

---

## Multi-dimensional study on the corrosion resistance of inorganic phosphate coatings

**Abstract:** The multidimensional corrosion resistance of chromium-molybdenum heat-resistant alloy steel was studied by using TW-7 and AHP inorganic phosphate as coatings. TW-7 and AHP inorganic phosphate coatings are both water-based high-temperature resistant coatings composed of a bottom coating and sealing coating. The main component of the sealing paint is a mixture of water, chromate, and phosphate. The single dry hot air resistance, resistance to continuously sprayed synthetic sea water, and composite heat resistance/synthetic sea water salt spray conditions were tested. The corrosion resistance of TW-7 and AHP inorganic phosphate coatings was studied. The results of the dry/hot air test showed that the TW-7 coating on the AHP cannot endure long-term high-temperature corrosion from small to large degrees at 600 °C. The synthetic seawater spray test showed that the TW-7 coating had the least amount of corrosion. No obvious corrosion spreading or shedding of the two coatings was observed under the combined conditions of heat resistance and sea water salt spray. The results show that the cyclic resistance of the two coatings to heat-resistant/synthetic seawater salt spray is consistent.

**Key words:** inorganic phosphate coating; high temperature; synthetic seawater salt spray; corrosion resistance

---

## 1. Introduction

Inorganic phosphate is a kind of inorganic coating because the form of phosphorus in the solution is phosphate ion. It is widely used in various industries<sup>[1]</sup>. Because it has good heat resistance, corrosion resistance, oil resistance, high temperature resistance and other characteristics<sup>[6]</sup>. The coating can be used as anti-corrosion material in high humidity, wear-resistant material, and Refractory in high temperature for mechanical metal equipment. At present, inorganic phosphate coatings have been widely used in aerospace development, marine shipbuilding, automotive new energy industry and other fields and have achieved good results<sup>[8]</sup>.

At present, most of the equipment explored in the marine field are mainly metal mechanical equipment, and these mechanical equipment will inevitably be corroded to different degrees when they work in the harsh marine environment for a long time, at least, it will cause the corrosion of equipment and the damage of machinery. In the long run, it will not only consume time and energy but also restrict the development of marine economy in our country<sup>[9]</sup>. Therefore, the protection of metal equipment is imminent, and the anti-corrosion of mechanical metal equipment has been a hot research topic at home and abroad<sup>[11]</sup>. For metals, one of the effective ways to improve their corrosion resistance is to treat their surface substrates. The coating protection of

---

substrate surface is one of the most important and effective methods for surface treatment<sup>[14]</sup>. So far, the current corrosion protection methods for metals include coating protection, changing metal structure, electrochemical protection, surface treatment, dielectric treatment, corrosion inhibitor protection, temperature protection and maintenance<sup>[16]</sup>. These methods can be used alone or in combination to protect metal effectively, thus reducing the harm of corrosion to metal, but in practical application should be based on specific circumstances to select the most suitable method of protecting metal. Phosphate-based heat-resistant materials after a series of operations such as substrate surface treatment, coating and curing, corrosion-resistant, salt-resistant, heat-resistant and other related excellent properties of the coating, after a series of tests has proved to be an excellent turbine protective coating of the primary material<sup>[18]</sup>. Therefore, this paper mainly aims at TW-7 inorganic phosphate, AHP inorganic phosphate coating related samples, develop test methods to study the corrosion resistance of coating, the applicability evaluation is carried out for simulating the service environment of hightemperature, high humidity and high salt, which provides supplementary data for the production of turbine blades and the safety index and reliability of machinery and equipment.

## 2. Experimental

### 2.1. Experimental materials

The material used in the experiment was 17-4PH steel. 17-4PH stainless steel is a common low-carbon steel, and its yield strength is usually between 725 and 1180 MPa; it has high strength and corrosion resistance and good weldability and processability, widely used in construction, machinery, roads and bridges and other fields, its chemical composition includes carbon, silicon, manganese, sulfur, phosphorus and so on (reference). The specific components are shown in Table 1. What equipment or analytical methods were used in your study?

Table 1 Composition of the experimental materials (%)

C	Si	Mn	S	P	Other
≤0.22	≤0.35	≤1.40	≤0.045	≤0.045	Fe

TW-7 coating and AHP coating are made of a high-temperature resistant topcoat that consists of silicone, high temperature resistant pigments and fillers, additives and organic solvents.

## 2.2 Method for preparing coating

According to the technical standard of inorganic phosphate coating, the process is made of 17-4PH stainless steel was prepared and exposed to ambient temperature of 20-40 °C, and the relative humidity is controlled to 40% -70%. Detailed operation as follows:

- (1) Sandblasting. The samples were sandblasted with a 40 mesh white corundum test forging sample, and then the Compressed air was

---

used to clean the external dust of the substrate and grind the material at the same time. When sandblasting a flat surface, the angle should be  $65^{\circ} \sim 75^{\circ}$  and the distance between the nozzle and the workpiece should be 250 ~ 280 mm. The process should keep the environment clean to avoid pollution.

(2) Bottom slurry agitation spraying. Use mechanical agitator **was used** to mix the slurry for three hours, filter with a 150 mesh filter to remove impurities, to ensure that the slurry **was** uniform without layering, and precipitation and shelf life of the slurry. A total of two times, ensure that the full spray and each spray interval of 20 minutes, ensure that the specimen completely before spraying.

(3) The substrate is solidified and shot-peened. After spraying, the sample is cured in a heat treatment furnace. The performance parameters are: keep at  $200^{\circ}\text{C}$  for 70 minutes, then heat to  $380^{\circ}\text{C}$  for 70 minutes. Cool the air in the heat treatment furnace to room temperature. Using spray pressure of 0.4-0.5 mpa, after curing in the bottom spray particles. Turn on the Compressed air and let go for 10-15 minutes. **The** surface for Compressed air, and shot peening should only be done without water.

(4) The coating is sprayed and cured. After holding temperature at  $100^{\circ}\text{C}$  for 50 min, it was heated to  $400^{\circ}\text{C}$  for 50 min and then cooled to room temperature in a heat treatment furnace. Repeat the

---

curing process. A total of two times, ensure that the full spray and each spray interval of 20 minutes, ensure that the specimen completely dry before spraying. **Could you clarify under which standard or methodology this coating preparation was conducted?**

### 2.3 Accelerated corrosion test

#### 2.3.1 Test for resistance to dry hot air

The specimen was kept at 600 °C for 100h. It is then cooled to room temperature and the paint layer is tested. The specimen was kept at 600 °C for 1000 h. **It was** then cooled to room temperature, and the paint layer **was** tested. Scanning electron **microscopy**, energy **spectroscopy** and X-ray diffraction were used to observe and analyze the structure, thickness and composition of the coating.

#### 2.3.2 **Resistance** to synthetic seawater spray

The experiment was carried out **with**  $35 \pm 2$  °C synthetic seawater salt spray for 100 h and 1000 h, respectively. Observe whether the coating (cross-cut sample: cut place) is damaged or seriously corroded, the structure, thickness, composition and corrosion products of the coating were observed and analyzed by SEM, EDS and X-ray diffraction.

#### 2.3.3 Heat resistant/synthetic seawater salt spray cycle

The specimens were subjected to ten cycles, each of which was heated at 450 °C for 2 hours in an air-circulating oven, cooled to room

---

temperature, and then exposed to  $35 \pm 2$  °C synthetic seawater for 20 hours. The damage of the film surface and the extent of corrosion spread were observed, and the structure, thickness, composition and microstructure of the corrosion products were tested and analyzed by SEM and EDS to determine the effect of the above exposure environment on the coating.

### 3. Results and discussion

#### 3.1 Analysis of physical and chemical properties of coating

Figure 1a and b shows the EDX spectra of TW-7 and AHP coatings, respectively. The energy spectrum showed that the chemical element in TW-7 coating were mainly O, C, Cr, P, Mg, and Al. According to the content of metal elements, the content of CR is higher than that of Al and Mg. It is inferred that the original composition of the coating is aluminum-chromium phosphate and Monomagnesium phosphate composite<sup>[19]</sup>. At a certain temperature, the coating is decomposed into  $P_2O_5$ ,  $Al_2O_3$ ,  $Cr_2O_3$  and MgO composite coatings. The main chemical element in AHP coating are O, C, Cr, P, Mg and Al. According to the content of metal elements, the content of CR is higher than that of Al and Mg. It is inferred that the original composition is aluminum-chromium phosphate, phosphorus and magnesium dihydrogen phosphate composite coating<sup>[20]</sup>. At a certain temperature, the coating is decomposed into  $P_2O_5$ ,  $Al_2O_3$ ,  $Cr_2O_3$  and MgO composite coatings.

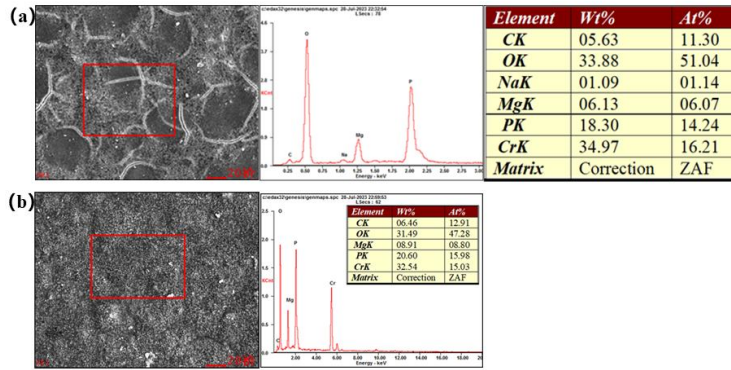


Fig. 1 (a)EDX spectrum of TW-7. (b) AHP of EDX spectra. CK, OK, NaK???. SEM images are too small.

### 3.2 Analysis of dry hot air resistance

The specimens were kept at 600 °C for 100h and 1000 h, respectively, and then cooled to room temperature. Figure 2 a b after continuous heating in 600 °C dry air for 100 hours, TW-7 coating did not change significantly, only the edge of the visible slight burn marks. AHP coating ablation appears in the lower part of the sample. After continuous heating in 600 °C dry air for 1000 hours, a large area of oxidation appeared on the surface of TW-7 sample, and so did AHP sample, but the oxidation area was smaller than that of TW-7 sample, and the coating cracked, this indicates that TW-7 is best tolerated by short-time heating in 600 °C dry air. Next is AHP sample, with the heating time prolonged, TW -7 sample can still maintain a good tolerance, paint layer is still retained, non-oxidation discoloration. Figure 2 c and d are TW-7. The surface of AHP sample after 100h and 1000h is compared with the original sample. It can be seen that the surface of TW-7 AHP sample before being heated by high temperature dry air is dense pits, but it is still relatively flat, after

100h high-temperature drying hot air, the surface of the samples have traces of oxidation and peeling off the coating<sup>[21]</sup>.As can be seen in the figure after 1000 hours of continuous heating, the surface of all samples appear more serious oxidation and coating shedding. This shows that the coating can not withstand long-lasting high temperature effect, high temperature corrosion<sup>[22]</sup>.

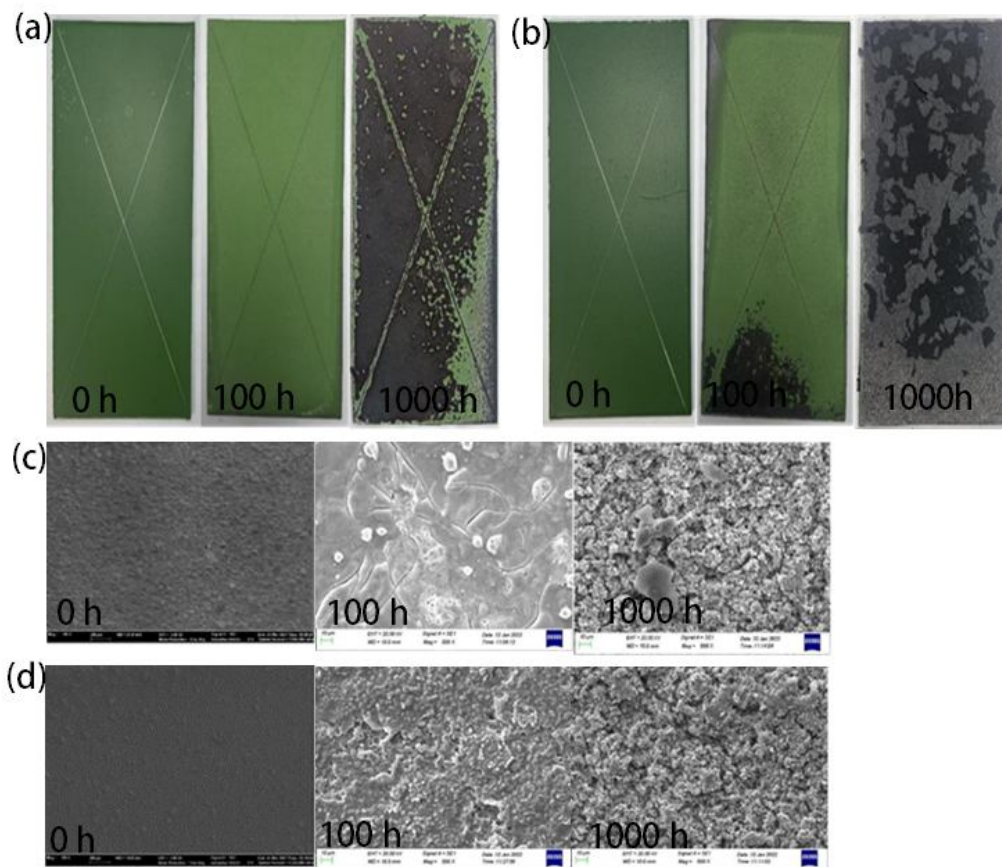


Fig. 2 (a) (b) TW -7, AHP heat-resistant dry air macro-contrast diagram. (c) Comparison of scanning electron microscopy(SEM) morphology of TW-7 specimen. (d) Comparison of SEM morphology of AHP sample surface. Some letters are indistinguishable; SEM images are too small.

---

### 3.3 Experimental Analysis of resistance to continuous spray of synthetic seawater

In  $35 \pm 2$  °C synthetic seawater spray for 100 h and 1000 h, respectively, It can be seen from figure 3a that there are many speckled corrosion marks on the surface of TW -7 coating, and the coating does not show obvious rust wear<sup>[23]</sup>. From figure 3b can see there is no obvious corrosion mark on the surface of AHP coating, and there is corrosion mark on the edge<sup>[24]</sup>. Figure 3c and d are the scanning electron microscopy (SEM) images of 17-4PH stainless steel samples coated with TW-7 after 100 hours and 1000 hours of sea water spray test were obtained<sup>[25]</sup>. Whether the spray lasts 100 hours or 1000 hours, the surface of the sample is coated with dissolved salt from seawater. When the synthetic seawater was sprayed for 100 hours, the cracks on the surface of the AHP coating sample expanded and the coating bulged, and when the synthetic seawater was sprayed for 1000 hours, there were more salt deposits on the surface of the sample and cracks on the coating<sup>[26]</sup>. There was no obvious corrosion on the surface of the samples after 1000h continuous spray of synthetic seawater. After 1000h continuous spray of synthetic seawater, the surfaces of the two samples were covered by a thick layer of sedimentary salt, there are yellow-brown rust marks on the edge of the samples<sup>[27]</sup>.

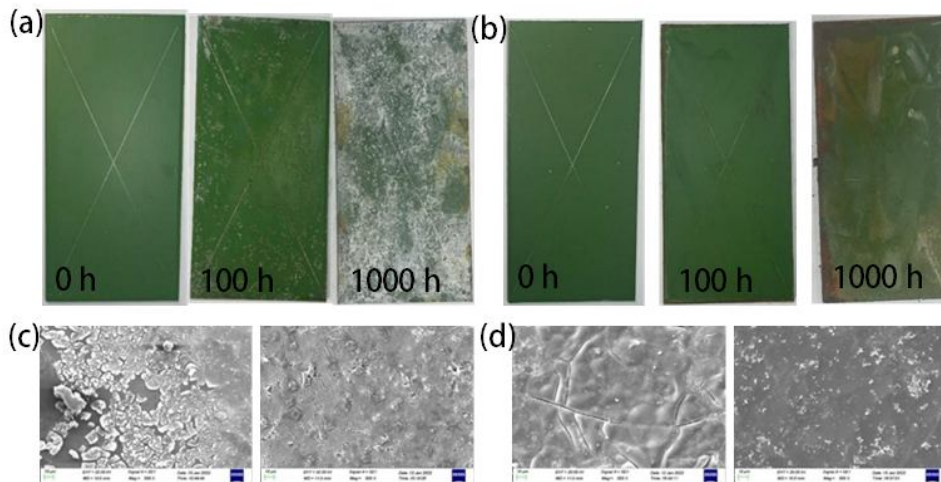


Fig 3 (a) (b) Comparison of TW-7 AHP resistance to synthetic seawater continuous spray. (c) Scanning electron microscopy (SEM) images of spray test of TW-7 AHP synthetic sea water (100h 1000h) SEM images are too small.

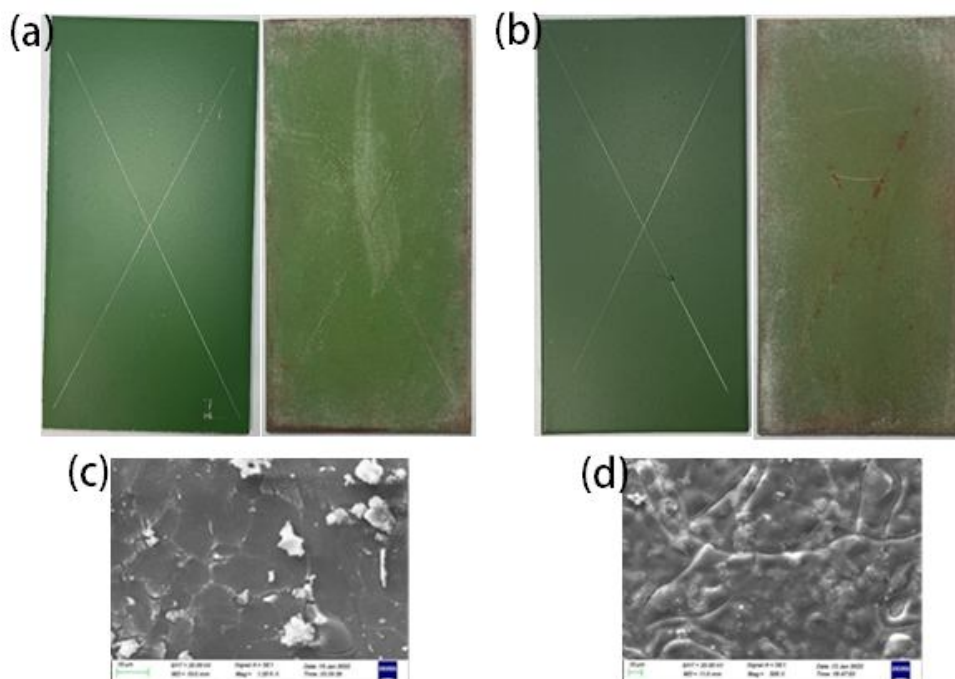
### 3.4 Experimental analysis of heat-resistant/synthetic seawater salt spray cycle

The heat-resistant/synthetic sea water salt spray cycle is a cycle of Heating at 450 °C in an air cycle oven for 2 hours, air cooling to room temperature, and then exposure to 35 ± 2°C synthetic sea water salt spray for 20 hours”, 10 consecutive cycles. Fig. 4a b is TW-7, and the surface of AHP coating is macroscopically photographed before and after the test of heat resistance/synthetic seawater salt spray cycle. It can be seen that after the compound alternating action of high temperature and seawater salt spray, the surface of the sample appears more obvious corrosion marks, especially the edge part of the sample. corrosion is more serious, the coating corrosion exposed the substrate, there is a distinct rust color on the base. The corrosion products were obviously distributed

---

along the cross-cut of AHP coating. Fig. 4c d is a SEM image of the surface of TW-7 and AHP coating. After 10 cycles of heat-resistant/synthetic seawater salt spray cycles, the surface cracks of TW-7coated samples deepened and shed, and more salt in seawater dissolved and deposited on the surface of samples. The crack on the surface of AHP coating deepens and falls off, and the coating bulges.

After the compound alternating action of high temperature and seawater salt spray, the corrosion marks on the surface of the sample appear obviously, especially on the edge of the sample, there is a distinct rust color on the base<sup>[28]</sup>. The corrosion resistance of TW-7 coating and AHP coating under hightemperature and seawater salt spray cycling conditions is acceptable, and there no obvious difference in surface state between the two coatings.



---

Fig. 4 (a) (b) TW-7, AHP coating by heat resistance/synthetic sea water salt spray cycle before and after the macro-photos. (c)(d) SEM photographs of the surface of TW-7 and AHP coatings. **SEM images are too small.**

#### 4. Conclusions

In this paper, TW-7 inorganic phosphate coating, AHP inorganic phosphate coating, dry hot air test, synthetic seawater continuous spray test were carried out, heat resistance/salt spray cycle test of synthetic seawater. The problems found in the research process are discussed in detail. At 600 °C, after 1000 hours of hot air drying test, the coating has serious peeling off, most areas of the top coat and primer have peeling off, the exposed metal substrate has serious oxidation. This shows that the coating can not withstand long-lasting high temperature effect, high temperature corrosion. After 1000h continuous spray of synthetic seawater, the surface of the samples was covered by a thick layer of sedimentary salt, and the edges of the samples showed **yellow–brown** corrosion marks. After the compound alternating action of high temperature and seawater salt spray, the corrosion marks on the surface of the sample appear obviously, especially on the edge of the sample, there is a distinct rust color on the base. The study of corrosion and wear resistance of inorganic phosphate coatings can provide guidance and reference for the preparation and application of phosphate coatings in industry, is of great significance. **A more in-depth discussion on the underlying mechanisms of coating degradation could further enrich the**

---

manuscript.

UNDER PEER REVIEW

---

## Update References

### References

- [1] Liu, Y., Chen, G., Yang, H., Bian, D., Zhao, Y. Tribological Performance of Chemically Bonded Phosphate Ceramic Coatings with Different Curing Agents on Mild Steel. *Russian Journal of Applied Chemistry*, 2019, 92(7), 909–917.
- [2] Mori, M., Masuno, T., Kozaki, D., Nakatani, N., Tanaka, K., Itabashi, H. Cations on Ion Chromatography by Phosphate-Coated Zirconia Stationary Phase Column. *Acta Chromatographica*, 2015, 27(4), 767–773.
- [3] Coto, B., Mendizabal, L., Pagano, F., Kling, H., Azpitarte, I., Barriga, J., Selegård, L. Role of surface finishing and interfacial lacquer layer on particle erosion mechanisms of Ti/TiN multilayer PVD coatings for carbon fibre reinforced polymer substrates protection. *Materials Letters*, 2021, 285, 129187.
- [4] Cazzola, M., Ferraris, S., Banche, G., Gautier Di Confiengo, G., Geobaldo, F., Novara, C., Spriano, S. Innovative Coatings Based on Peppermint Essential Oil on Titanium and Steel Substrates: Chemical and Mechanical Protection Ability. *Materials*, 2020, 13(3), 516.
- [5] Mokhtarian, J., Allafchian, A., Atapour, M. Effect of silane coating containing SiC nanoparticles on the corrosion behaviour of stainless

- 
- steel 304. *Micro & Nano Letters*, 2018, 13(8), 1203–1208.
- [6] An, S., Lee, M. W., Yarin, A. L., Yoon, S. S. A review on corrosion-protective extrinsic self-healing: Comparison of microcapsule-based systems and those based on core-shell vascular networks. *Chemical Engineering Journal*, 2018, 344, 206–220.
- [7] Karimova, S. A., Pavlovskaya, T. G., Chesnokov, D. V., Semenova, L. V. Corrosion activity of carbon plastics and protection of metal power structures in contact with carbon plastics. *Russian Journal of General Chemistry*, 2011, 81(5), 1061–1067.
- [8] Park, S., Choi, G. R., Lee, J. C., Kim, Y. C., Oh, D., Cho, S., Lee, J.-H. Organic and inorganic binder-coating properties for immobilization of photocatalytic ZnO nanopowders. *Research on Chemical Intermediates*, 2010, 36(6-7), 819–825.
- [9] Zhang, X., Wei, L., Wang, X., Fu, G., Liu, Z., Yu, B., Ye, S. Corrosion Resistant of Inorganic Coating for 50CrVA Spring Steel at Elevated Temperatures. *ISIJ International*, 2017, 57(4), 730–736.
- [10] Nijhuis, A. W. G., Leeuwenburgh, S. C. G., Jansen, J. A. Wet-Chemical Deposition of Functional Coatings for Bone Implantology. *Macromolecular Bioscience*, 2010, 10(11), 1316–1329.
- [11] Anufriev, N. G., Oleinik, S. V., Sinegribova, O. A., Nezgovorova, N. N., Sinegribov, V. A., Smetannikov, A. F., & Novikov, P. Y. Corrosion

---

of titanium in hydrochloric acid media of potassium ore processing in the process of precious metals sorption. *Theoretical Foundations of Chemical Engineering*, 2012, 46(4), 384–386.

- [12] Kumar, S. S. A., Bashir, S., Ramesh, K., & Ramesh, S. New perspectives on Graphene/Graphene oxide based polymer nanocomposites for corrosion applications: The relevance of the Graphene/Polymer barrier coatings. *Progress in Organic Coatings*, 2021, 154, 106215.
- [13] Seidi, F., Jouyandeh, M., Taghizadeh, M., Taghizadeh, A., Vahabi, H., Habibzadeh, S., Saeb, M. R. Metal-Organic Framework (MOF)/Epoxy Coatings: A Review. *Materials*, 2020, 13(12), 2881.
- [14] Zhang, C., Liu, B., Yu, B., Lu, X., Wei, Y., Zhang, T., Wang, F. Influence of surface pretreatment on phosphate conversion coating on AZ91 Mg alloy. *Surface and Coatings Technology*, 2019, 359, 414–425.
- [15] Kocijan, A., Conradi, M., Mandrino, D., Kosec, T. Comparison and characterization of biocompatible polymer coatings on AISI 316L stainless steel. *Journal of Coatings Technology and Research*, 2015, 12(6), 1123–1131.
- [16] An, S., Lee, M. W., Yarin, A. L., Yoon, S. S. A review on corrosion-protective extrinsic self-healing: Comparison of microcapsule-based systems and those based on core-shell vascular

- 
- networks. *Chemical Engineering Journal*, 2018, 344, 206–220.
- [17] Lavanya, K., Saranya, J., Chitra, S. Recent reviews on quinoline derivatives as corrosion inhibitors. *Corrosion Reviews*, 2018, 36(4), 365–371.
- [18] Zhang, X., Wang, M., Jia, T., Ma, X., Song, Q., Zhou, Q., Guo, A. A heat-resistant glass-modified multi-component phosphate adhesive for repair and connection of superalloy in extreme environment. *Journal of Alloys and Compounds*, 2018, 745, 868–873.
- [19] Chen, W., Xue, S., Wang, H., Hu, Y. Effects of Ag on Properties of Sn-9Zn Lead-Free Solder. *Rare Metal Materials and Engineering*, 2010, 39(10), 1702–1706.
- [20] Liu, Z., Sun, Q., Song, Y., Yang, J., Chen, X., Wang, H., Jiang, Z. High-emissivity composite-oxide fillers for high temperature stable aluminum chromium phosphate coating. *Surface and Coatings Technology*, 2018, 349, 885–893.
- [21] Yu Zheng, Mohammad Hassan Shirani Bidabadi, Guofeng Wang, Chi Zhang, Hao Chen Zhigang Yang, Coordination of Pre-oxidation Time and Temperature for a Better Corrosion Resistance to CO<sub>2</sub> at 550 °C, *Oxidation of Metals*, 2019, 91, 657-675.
- [22] Gießgen, T., Mittelbach, A., Höche, D., Zheludkevich, M., Kainer, K. U. Enhanced predictive corrosion modeling with implicit corrosion products. *Materials and Corrosion*. 2019, 7(12).

- 
- [23] Zhang, Z., Jiang, P.-X., Hu, Y.-T., Li, J. Experimental Investigation of Continual- and Intermittent-Spray Cooling. *Experimental Heat Transfer*, 2013, 26(5), 453–469.
- [24] Fu, H., Chen, C., Li, J., Lan, Y., Wang, L., Yuan, J. Influence of Na<sub>2</sub>S on the corrosion behavior of Q345 steel in sodium aluminate solution. *Materials Research Express*. 2019, 6, 1065a9.
- [25] Safari, M., Mostaan, H., Ghaderi, A. Dissimilar resistance spot welding of AISI 304 to AISI 409 stainless steels: mechanical properties and microstructural evolutions. *Metallurgical Research & Technology*, 2018, 115(6), 610.
- [26] Khan, A., Patil, A. P., Rao, T. S. Effect of zinc addition to copper in improving its corrosion resistance in sulfide polluted synthetic seawater. *Transactions of the Indian Institute of Metals*, 2011, 64(1-2), 99–103.
- [27] Schuerch, M., Dolch, T., Reise, K., Vafeidis, A. T. Unravelling interactions between salt marsh evolution and sedimentary processes in the Wadden Sea (southeastern North Sea). *Progress in Physical Geography*, 2014, 38(6), 691–715.
- [28] Korobeynikov, S. M., Ridel, A. V., Medvedev, D. A. Deformation of bubbles in transformer oil at the action of alternating electric field. *European Journal of Mechanics - B/Fluids*, 2019, 75, 105–109.