refinement in crystal size and hence more corrosion resistance is as shown in Fig. 3(b).



Fig. 3. SEM photomicrographs of the deposits obtained at 3 Adm⁻²: (a) Pure Zn coating (b) Zn-Gnps composite coating

In Fig. 4, the images of corrosion morphology of pure Zn and composite Zn showed after weight-loss measurements in 3.5 wt.% NaCl solution for 15 days. The large number of corrosion spots and its products were noticed on the SEM image of pure Zn coated sample [Fig. 4(a)]. Very little corrosion was observed on the Zn coated surface in presence of the Gnps [Fig. 4(b)].



Fig. 4. SEM photomicrographs of the deposits after 15 days weight loss measurements: (a) Pure Zn coating (b) Zn-Gnps composite coating

Fig. 5(a) and 5(b) represents the SEM images of pure Zn and Zn in presence of Gnps respectively, after cathodic polarization in 3.5 wt.% NaCl solution.

SEM images of coated steel articles of coating thicknesses 7.5 and 15 μ m after potentiodynamic polarization in 3.5 wt.% NaCl solution is shown in the Fig. 6 [(a), (b), (c), (d)] respectively. The SEM studies indicated that the deposit in presence of Gnps showed higher corrosion resistance similar to the results obtained by weight-loss method and electrochemical measurements.



Fig. 5. SEM images for two samples after cathodic polarization: (a) Pure Zn coating (b) Zn-Gnps composite coating.



Fig. 6. SEM images of coating thickness 7.5 µm and 15 µm after potentiodynamic Polarization: (a, c) Pure Zn coating (b, d) Zn-Gnps composite coating.

Electrochemical measurement results

Fig. 7 shows the cathodic polarization behaviour of pure Zn coated and Zn-Gnps in 3.5 wt.% NaCl solution. It was observed that the potential of the composite coated sample was more negative than that of pure Zn coated sample at all current densities. This indicates that addition of Gnps in to the Zn coating surface increases the corrosion resistance.



Fig. 7. Variation of cathode polarization curves in 3.5 wt.% NaCl solution: (a) Pure Zn coating (b) Zn-Gnps composite coating

Fig. 8 shows corrosion rate of coated specimens in 3.5 wt.% NaCl solution. In both the cases, corrosion rate slightly increased in the beginning and remains constant after 100 h of immersion. The corrosion rate was higher for pure Zn coating when compared that of composite Zn coating. Further it inferred that Zn-Gnps improves the corrosion resistance property.



Fig. 8. Variation of cathode polarization curves in 3.5 wt.% NaCl solution: (a) Pure Zn coating (b) Zn-Gnps composite coating

The corrosion potential values of the steel plates in 3.5 wt.% NaCl solution were monitored as a function of immersion time. Fig. 9 compares the corrosion potential values of the steel plates with time. At the onset of corrosion, Gnps incorporated Zn coatings exhibited lower cathodic potential values than that of the pure Zn coating. Gnps present on the coating surface reduces the active corrosion sites and it makes the coating more corrosion resistant. This indicated a good chemical stability of the deposit from optimum bath.



Fig. 9. Variation of the corrosion potential (E_{corr}) with the immersion time for zinc coated samples in 3.5 wt.% NaCl solution: (a) Pure Zn coating (b) Zn-Gnps composite

Corrosion resistance results

Fig. 10 and 11 present the effect of Gnps on Zn deposits of 7.5 and 15 μ m thicknesses with respect to corrosion behavior in 3.5 wt.% NaCl solution using galvanostatic polarization technique and the values are given in Table 1. From the figures it can be seen that the i_{corr} values for Zn deposits were considerably lowered when plated in presence of Gnps, irrespective of the deposit thicknesses. Hence the deposit obtained in presence of Gnps bath showed maximum corrosion resistance.



Fig. 10. Potentiodynamic polarization curve for coating thickness 7.5 μm in 3.5 wt.% NaCl solution: (a) Pure Zn coating (b) Zn-Gnps composite coating.



Fig. 11. Potentiodynamic polarization curve for coating thickness 15 µm in 3.5 wt.% NaCl solution: (a) Pure Zn coating (b) Zn-Gnps composite coating.

Table- 1	1: Ga	lvanostatic	polarization	in 3.5	wt.%]	NaCl solution
----------	-------	-------------	--------------	--------	--------	---------------

Bath system	Deposit thickness (µm)	E _{corr} (-mV vs SCE)	i_{corr} ($\mu A \ cm^{-2}$)
Pure Zn coating	7.5	1025	17.7
Zn-Gnps composite coating	15	1045	12.5
Pure Zn coating	7.5	1090	31.6
Zn-Gnps composite coating	15	1100	10

Salt-spray test results

The industrial method of testing the corrosion behavior of Zn-plated object was salt spray test. The test was conducted by spraying 5 wt.% NaCl solution. The fog of droplets accumulated on the surface of the articles facilitates the corrosion resulting in Zn salts called white rust. The number of hours for the formation of white rust was the indication of the corrosion resistance. The higher corrosion resistance delays the production of white rust. In the present case pure Zn deposit produced white rust after 24 h and the Zn deposit in presence Gnps produced white rust after 96 h. This test confirms the enhancement of corrosion of Zn coatings in presence of the Gnps.

Adhesion, porosity results

Standard bend test was used to measure both adherence and ductility of Zn deposits. Mild steel panels of 1mm thick (1 x 10 cm² area) were electroplated with Zn to a different thicknesses (5-20 μ m). The samples were subjected to bending through 180⁰. No crack or peel off in the deposit was noticed even after 180° bending. This indicated good adherence and ductility of Zn deposit on steel.

The porous nature of the coated specimens were examined by adopting porosity test. The specimens after plating were subjected to bright dip in 1% nitric acid followed by water wash. The porosity of the deposit was assessed by ferroxyl test [13]. This test indicated porous free nature of the deposit.

H. B. Muralidhara et al

X-ray diffraction results

Fig. 12 shows the XRD pattern of pure Zn coating and Fig. 13 shows the XRD pattern of Zn-Gnps composite coating. Crystalline size was determined from the full wave at half maximum (FWHM) of the X-ray peaks present on the diffractogram and corresponding results are presented in Table 2. The X-ray diffraction pattern of the coating containing Gnps showed a broadening of the diffraction peaks. This broadening is due to refinement of microstructure.



Fig. 12. X-Ray diffraction pattern of the pure zinc deposit



Fig. 13. X-Ray diffraction pattern of the Zn-Gnps composite coating

System	Pure Zn coating	Zn-Gnps composite coating	Pure Gnps	
	35.7	26.22		
Average crystal size (nm)	44.8	25.70	14	
	76.97	22.57		

Table- 2: Parameters derived from XRD data

CONCLUSION

A simple electrochemical method for the synthesis of Gnps is investigated and successfully codeposited with Zn. The distribution of Gnps is found to be uniform throught the Zn matrix giving a crystalline and increased corrosive resistance property for the deposits. Zn-Gnps composite coating possesses higher corrosion resistance when compared to pure Zn coating. The results of weight loss measurement, salt spray test and electrochemical methods were matching with each other. The porosity test indicated that inclusion Gnps in the Zn deposit reduces the porous nature of pure Zn coating. The Gnps inclusion in the Zn deposit shift the potential towards a more negative and leads to more uniform crystallization. SEM results confirms that more uniform nanocrysalline Zn deposit was obtained with the addition of Gnps in to an acid zincate electrolyte. XRD data also confirmed that addition Gnps in to an acid sulphate bath results refinement in the crystalline size. Over all, inclusion of Gnps in the Zn deposit brings down the corrosion rate and thus reducing the metal loss.

Acknowledgements

The authors are grateful to Visvesvaraya Technological University, Belgaum for providing financial support under research grant scheme (Project No. VTU/Aca./2010-11/A-9/11353). The authors wish to thank K.S. Institute of Technology, Bangalore for providing laboratory facility to bring about this research work.

REFERENCES

- [1] X Xia; I Zhitomirsky; JR McDermid, J. Mater. Process. Technol, 2009, 209, 2632-2640.
- [2] TJ Tuaweri; GD Wilcox, Surf. Coat. Technol, 2006, 200, 5921-5930.
- [3] SMA Shibli; VS Dilimon; SP Antony; R Manu, Surf. Coat. Technol, 2006, 200, 4791-4796.
- [4] BM Praveen; TV Venkatesha, Appl. Surf. Sci, 2008, 254, 2418-2424.
- [5] XH Chen; CS Chen; HN Xiao; FQ Cheng; G Zhang; GJ Yi, Surf. Coat. Technol, 2005, 191, 351-356.
- [6] BM Praveen; TV Venkatesha; Y Arthoba Naik; K Prashantha, Surf. Coat. Technol, 2007, 201, 5836-5842.
- [7] HY Zheng; MZ An; JF Lu, Appl. Surf. Sci, 2008, 254, 1644-1650.

[8] Y Wang; S Lim; JL Luo; ZH Xu, Wear, 2006, 260, 976-983.

- [9] C Muller; M Sarret; M Benballa, Surf. Coat. Technol, 2002, 162, 49-53.
- [10] S Hashimoto; M Abe, Corrosion Science, 1994, 36, 21-25.
- [11] CN Panagopoulos; EP Georgiou; AG Gavras, Surf. Coat. Technol, 2009, 204, 37-41.

[12] HB Muralidhara; Y Arthoba Naik, Bull. Mater. Sci, 2008, 31, 585-591.

[13] HB Muralidhara; Y. Arthoba Naik, Surf. Coat. Technol, 2008, 202, 3403-3412.

[14] HB Muralidhara; J Balasubramanyam; Y Arthoba Naik; K Yogesh Kumar; H. Hanumanthappa; MS Veena, J. Chem. Pharm. Res, **2011**, 3, 433-449.

- [15] HB Muralidhara; Y Arthoba Naik; HP Sachin; TV Venkatesha, Indian J Chem Technol. 2008, 15, 155-162.
- [16] K Vathsala; TV Venkatesha; BM Praveen; KO Nayana, Engineering, 2010, 2, 580-584.
- [17] M Ghorbani; M Mazaheri; K Khangholi; Y Khazari, Surf. Coat. Technol, 2001, 148, 71-76.
- [18] A Afshar; M Ghorbani; M Mazaheri, Surf. Coat. Technol, 2004, 187, 293-299.