

PROTECTION OF STEEL JISG 3141 WITH CHROMIUM-FREE CONVERSION COATING BASED ON INORGANIC SALT (Zr/Ti/Mo)

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ABSTRACT

Chromium-free conversion coatings based on Zr/Ti/Mo compounds were prepared to improve the corrosion resistance of the SPCC-JISG 3141 steels. Passivation layer containing Zr, Ti and Mo has been successfully carried out on steel by dipping in solution of 17 g/l Na₂MoO₄, 8 g/l K₂ZrF₆, 1 g/l H₂TiF₆ and pH = 5. Scanning electron microscopy couples with energy - dispersive spectroscopy (SEM/ EDX) were used to provide the microscopy structure information and presence of Zr/Ti/Mo on surface of the steels. The corrosion potential and current of coating in case of with and without passivation layer on the steels was determined by potentiodynamic polarization test, showed that the corrosion current density decreased when using Zr/Ti/Mo coating. The passivation layer provided the corrosion resistance of coating. Furthermore, the salt spray test (Model SAM Y90) evidenced the higher corrosion resistance of the coated samples compared to bare steel when electro - deposition coating (ED) applied. The treatment using inorganic salt could significantly increase the anticorrosion of steels with their environment-friendly.

Keywords: chromium-free, Molybdate, the salt spray, conversion coating, steel.

1. INTRODUCTION

SPCC-JISG 3141, which represents a commercial quality cold rolled steel, offers high corrosion resistance compared to other steels. However, they display poor resistance to localized pitting corrosion in aqueous solutions containing complex agents such as chloride ions [1 - 3]. JISG 3141 has been widely used for structural components because of the low absolute strength and higher material cost of aluminum alloys. Therefore, the improvement of JISG 3141 corrosion resistance has been a topic of great importance.

Among the various methods to avoid or prevent the destruction of metal surface, conversion coatings are one of the best known methods of improving corrosion protection and enhancing paint adhesion [4 - 6]. Chromate [7], nitrite [8]and phosphate-containing conversion

layers [9] have been commonly used for this purpose. However, there are some limitations to its several healthy, environmental and process disadvantages [10]. Thus, it is necessary to identify environmental-friendly conversion coating has become highly urgent [11 - 15]. Molybdate is classified an anodic inhibitor and good corrosion resistance, as possible replacement for chromate coating. Besides, molybdate is a little poisonous and non-poisonous. But unlike CrO_4^{2-} , MoO_4^{2-} ions have less oxidizing properties. Therefore, nitrite is an oxidizing agent that improves corrosion inhibition efficiency of molybdate. In recent years, Zr/Ti compounds have also gained acceptance as corrosion inhibitors.

Nevertheless, none of them provides sufficient corrosion protection to the steel substrates and the replacement of hexavalent chromium. Ti/Zr salt combined with molybdate, multi-metal system had been rarely reported. This study aims at studying the corrosion resistance of the chromium-free conversion based on Zr/Ti/Mo compounds on the steel SPCC-JISG 3141 surfaces. The corrosion protection offered by the Zr/Ti/Mo based conversion coating was evaluated by potentiodynamic polarization test and salt spray exposure. Scanning electron microscopy/ energy dispersive spectroscopy (SEM/ EDS) were used to provide complementary microstructural information. Moreover, the adhesion properties of the epoxy coating were also studied.

2. MATERIAL AND METHODS

2.1. Materials

JISG 3141 substrates with different sizes were used depending on the characterization method, it would be subjected to: panels (200 mm × 70 mm × 1 mm) for salt spray exposure test and tape adhesion test; panels (40 mm × 15 mm × 1 mm) for electrochemical tests; panels (25 mm × 10 mm × 1 mm) for SEM/EDS analysis. Table 1 shows the percentage weight composition of the steel, sources from China steel Sumikin Vietnam Joint Stock Company.

Table 1. Percentage weight composition of SPCC-JISG 3141 steel alloys.

C	Mn	P	S	Cu	Ni	Cr	Mo	V	Nb	Ti	Si
0.15	0.6	0.1	0.035	0.2	0.2	0.15	0.06	0.008	0.008	0.02	0.001

Potassium hexafluorozirconate (K_2ZrF_6), sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), hexafluorotitanic acid (H_2TiF_6) were obtained from Aldrich. Nitric acid (HNO_3) and sodium hydroxide (NaOH) were prepared from Xilong scientific Co.

2.2. Experimental

2.2.1. Sample preparation

The conversion coating of all steel was carried out in the following manner (ASM Metal Handbook [16]):

1. After degreasing, soak the parts for 30 minutes in 5 wt% of NaOH at 70 - 80 °C.
2. Distilled water rinse

3. Immerse the part for 5 minutes in solution of 17 g/l Na₂MoO₄, 8 g/l K₂ZrF₆, 1 g/l H₂TiF₆, HNO₃ and pH = 5.
4. Distilled water rinse
5. Immerse for 30 minutes in 5 wt% NaOH at 70 - 80 °C.
6. Distilled water rinse

For tape adhesion and salt spray test, the sample surfaces were deposited film by electro-deposition (ED) coating that was fully crosslinked by reaction of the epoxy-amine backbone with the crosslinker. In this case, carbon black was pigment paste. All of process was processed by P.I.G.O Vietnam.

2.2.2. Characterization methods

The corrosion resistance was evaluated by electrochemical tests. The electrochemical measurements were carried out with PGS.HH10 potentiostat/galvanostat. A conventional three-electrode cell with Ag/AgCl reference electrode and a platinum counter electrode was used for all the electrochemical tests. During the potentiodynamic tests, the samples were immersed into a 3.5 wt% KCl solution. The (25 mm × 10 mm × 1 mm) panels were inserted in a sample holder exposing 1 cm² of the surface.

Additional, salt spray tests (Model SAM Y90) were also performed to further evaluate the coating corrosion resistance. As in salt spray chamber, the panels were scribed with an X. That tests in accordance with the ASTM-B117 standard, except that the surface of the panels was inclined 60 from vertical.

Panels were used a dimension of 200 mm × 70 mm × 1 mm for tape adhesion following ASTM D3359-97 and quantitatively indicates of the damage caused by pitting outwards from the scribe (ASTM-D1654-79A).

The morphology and the chemical composition of the treated steel substrates were investigated using a scanning electron microscopy (SEM, JEOL JED-2300) coupled with an energy dispersive X-ray (EDS).

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical tests

Polarization curves for untreated and Zr/Ti/Mo process treated steel in 3.5 wt% KCl solution with different dipping time are shown in Fig.1. The anodic reaction (1) is related to the dissolution of ferrous substrate. The cathodic ones (2) and (3) correspond to the evolution of hydrogen and reduction of oxygen dissolved in the solution, respectively. Compared to bare steel, the treated samples in conversion solutions with dipping time $t_d = 1, 2, 3$ and 4 minutes had polarization curves shifting to positive potential. Corrosion current was decreased with the different t_d . The highest E_{corr} value (-0.33 V) was observed for the sample coated through immersion in conversion bath for 3 minutes.

Anodic reaction:



Cathodic reactions





During the dipping time, the precipitation of insoluble product layers (e.g., FeMoO_4 , $\text{Fe}_2(\text{MoO}_4)_3$, $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$, $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$) was formed on the steel surface. The higher t_d was, the thicker precipitation layer was. However, the conversion layer could be dissolved back if the dipping time was prolonged. It could be seen the corrosion potential was shifted more negative direction (-0.53V at $t_d = 4$ minutes). Of course, the thinner conversion layer could not protect substrate from corrosion. Dipping the steel sample for 3 minutes should be enough to produce the best conversion layer protected steel substrate.

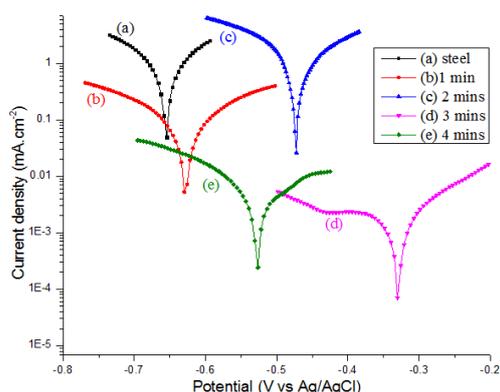


Figure 1. The polarization curves for base steel and Zr/Ti/Mo-treated steel samples with different dipping time ($t_d = 1; 2; 3$ and 4 minutes) in 3.5 wt% KCl.

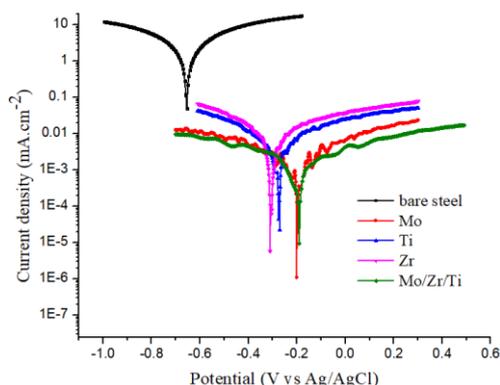


Figure 2. The polarization curves for base and treated steel samples in solution containing $\text{Na}_2\text{MoO}_4 + \text{HNO}_3$; K_2ZrF_6 ; H_2TiF_6 , and Zr/Ti/Mo solution with $\text{pH} = 5$.

Table 1. Obtained data from Tafel extrapolation for base and four treated samples in different conversion baths for 3 minutes at room temperature (immersed in 3.5 wt% KCl).

Samples	$I_{\text{corr}} \times 10^6 \text{ (mA.cm}^{-2}\text{)}$	$E_{\text{corr}} \text{ (V vs Ag/AgCl)}$
Base steel	46570	-0.650
8g/l K_2ZrF_6 solutions, $\text{pH} = 5$	6.041	-0.310
1 g/l H_2TiF_6 solutions, $\text{pH} = 5$	21.668	-0.269
17g/l $\text{Na}_2\text{MoO}_4 + 8 \text{ ml HNO}_3$ 0.2 M solutions, $\text{pH} = 5$	1.145	-0.203
Zr/Ti/Mo solutions, $\text{pH} = 5$	9.247	-0.189

The processes of conversion coating were speculated on the micro-cathodic sites [18-21], as followed Eq. (4) - (8):

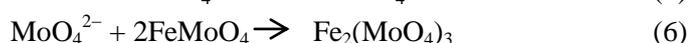
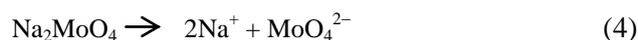




Figure 2 showed the polarization curves for base and treated steel samples in solution containing 17 g/l Na₂MoO₄ + 8 ml HNO₃ 0.2 M, 8 g/l K₂ZrF₆, 1 g/l H₂TiF₆ and Zr/Ti/Mo solution with pH = 5. The corrosion potential of Zr-treated, Ti-treated, Mo-treated and Zr/Ti/Mo-treated was shifted toward more positive values compared to untreated steel, respectively (Table 1). The present of Zr, Ti and Mo compound at the same time in conversion solution could improve the corrosion resistance of coating. It could be a synergic effect in forming the better conversion layer.

3.2. Surface morphology and EDS analyses

Surface morphology and composition of base and Zr/Ti/Mo treated steel with three different sites were demonstrated in Fig. 3 and Fig. 4. The surface of the bare steel showed noticeable lines of grit papers (Fig. 3a). After dipping in a Zr/Ti/Mo conversion bath, all the scratches were disappeared. Fig. 3b and c showed the EDS spectra of the roughly spherical deposits on the sample surfaces. However, no aggregation was seen in Fig. 3d due to some aggregation are still present on the coating surface.

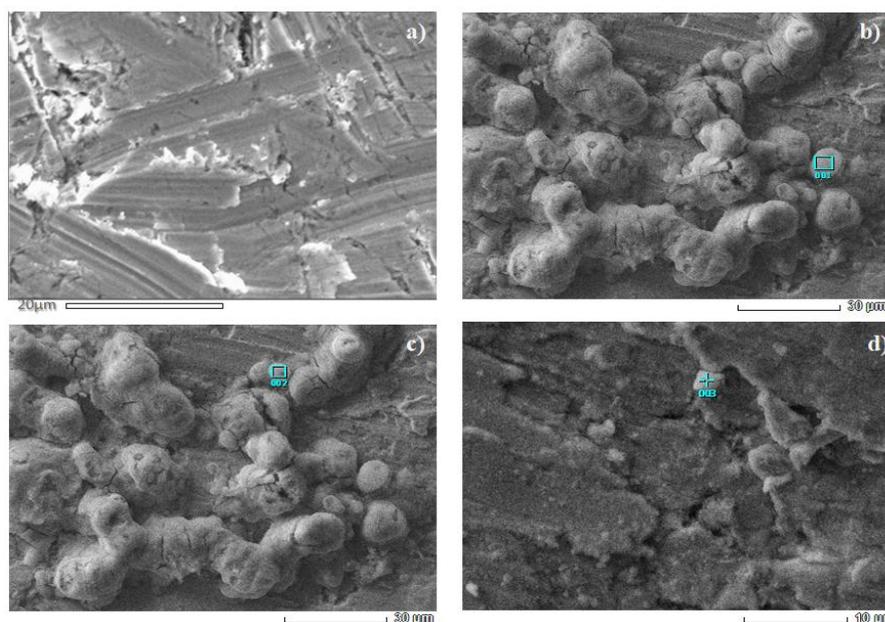


Figure 3. SEM images of (a) untreated and treated steel surface: (b) site 1, (c) site 2 and (d) site 3.

Table 2. Semiquantitative EDS analysis on intermetallic particles of treated samples.

Memo	C	O	Ti	Fe	Zr	Mo	Total (Mass %)
1	5.33	37.85	0.19	55.74	-	0.89	100
2	4.12	39.15	0.05	55.95	0.16	0.57	100
3	2.35	12.31	1	77.53	0.59	6.22	100

The EDS analysis also reported that Fe, Ti, Zr, Mo and O were the main composite elements (see Table 2). No peak Zr in site 1 could be seen (Fig. 4b). It may be explained that K_2ZrF_6 affect the reaction as catalytic action, consequently, there is no signal about Zr element at random [22].

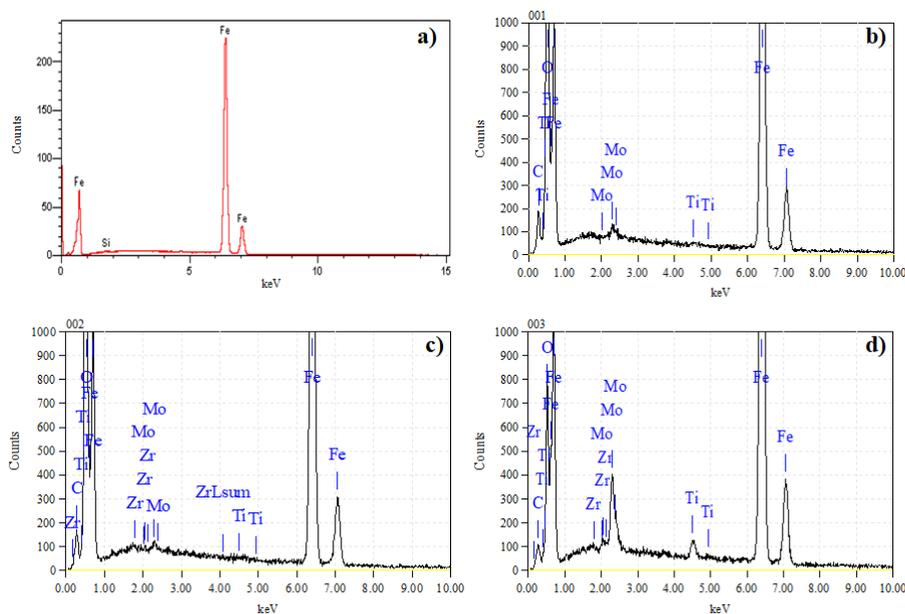


Figure 4. EDS spectrum of Zr/Ti/Mo coated on JISG 3141 substrates.

3.3. Adhesion measurements



Figure 5. Aspect of the Zr/Ti/MoCC-ED coating sample after the tape adhesion tests .

The major use of Zr/Ti/Mo conversion coating (Zr/Ti/MoCC) filming of steels in the industry is as a pretreatment to provide a uniform, stable metal surface with good adhesion to subsequently applied paint schemes. The ED paint thickness is 15 - 17 μm . Tape adhesion test (ASTM D3359-97): inspect the grid area for removal of coating from the substrate. The samples were obtained 0 % percent area removed (5B classification): the edges of the cuts are completely smooth; none of the squares of the lattice is detached (Fig. 5). The adhesion between the steel and the organic coating with employing Zr/Ti/MoCC was initially good as a surface treatment.

3.4. Corrosion tests

It can be seen from Fig.6 indicating the presence of corrosion products formed near the incision after 272, 361, 462 and 529 h exposure to salt spray. Table 3 shows the results for salt sprays tests of the untreated/ED coatings and Zr/Ti/MoCC/ED-coatings. At the same time of exposure, untreated-ED coating reveals the appearance of rusting and blistering along the scribe mark as shown in Fig. 6a, but Zr/Ti/MoCC-ED coating exhibited no blistering (Fig. 6b). At 529 h exposure, Zr/Ti/MoCC-ED coating was reached to the scribe failure rating number 4, near twice resistance time in salt spray chamber compared to untreated steels. Therefore, the Zr/Ti/MoCC improved the corrosion resistance properties of the steel as compared to untreated steels.

Table 3. Corrosion resistance performance of untreated-ED coating and Zr/Ti/MoCC-ED coating on JISG 3141 substrates after time of exposure in salt spray cabinet.

Samples	Time of exposure (h)	Scribe failure rating no. (ASTM-D1654)
Untreated/ED coating	272	4
Zr/Ti/MoCC-ED coating	272	10
Zr/Ti/MoCC-ED coating	361	8
Zr/Ti/MoCC-ED coating	529	4

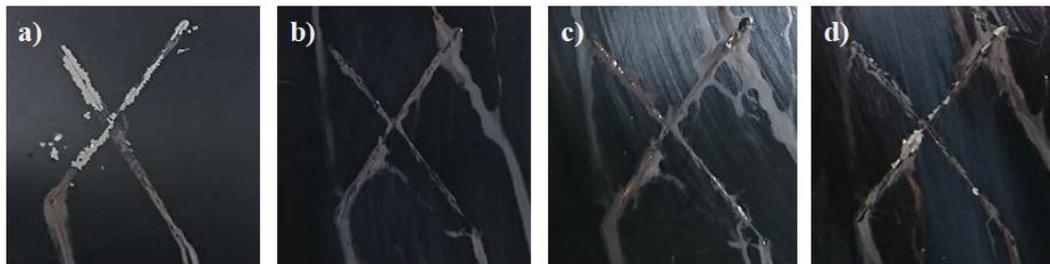


Figure 6. Salt spray corrosion test of untreated- ED coating after (a) 272 h exposure and Zr/Ti/MoCC-ED coating surfaces after (b) 272 h, (c) 361 h and (d) 529 h exposure.

4. CONCLUSION

The SPCC-JISG 3141 was treated successfully by Zr/Ti/Mo- based conversion coating. The surface morphology and composition of Zr/Ti/Mo-treated samples were studied. Results obtained from SEM/EDS revealed that Zr/Ti/MoCC formed did not uniformly cover the surface of steels. Moreover, the adhesion and corrosion protection properties of the ED coating were also studied on the surface treated samples. Results showed that the adhesion of the ED coating to the steel surface was particularly good after that conversion coating treatment of the steel surface. From the results of salt spray tests, Zr/Ti/Mo conversion coating could significantly improve the corrosion protection properties of the ED coating even at long immersion times.

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REFERENCES

1. Krakowiak S., Darowicki K., and Ślepski P. - Impedance of metastable pitting corrosion, *J. Electroanal. Chem.* **575** (1) (2005) 33-38.
2. Rasouli S. and Danaee I. - Effect of preparation method on the anti-corrosive properties of nanocrystalline Zn-CoO ceramic pigments, *Mater. Corros.* **62** (5) (2011) 405-410.
3. Samiento-Bustos E., Rodriguez J. G. G., Uruchurtu J., Dominguez-Patino G., Salinas-Bravo V. M. - Effect of inorganic inhibitors on the corrosion behavior of 1018 carbon steel in the LiBr+ethylene glycol+H₂O mixture, *Corros. Sci.* **50** (8) (2008) 2296-2303.
4. Al-Otaibi M. S., Al-Mayouf A. M., Khan M., Mousa A. A., Al-Mazroa S. A., Alkhatlan H. Z. L. - Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media, *Arab J. Chem.* **7** (3) (2014) 340-346.
5. Obot I. B., Obi-Egbedi N. O., and Umoren S. A. - Antifungal drugs as corrosion inhibitors for aluminium in 0.1M HCl, *Corros. Sci.* **51** (8) (2009) 1868-1875.
6. Yıldırım A. and Çetin M. - Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors, *Corros. Sci.* **50** (1) (2008) 155-165.
7. Zhang F., Pan J., and Claesson P. M. - Electrochemical and AFM studies of mussel adhesive protein (Mefp-1) as corrosion inhibitor for carbon steel, *Electrochimica Acta* **56** (3) (2011) 1636-1645.
8. Berke N. S. and Hicks M. C. - Predicting long-term durability of steel reinforced concrete with calcium nitrite corrosion inhibitor, *Cem. Concr. Compos.* **26** (3) (2004) 191-198.
9. Shin A. and Shon M. - Effects of coating thickness and surface treatment on the corrosion protection of diglycidyl ether bisphenol-A based epoxy coated carbon steel, *J. Ind. Eng. Chem.* **16** (6) (2010) 884-890.
10. Narayanan T. S. - Surface pretreatment by phosphate conversion coatings—a review, *Rev. Adv. Mater. Sci.* **9** (2) (2005) 130-177.
11. Zhu L., Yang F., and Ding N. - Corrosion resistance of the electro-galvanized steel treated in a titanium conversion solution, *Surf. Coat. Technol.* **201** (18) (2007) 7829-7834.
12. Lunder O., Simensen C., Yu Y., Nisancioglu K. - Formation and characterisation of Ti-Zr based conversion layers on AA6060 aluminium, *Surf Coat Technol.* **184** (2-3) (2004) 278-290.
13. Allachi H., Chaouket F., and Draoui K. - Protection against corrosion in marine environments of AA6060 aluminium alloy by cerium chlorides, *J. Alloys Compd.* **491** (1) (2010) 223-229.
14. Hamdy A. S., Doench I., and Möhwald H. - Vanadia-based coatings of self-repairing functionality for advanced magnesium Elektron ZE41 Mg-Zn-rare earth alloy, *Surf Coat Technol.* **206** (17) (2012) 3686-3692.
15. Yong Z., Zhu J., Qiu C., Liu Y. - Molybdate/phosphate composite conversion coating on magnesium alloy surface for corrosion protection, *Appl Surf Sci.* **255** (5) (2008) 1672-1680.
16. ASTM, *Metals Handbook, Ninth Edition: Volume 13 - Corrosion*, Asm Intl, Materials Park, Ohio, 1987.

17. Eivaz Mohammadloo H., Sarabi A. A., Sabbagh Alvani A. A., Sameie H., Salimi R. - Nano-ceramic hexafluorozirconic acid based conversion thin film: Surface characterization and electrochemical study, *Surf Coat Technol.* **206** (19) (2012) 4132-4139.
18. Nordlien J. H., Walmsley J. C., Østerberg H., Nisancioglu K. - Formation of a zirconium-titanium based conversion layer on AA 6060 aluminium, *Surf Coat Technol.* **153** (1) (2002) 72-78.
19. Schroeder T., Zegenhagen J., Magg N., Immaraporn B., Freund H. - Formation of a faceted MoO₂ epilayer on Mo(112) studied by XPS, UPS and STM. *Surf Sci.* **552** (1) (2004),85-97.
20. Yi A., Li W., Du J., Mu S. L.. - Preparation and properties of chrome-free colored Ti/Zr based conversion coating on aluminum alloy, *Appl. Surf. Sci.* **258** (16) (2012) 5960-5964.
21. Ishizaki T., Masuda Y., and Teshima K. - Composite film formed on magnesium alloy AZ31 by chemical conversion from molybdate/phosphate/fluorinate aqueous solution toward corrosion protection, *Surf Coat Technol.* **217** (2013) 76-83.
22. Zhan W., Liu X., and OuYang G. - Film-forming mechanism and properties of Ti/Zr/Mo colored conversion coating prepared on aluminum alloy, *Int J. Precis. Eng. Manuf-Green Technol.* **3** (3) (2016) 297-302.