Research Status and Progress of Nano Coatings for Steel Bridges

Juan Wen\textsuperscript{1*}, Zheng Li\textsuperscript{1}, Tao Hu\textsuperscript{1}, Cunfang Lu\textsuperscript{2*}, Quan Gong\textsuperscript{2}, Deng Wu\textsuperscript{2}, Jun Chen\textsuperscript{2}, Shaolin Zhang\textsuperscript{2}

\textsuperscript{1}Chongqing Cheng Tou Road and Bridge Administration Co.Ltd, Chongqing, 400060, China
\textsuperscript{2}School of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing, 400050, China

*Corresponding author’s e-mail: lucunfang@cqut.edu.cn

Abstract: The coating systems of steel bridges all over the world generally include primer, intermediate and top-coat. The performance of the coatings could be promoted drastically by adding the specific nano particles into the coatings. In this paper, the research status and progress of nano coatings for steel bridge were summarized. Previous research showed that graphene and nano scale Al\textsubscript{2}O\textsubscript{3} had significant effects on improving the adhesion performance and corrosion resistance performance of epoxy Zn-rich primer. Nano particles of ZnO, TiO\textsubscript{2} and SiO\textsubscript{2} could promote the weather resistance performance of top coatings, while nano-scale SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} substance could facilitate the mechanical properties of top coatings. Other nano-scale substance properties enrich the coating some further functions, such as self-cleaning, light storage, self-repair and so on.

1. Introduction
The development of anticorrosive technologies of steel bridge coatings in China underwent several stages. In the 1950s, the using life of steel bridges coating was only 2-3 years. From the late 1960s to the 1980s, red lead antirust primer and grey aluminum zinc alkyd topcoat were successively adopted, and the using time was improved to about 10 years. In the 1990s, coating system of epoxy zinc-rich antirust primer, cloud-iron epoxy intermediate and grey aluminum graphite alkyd topcoat were applied gradually, and the service life of the coating reached more than 15 years.

Nowadays, coating system of epoxy zinc-rich antirust primer, cloud-iron epoxy intermediate paint and fluorocarbon topcoat were extensive used on steel bridges. And the service time of the coating system could be prolonged to about 30 years. Coating systems commonly used in China and other countries were summarized in Table 1.

Table 1 Common coating system in the world

| Country | Primer                                      | Intermediate                        | Top-coat                                           |
|---------|---------------------------------------------|-------------------------------------|---------------------------------------------------|
| China   | Red lead primer, Epoxy zinc-rich            | Micaceous iron epoxy paint          | Polyurethane lacquer, Fluorocarbon                 |
|         | Red lead alkyd primer, Oil red lead paint   |                                     | Micaceous iron aluminum powder, Alkyd top-coat     |
| UK      | Zinc yellow phenolic primer, Zinc rich primer |                                     | Micaceous iron phenolic topcoat, Micaceous iron Polyurethane |

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd
2. Research status of nano coating

Compared with the traditional coatings, nano coatings have some outstanding advantages in the performance of adhesion force, anticorrosion, weather resistance, mechanical properties, self-cleaning and other functional properties.

2.1 Adhesive force Performance

There is still no agreement on the coating adhesion mechanism. The so far understanding of adhesion is that adhesion is caused by the combination of polar groups (such as carboxyl group and hydroxyl group) of the polymer in the coating film and polar groups on the surface of the steel matrix. Therefore, factors that reduce this polar bonding would result in a decrease in adhesion. Previous studies have shown that blistering, peeling and filamentous corrosion of organic coating all result from the failure of wet adhesion of coating [11-14]. Wet film theory holds that under the action of environmental humidity or water, water molecules penetrate into the interface between the coating and the substrate, breaking the bond between the coating and the substrate, resulting in a decrease in wet adhesion. After the restoration of drying, the water molecules on the interface escaped from the coating, and the combination between the coating and the substrate could be restored. The adhesion was still good, but its protective ability had been greatly damaged. In other words, when water is present in the coating, the failure process of wet adhesion has occurred before any macroscopic changes [15].

For epoxy zinc rich primers, the zinc dust protects the steel structure from corrosion by cathodic protection, physical shielding effect and self-healing and passivation of the film. Thus, the adhesion performance is the foundation of anticorrosion of the steel bridge especially for primers. Many sorts nano-scale oxide particles were sprayed on the surface of steel structure through arc spraying, industrial application showed that the adhesion of nano Al containing coating was improve by 40% [16]. When nano alumina sol was added as binder to prepare an anticorrosive coating, using for high-temperature refractory lining, the adhesion level of the coating increased to grade 0[17]. It was reported that Si-Al composite coating resin was synthesized by hydroxylation condensation polymerization with silica sol and methyl triethoxysilane (MTES) as the precursor and acetic acid as the catalyst and with nanoparticles of Al$_2$O$_3$ added. When m(Al$_2$O$_3$)/m(MTES) was 0.010, the adhesion of the Si-Al composite coating reached level 0 [18].

2.2 Property of the anticorrosive

Currently there is a growing interest in the application of graphene nano-anticorrosive coatings. By introducing the graphene into zinc-rich epoxy coatings, graphene nanosheets could enhance the conductivity of zinc particles and improve the utilization of zinc powders. Thus, the life of zinc-rich epoxy coating was prolonged. The experiments showed that when the graphene content was 2 wt% and the zinc content is 35wt %, the salt spray resistance test of the coating reached 1000h [19]. And recently, Ningbo institute of materials, Chinese Academy of Sciences had achieved mass production of the graphene based heavy anticorrosive coating [20]. The image of the graphene particles [21] and modified zinc rich primer were showed in Fig.1.

| Country    | Primer Type          | Top-coat Type              |
|------------|----------------------|----------------------------|
| France     | Red lead primer      | Micaceous iron topcoat     |
|            |                      | Aluminum powder phenolic   |
|            |                      | topcoat,                   |
|            |                      | Aluminum powder            |
|            |                      | Polyethylene top-coat      |
| United     | Zinc rich primer     | Epoxy                      |
| States     |                      | Polyurethane top-coat      |
|            |                      | Polyurethane top-coat      |
|            |                      | Fluorocarbon top-coat      |
| Japan      | Zinc rich primer, Red lead primer | Epoxy                  |
Besides the primers, graphene was also used in some top-coats. Previous investigation showed that when graphene, with 0.4-1 wt%, was added to polyurethane coating [22-23], alkyd resin coating [24], epoxy resin topcoat [25] and fluorocarbon [26], the anti-corrosion performance of the coatings were significantly improved. Except for the graphene material, some other nano-scale materials were also used to improve anti-corrosion resistance of coatings, include TiO$_2$, ZnO, SiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, CaCO$_3$, ZrO$_2$, Cr$_2$O$_3$, MnAl$_2$O$_4$, nano-polyaniline, layered clay, etc.

2.3 Property of weather resistance
Weather resistance performance of outdoor coatings was an important indicator especialy for top-coat of steel bridges. The phenomenon of aged coatings commonly were fade, color change, crack and strength decrease. Among various weather conditions, sunshine and rainfall were the main factors influencing the coating properties. Thus, particles with excellent optical performance, such as UV shielding effect, could be investigated as nano coating additives.

Elementis Company in U.S. [26] added some ZnO particle with an average size of 80nm into a general anti-UV coating, and the anti-UV property of the modified coatings was significantly improved. Foster company [27] in U. S. had synthesized a nano ZnO particle containing acrylic coatings, which had a better performance of weather resistance. Yang pei et al. [28] studied water-based exterior wall coating containing nano ZnO-CeO$_2$, and the results showed that its anti-UV aging performance was significantly improved, while its water resistance and alkaline properties were also improved.

Adding nano TiO$_2$ into the coating could also improve its UV resistance and aging resistance due to its special nano effect [29]. Polyurethane coating with nano TiO$_2$ particles prepared by Sabzi et al. [30] had an excellent UV aging resistance. Fu xinhe et al. [31] prepared polyurethane waterproof coating by modifying nano SiO$_2$, and its weather resistance was improved.

2.4 Mechanical performance
Particle size of coating filler could influence its rheology performance. Therefore, the construction performance of nano coatings was better than that of the ordinary coating. Due to the large specific surface area of the nanoparticles and the good interface adhesion between them and the organic resin, the mechanical properties of the organic coating can be greatly improved, such as the abrasion resistance, scratch resistance, hardness, strength and toughness of the coating. With silane coupling agent KH560 as modifier, dispersed by ultrasonic wave and mechanical stirring, an epoxy anticorrosive coating modified by SiO$_2$ and Al$_2$O$_3$ was prepared. The swinging rod damping hardness and impact strength of the prepared coating were 1.04 and 38kg.cm/cm [32]. A new type of zinc-rich silicate anticorrosive coating with graphene was prepared. The mechanical property test results indicated that, the impact strength and hardness of the coating increased with the graphene addition.
amount increased in the range of 0.8~2.0 wt % [33].

2.5 Self-cleaning Performance
By importing substances of low surface energy into the coatings, the surface energy of the coatings could be reduced and the self-cleaning property of the coating could be improved. At present, organic silicone coatings and fluorinated compounds are widely applied as low surface energy materials, and the corresponding coating was used as anticorrosive coating for steel bridges, pipes and glassed to improve their self-cleaning performance [14][17] [26]. The Si-O bonds in organic silicone coatings have a long bond length and a large bond angle, which is conducive to the internal rotation of the molecular chain so that the molecular chain has a good smoothness. Therefore, silicone coating is easy to be adjusted into a low-surface energy structure. C-F bond in fluorocarbon coatings has higher bond energy than Si-O bond in siloxane coatings, and the van der Waals force among molecular is smaller. Therefore, the surface energy of fluorocarbon materials is lower, which is also the material of lowest surface energy reported [34-37].

2.6 Functional Performance
When nano aluminate is used in coatings, it can store the light energy of natural light or light. When the external light stops, it is released slowly in the form of light. Moreover, the duration of luminescence is dozens of times longer than that of traditional luminescent materials. In recent years, there are more intelligent anticorrosive coatings proposed, can quickly respond to environmental changes, such as pH value, light and other environmental changes, and selectively make the best response, preventing the metal further corrosion coating system. For example, organic corrosion inhibitor is introduced into the coating of siloxane system to make the coating self-repairing. At present, the research on intelligent coating mainly focuses on microcapsule technology, while the development of microcapsule technology focuses on self-repair of coating, and there are few reports on self-diagnosis [36]. There are few reports about intelligent anticorrosive coatings with self-repair, self-diagnosis and other functions [39-41].

3. Conclusions
Anticorrosive coating is an effective measure to solve the corrosion failure problem of bridge steel structure. Epoxy zn-rich primer with graphene has been applied in engineering, and the addition of graphene was proved effective to improve the adhesion and weather resistance of the primer. Other nano materials, such as TiO₂, SiO₂ and ZnO, have a significant effect on improving the anticorrosion, mechanical properties, self-cleaning and functionality of coatings, but engineering applications still need further investigation.

Reference
[1] J. Liu, T. Liu, Z. Guo, N. Guo, Y. Lei, X. Chang, Y. Yin. (2018) Promoting barrier performance and cathodic protection of zinc-rich epoxy primer via single-layer graphene, Polymers 10: 591.
[2] H. Hayatdavoudi, M. Rahsepar. (2017) A mechanistic study of the enhanced cathodic protection performance of graphene-reinforced zinc rich nanocomposite coating for corrosion protection of carbon steel substrate, J. Alloy. Comp. 727: 1148-1156.
[3] S. Park, M. Shon. (2015) Effects of multi-walled carbon nano tubes on corrosion protection of zinc rich epoxy resin coating, J. Ind. Eng. Chem. 21: 1258-1264.
[4] A. Gergely, Z. Paszti, J. Mihaly, E.et al. (2014) Galvanic function of zinchrich coatings facilitated by percolating structure of the carbon nanotubes. Part II: protection properties and mechanism of the hybrid coatings, Prog. Org. Coating, 77: 412-424.
[5] K. Schaefer, A. Miszczyk. (2013) Improvement of electrochemical action of zinc-rich paints by addition of nanoparticulate zinc, Corrosion Science, 66: 380-391.
[6] A. Meroufel, S. Touzain, (2007) EIS characterisation of new zinc-rich powder coatings, Prog. Org. Coating 59 197-205.
[7] Ronert F., Sharrock J. (1990) European approach to UV protection with a novel pigment [J]. Journal of Coatings Technology, 62: 125-130.

[8] C. Fernandez-Sanchez, C.J. McNeil, K. Rawson, (2005) Electrochemical impedance spectroscopy studies of polymer degradation: application to biosensor development, Trac. Trends Anal. Chem. 24: 37-48.

[9] X.W. Liu, J.P. Xiong, Y.W. Lv, Y. Zuo, (2009) Study on corrosion electrochemical behavior of several different coating systems by EIS, Prog. Org. Coating 64: 497-503.

[10] M. Jalili, M. Rostami, B. Ramezanzadeh, (2015) An investigation of the electrochemical action of the epoxy zinc-rich coatings containing surface modified aluminum nanoparticle, Appl. Surf. Sci. 328: 95-108.

[11] W.B. Chen, P. Chen, H.Y. Chen, J. Wu, W.T. Tsai. (2002) Development of Al-containing zinc-rich paints for corrosion resistance, Appl. Surf. Sci., 187: 154-164.

[12] Y. Cubides, H. Castaneda, (2016) Corrosion protection mechanisms of carbon nanotube and zinc-rich epoxy primers on carbon steel in simulated concrete pore solutions in the presence of chloride ions, Corros. Sci. 109: 145-161.

[13] B. Ramezanzadeh, S.Y. Arman, M. Mehdipour, (2014) Anticorrosion properties of an epoxy zinc-rich composite coating reinforced with zinc, aluminum, and iron oxide pigments, J. Coat. Technol. Res. 11: 727-737.

[14] A. Gergely, I. Bertoti, T. Torok, E. Pfeifer, E. Kalman, (2013) Corrosion protection with zinc-rich epoxy paint coatings embedded with various amounts of highly dispersed polypyrrole-deposited alumina monohydrate particles, Prog. Org. Coating. 76:17-32.

[15] L. Zhang, X.Y. Lu, Y. Zuo, (2014) The influence of cathodic polarization on performance of two epoxy coatings on steel, Int. J. Electrochem. Sci. 9: 6266-6280.

[16] H. Marchebois, M. Keddam, C. Savall, J. Bernard, S. Touzain. (2004) Zinc-rich powder coatings characterisation in artificial sea water-EIS analysis of the galvanic action, Electrochim. Acta, 49: 1719-1729.

[17] B. Ramezanzadeh, M.H.M. Moghadam, N. Shohani, M. Mandavian, (2017) Effects of highly crystalline and conductive polyaniline/graphene oxide composites on the corrosion protection performance of a zinc-rich epoxy coating, Chem. Eng. J. 320:363-375.

[18] F. Yang, T. Liu, J.Y. Li, S.H. Qiu, H.C. Zhao, (2018) Anticorrosive behavior of a zinc-rich epoxy coating containing sulfonated polyaniline in 3.5% NaCl solution, RSC Adv. 8: 13237-13247.

[19] Q. Liu, X. Qu, H. Xu. (2013), A method to prepare a zinc rich oxy anticorrosive coating [P].China, 103173095 A.

[20] W. Zhao. (2016) Graphene based heavy anti-corrosive coating in the stage of big scale application [J]. Surface engineering and remanufacture, 16(5):67.

[21] Shengrong WANG, Jianwei Yang, Jianping Cao et al. (2019) A mechanistic study of corrosion of graphene and low zincrich epoxy coating on carbon steel in salt environment. International Journal of Science, (14), 9671-9681.

[22] Li Y., Yang Z., Qiu H., et al. (2014) Self–aligned graphene as anticorrosive barrier in waterborne polyurethane composite coatings[J]. Journal of Materials Chemistry A, 14: 139-14 145.

[23] Mo M., Zhao W., Chen Z.. (2015) Excellent tribological and anticorrosion performance of polyurethane composite coatings reinforced with functionalized graphene and graphene oxide nanosheets [J]. RSC Advances, 5: 564-586

[24] Krishamoopthy K., Jeyasubramanian K., Premanathan M., et al. (2014) Graphene oxide nanopaint [J]. Carbon, 72: 328-337.

[25] Mohaammadi S., Taromi A., Shariatpanahi H.,et al.. (2014) Electrochemical and anticorrosion behavior of functionalized graphite nanoplatelets epoxy coating [J]. Journal of Industrial and Engineering Chemistry, 20: 4124-4139.

[26] Fang Y., Liu S., Zhao J.. (2016) Preparation and corrosion resistance of graphene/fluorocarbon coating [J]. Surface and Technology, 11: 67-72.
[26] Li Y., Hu X., Shen B. et al. (2008) The Properties of Modified Nano SiO2/ Acrylics Composite Coating [D]. Journal of Xiamen University(Natural Science), 05: 696.

[27] H.W. Shi, F.C. Liu, E.H. Han, (2011) The corrosion behavior of zinc-rich paints on steel: influence of simulated salts deposition in an offshore atmosphere at the steel/paint interface, Surface Coating. Technology, 205: 4532-4539.

[28] Yang P., Zhang J., Li L.. (2014) study on the property of anti-ultraviolet agingof nano-coating [J]. Applied Chemistry Engineering, 43: 1240-1242.

[29] Wang Z., Zhang P., Lin X.. (2015) Corrosion Protection Engineering [M].Beijing: Chemical Industry Press.

[30] Sabzi M., Zohuriaanmehr J., Atai M.. (2009) Surface modification of Ti O2nano-particles with silane coupling agent and investigation of its effect on the properties of polyurethane composite coating [J]. Progress in Organic Coatings, 65: 222-228.

[31] J. He, J. Hu, X. Mo, et al. (2019) Novel photocatalyst nitrogen-doped simonkolleite Zn5(OH)8Cl2H2O with vis-upconversion photoluminescence and effective visible-light photocatalysis, Appl. Phys. A, 125:3.

[32] W. Gao. (2012) Evaluation and preparation of nano modified epoxy anticorrosive coating. Southwest petroleum University [M], Chengdu.

[33] S. Zhao, H. Chen, et al. (2018) Effects of graphene on properties of silicate zinc-rich anti-corrosion coating, Corrosion & Protection, 39: 930-936.

[34] Y. Cubides, S.S. Su, H. Castaneda, (2016) Influence of zinc content and chloride concentration on the corrosion protection performance of zinc-rich epoxy coatings containing carbon nanotubes on carbon steel in simulated concrete pore environments, Corrosion 72: 1397-1423.

[35] A. Sofian, K. Noda, (2014) Corrosion resistance and mechanism of zinc rich paint in corrosive media, ECS Trans., 58: 29-37.

[36] C. Abreu, M. Izquierdo, P. Merino, et al., (1999) A new approach to the determination of the cathodic protection period in zinc-rich paints, Corrosion 55: 1173-1181.

[37] J. R. Scully. (2015) Corrosion chemistry closing comments: opportunities in corrosion science facilitated by operando experimental characterization combined with multi-scale computational modelling, Faraday Discuss 180: 577-593.

[38] Guo H., Zhou J., Lin Z., (2008) ZnO nanorod light-emitting diodes fabricated by electrochemical approaches, Electrochem. Commun. 10: 146-150.

[39] A. Janotti, C.G. Van de Walle, (2009) Fundamentals of zinc oxide as a semiconductor, Rep. Prog. Phys., 72:126501.

[40] L. Zhang, Y. Jia, S. Wang, Z.,et al. (2010) Carbon nanotube and CdSe nanobelt Schottky junction solar cells, Nano Lett. 10: 3583-3589.

[41] A. K. Sharma, R. Sharma, (2018) Fabrication and characterization of zinc oxide/multiwalled carbon nanotube Schottky barrier diodes, J. Electron. Mater. 47: 3037-3044.