

Thermal Sprayed Alumina Nanocoatings for Corrosion Prevention

Nitu Bhatnagar

Abstract—The demand to minimize maintenance of metallic structures while optimizing performance requires protective coatings that can last long and respond well to the very corrosive conditions in marine environment. Nanocoatings represent an engineering solution to prevent corrosion of the structural parts of ships which are inaccessible and are exposed to marine environment. Carbon nanofibers (CNF's) have been of great interest due to their extraordinary mechanical and electronic properties but for the problems related to their uniform dispersion. In this work, the critical issue of uniform dispersion is solved by growing dispersed CNF's on Al_2O_3 powder particles in situ by the catalytic chemical vapor deposition (CCVD) technique which is successfully thermal sprayed to obtain uniform coating on the steel substrate. This paper also discusses the results pertaining to contact angle value which increases with the alumina nanocoating on the steel surface.

Keywords—Nanocoatings, marine environment, carbon nano fiber, Al_2O_3 , Catalytic Chemical Vapor Deposition (CCVD), Thermal spraying.

I. INTRODUCTION

MOST of the maritime steel structures are always exposed to extreme marine environment such as moisture, salt water, oxygen, ultraviolet light, and high temperature which present severe and costly corrosion problems for these structures and provide a severe test of durability of the materials used. The need to minimize maintenance of metallic structures while optimizing performance requires protective coatings which can last long and respond well to the corrosive conditions in marine environment by providing a barrier between the steel and the corrosive environment. Therefore, nanocoatings represent an engineering solution to protect the structural parts of ships which are inaccessible and are exposed to aggressive marine environment. These coatings act as a barrier to avoid the transportation of corrosive species, such as chlorine and hydroxyl ions, water, oxygen, pollutants and pigments, which otherwise have high affinity to react with the surfaces when they interact with the interfaces of the materials [1-3]. Nanocoatings are coatings that are produced by usage of some component at nanoscale to obtain desired properties [4]. Nanoparticles / fillers find application in wear-resistant, erosion-resistant and corrosion resistant [5]. Because

of greater surface activity of nano particles, they can absorb more resins compared to conventional pigments and thus reduce the free space between the pigment and the resin. Thus, nanoparticles increase the transport path of corrosive species and enhance the protective properties and performance.

Many research dedicated to coating systems containing nanofillers such as epoxy/ TiO_2 , Latex/silica [6, 7] show that the nanofillers offer advantages such as improvement in scratch, abrasion, heat, radiation and swelling resistance and decrease in water permeability and increase in hardness, weatherability, modulus [8] compared to conventional organic coatings containing microfillers. The analysis of epoxy-clay nanocomposite coating by Bagherzadeh et al [9] had shown that incorporating nanoclay particles into organic coatings improves anti-corrosive properties of coating. In the past few years, a lot of research has been done on the use of carbon nano tube and carbon nano fiber, whose unimaginable high strength make them potential reinforcement for the composite materials. Besides, the nanosized carbon tubes also provide superior dispersion strengthening to the composite structures [10]. CNT and graphene based nanocomposite coatings were developed against UV degradation and corrosion [11]. It was observed that a small weight percentage of carbon nanotubes and graphene in the polymeric coating increase the film resistance against UV light. At 0% MWCNT coating, percent reduction between 0 and 8 days of UV exposure is at lower level, and then significantly increased. At 16 days of UV exposure and 80 days of salt fog, nearly 23% of film is removed from the surface. However, at 1% and 2% MWCNT coatings, the film thickness reductions are 13% and 7%, respectively, at the same UV and corrosion test conditions. This indicates that in the presence of nanoscale inclusion, film thickness also stays more stable, which may be another reason of receiving higher performance against UV light and salt fog.

It has also been reported by Bob Gemmer [12] that nanocoating significantly not only reduces erosion and corrosion, but also helps in extending the life cycle of the airfoils; thereby reducing the need for costly replacements or repair. Thus, it is expected that the use of these nanoparticles in coating will also prove to be effective in extending the life cycle of these maritime structures; thereby reducing the need for replacements or repair which is a costly affair.

Balani et al. [13] have grown 0.5 wt.% CNTs on Al_2O_3 in situ by the catalytic chemical vapor deposition (CCVD) technique. They were successfully plasma sprayed to obtain a 400 μm thick coating on the steel substrate which resulted in

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an enhancement in hardness and fracture toughness of the plasma-sprayed coating. Hardness increased from 806 to 906 VH and fracture toughness from 4.14 ± 0.22 to 4.62 ± 0.27 MPa m^{-1/2}.

Carbon nanofibers possess an important technological thrust in the development of nanofiller based polymer nanocomposite materials as it aims to provide solutions to many vexing problems in many high technological applications at a relatively low cost compared with carbon nanotubes (CNT) counterpart. The same level of improvement in important properties may be achieved with less than 5wt% loading of a well dispersed nanoscale filler as compared to conventional microscale filler based polymer composites with over 30 wt% loading [14]. It has been reported [15] that the lap shear tensile strength of atmospheric pressure plasma treated adhesive joint increases from 8 MPa to 10 MPa, 12.5 MPa and 12 MPa respectively with dispersion of 1%, 2% and 3% CNF in to the epoxy adhesive, resulting in considerable improvement in the adhesion properties due to dispersion of CNF in to the epoxy adhesive.

Nanofibres exhibit properties between those of nanotubes and carbon fibers. Average diameter of carbon nano fiber ranges from 150nm- 200nm and length varies from 50-200 nm. Mechanical properties is about 20 times stronger than steel with melting point of 1300 °C, and density of 1.3 gm/cm³. Addition rates in compounds range from 3-8% by weight.

II. METHODOLOGY

In line with the results that had been achieved with carbon nano tube, carbon nano fiber is also expected to increase the fracture toughness and hardness of the substrate with its exceptional low weight and excellent mechanical properties. Moreover with the use of CVD technique, it is easier to use carbon nano fibers directly without further purification unless the catalyst particle is required to be removed.

Researchers have reported that nanoparticles are grown onto Al₂O₃ surface using the catalytic chemical vapor deposition (CCVD) process as shown in figure 1. The CVD method requires catalyst nanoparticles (usually Fe, Co, Ni), a carbon feedstock (hydrocarbon or CO) and heat. This helps in creating a metallurgical bond between Al₂O₃ powder particles and nanoparticles.

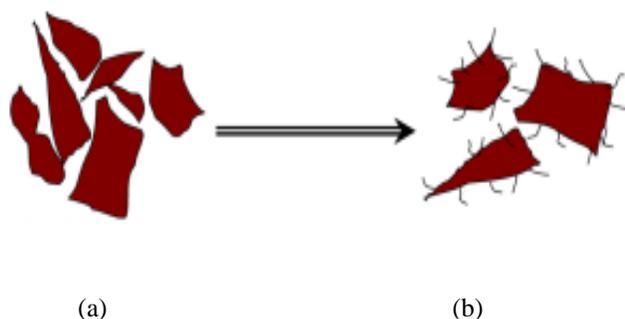


Fig.1. (a) Micron sized Al₂O₃ (b) CCVD grown CNF

A simple CVD method involves passing a hydrocarbon vapor through a tubular reactor in which a catalyst material is present at a temperature of (300–1200 °C) to decompose the hydrocarbon as shown in Figure 2. Nanoparticles grow on the catalyst in the reactor, which are collected upon cooling the system to room temperature.

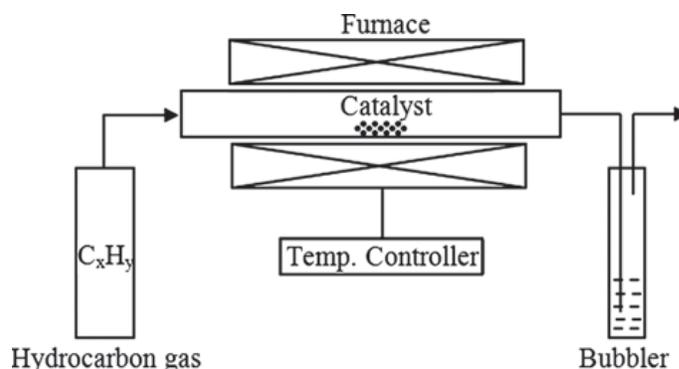


Fig.2. Schema of simple CVD method [16]

To apply such protective coatings a highly versatile, low cost technique is selected that can be performed with a minimum in equipment investment and maintenance, and that does not require overly sophisticated training for the operator. Such a technique has been found in thermal spraying [17] which offers an effective and economic way to make the coating without affecting any other properties of the component. Thermal spray coatings are produced by rapidly heating the feedstock material in a hot gaseous medium and simultaneously projecting it at a high velocity onto a prepared surface where it builds up to produce the desired coating [18]. Fig. 3 shows the typical thermal spray process and coating.

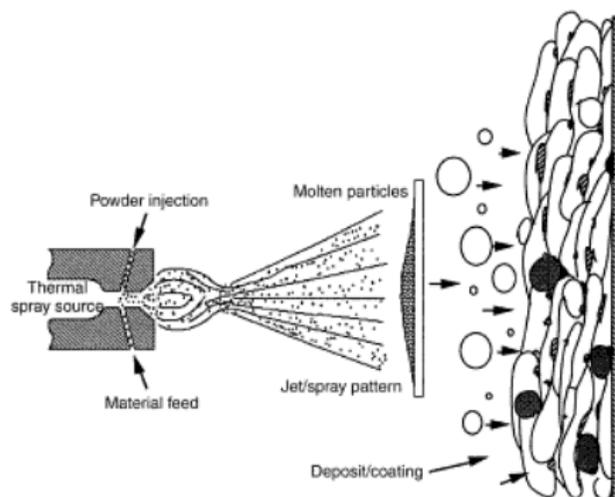


Fig. 3. Typical thermal spray process and coating [19]

Prior to spraying the material, grit blasting of the steel substrate is done to help improve the mechanical interlocking between the substrate and the coating.

After the thermal spraying has been done, the different characterization techniques will be used to analyze the corrosion behavior of the steel surface before and after application of alumina coating on the steel surface. The initial findings on this coating in the form of contact angle measurement have been reported in the subsequent paragraph.

III. RESULT AND DISCUSSION

3.1 Surface Characterization

This paragraph demonstrates the use of contact angle measurement as a simple, fast, inexpensive and accessible tool for the study of surfaces with and without alumina nanocoating. It is observed that the contact angle (θ) on the steel surface without alumina nanocoating is 25° which increases to 62° after the alumina nanocoating is applied on the surface as shown in figures 4 (a) and 4(b).



Fig. 4 (a) Wetting of a steel surface by water before coating, $\theta = 25^\circ$

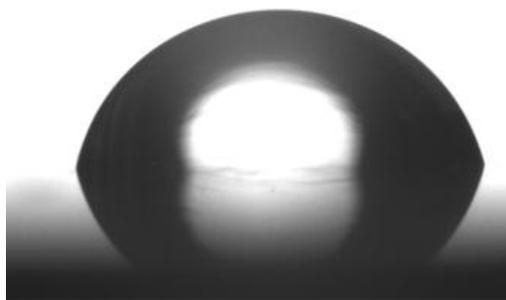


Fig. 4 (b) Wetting of a steel surface by water after coating, $\theta = 62^\circ$

This shows that the alumina naocoating was effective in imparting hydrophobic properties to the steel surface which is an important criterion to judge the corrosion behavior of a surface. The further studies will include tribological and electrochemical corrosion properties of Al_2O_3 /polymer nanocomposite coatings which can be studied by using micro-hardness test, single-pass scratch test, abrasive wear test, and finally electrochemical technique such as potentiodynamic polarization measurement [20]. The coatings containing Al_2O_3 is expected to show improvement in scratch and abrasive

resistance which is attributed to the dispersion hardening of Al_2O_3 particles.

IV. CONCLUSION

In this work, it has been envisaged that when CNF-reinforced Al_2O_3 particles grown by CCVD technique is thermally sprayed on a steel substrate it will provide a tough, durable, chemically and radiation resistant coating. From the contact angle measurement, it is clear that the nanocoating already helps in imparting hydrophobic characteristics to the surface. Further, this type of coating will help advance the service life and safety of the maritime structures. In addition, the novel coating process could be economic, environmental friendly, and easy to use compared to other methods currently employed for prevention of corrosion by the marine industry.

REFERENCES

- [1] Mahmud, G.A. "Increasing the coating resistance against UV degradation and corrosion using nanocomposite coating," MS Thesis, Wichita State University, 2009.
- [2] Rabek, J. R., Photodegradation of Polymer, New York: Springer, 1996.
- [3] Guillet, J. E., "Fundamental Processes in the UV degradation And Stabilization of Polymers," Pure Appl. Chem., Vol. 30, No. 1-2, 1972, pp. 135-144.
- [4] Gleiter, H., Nanostructured materials, Basic concepts & microstructure, Acta Materialia, Vol 48, Issue 1, pp1.2000.
- [5] Wilson, M., Kannangara, K., Nanotechnology-basic science and emerging technologies, Overseas press India pvt Ltd New Delhi.
- [6] Ng, C.B., Schadler, L.S., Siegel, R.W. Nanostruct. Material 12(1-4)(1999) 507.
- [7] Ng, C.B., ASH, B.J., Schadler, L.S., Advanced composites Lett. 10(3) (2001)101.
- [8] Sanchez, C., Ribot, F., proceedings of the first Eurobion work-shop on hybrid organic-inorganic materials, chimie de la matiere, France, 1993.
- [9] Bagherzadeh, M.R., Mahdavi, F., Preparation of epoxy -clay nanocomposite coating , Progress in Organic Coating, Vol-60 pp-117-120 ,issue 2, Sep-2007.
- [10] Laha, T., Agarwal, A., McKechnie, T., Seal, S., Synthesis and characterization of plasma spray formed carbon nanotube reinforced aluminum composite Materials Science and Engineering A 381 (2004) 249-258.
- [11] Asmatulu, R., UV Degradation Prevention on Fiber-Reinforced Composite Blades, Sustainable Energy Solutions, Wichita State University, 2010
- [12] Gemmer, B., <http://energy.gov/articles/innovative-nanocoatings-unlock-potential-major-energy-and-cost-savings-airline-industry>, 2012
- [13] Balani, K., Zhang, T., Karakoti, A., Li, W.Z., Seal, S., Agarwal, A., In situ carbon nanotube reinforcements in a plasma-sprayed aluminum oxide nanocomposite coating, Acta Materialia 56 (2008) 571-579
- [14] Barick, A. K.; Tripathy, D. K., Int. Conf. on Advances in Polym. Tech., India, pp. 75 - 78, 2010.
- [15] Bhatnagar, N., Effect of Nano Fillers on the Joint Strength of High Performance Polymeric Nanocomposite International Journal of Chemical, Environmental & Biological Sciences (IJCEBS) Volume 1, Issue 2 (2013) ISSN 2320-4087 (Online)
- [16] Kumar M. and Ando, Y., Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production Journal of Nanoscience and Nanotechnology, 10 (2010) 3739-3758.
- [17] Chatha, S.S., Sidhu, H.S., Sidhu, B.S., Journal of Minerals & Materials Characterization & Engineering, 11(6), (2012) 569-586.
- [18] Crawmer, D.E., In: Davis JR, editor. Hand book of thermal spray technology, ASM International, Materials Park, OH, USA; (2004) 43-46.
- [19] Zhang, G., Liao, H., Cherigui, M., Paulo, J., Davim, C., Coddet, Eur. Polym. J. 43 (2007) 1077-1082.

[20]Mathiazhagan, A.,Joseph, R., Nanotechnology-A New Prospective in Organic Coating -Review, International Journal of Chemical Engineering and Applications, 2 (2011).



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