Study on the Material Properties of Inorganic Silicate Coating and Protective Effect on Ship Metal Structure

Cheng Xia¹,a, Kehai Dong¹,b*, Shuaiguang Lai¹,c, Tong Zhang¹,d, Hongbo Yu¹,e

¹Coast Guard Academy of Naval Aviation University, Yantai, Shandong, P.R. China.
aemail: 986574686@qq.com, bemail: dongkh307@163.com, afhy.onexmail.com
cemail: 949433990@qq.com, demail: 894863040@qq.com eemail: 2986575128@qq.com

Abstract. In order to verify whether the coating can meet the stringent requirements of the ship’s long sailing cycle, harsh environment, and various unfavorable factors such as fire conditions, physical and mechanical performance tests, endurance tests, and Micro and micro tests of the three coating samples were carried out. The hardness of the ZS2000, ZS hybrid and ZS1000 coatings measured by the experiment were ≥8H, ≥7H, ≥3H, respectively; the thermal conductivity values of the three coatings are very low, respectively 0.074 W/(m⋅K), 0.034 W/(m⋅K) and 0.025 W/(m⋅K), which can meet the requirements of the engine in unexpected flame environment; the original adhesion of the coating is the best, but the adhesion of the coating is reduced after the damp heat cycle and the salt corrosion at room temperature, and the salt spray resistance, damp and heat resistance of the coating are good, and no obvious defect is observed; TG experiments have found that the remaining percentages of the three coatings ZS1000, ZS2000 and ZS hybrid are 85.29%, 80.72% and 77.90% respectively. The thermal stability of ZS1000 is the best, and the three coatings have the best remaining balance. The difference is not large, so they all have good thermal stability. Analyzing the results of a series of performance tests, it is found that the comprehensive performance of the ZS hybrid coating is better than that of the ZS2000 and ZS1000 coatings.

1. Introduction
Ships sailing at sea are affected by various unfavorable factors such as salt spray, high and low temperature differences, high heat and humidity, and radiation. Under the long-term adverse environmental impact, the metal structure on the ship will be oxidized and corroded, resulting in a decrease in structural strength and a decrease in circuit insulation performance, and, due to various accidental factors, the ship may catch fire. Therefore, in order to ensure the integrity of the metal structure of the hull, improve the reliability of the use of marine electrical appliances, and reduce the loss caused by fire, the application of excellent protective coating on the outer surface of the corresponding part of the hull can reduce the impact of the above-mentioned unfavorable factors on it. Reduce the possibility of economic losses and safety accidents.

In recent years, scholars have conducted research on the relevant properties of protective coatings. Silane coating has been used as a steel surface treatment to promote the adhesion between the substrate and the organic coating. However, the corrosion resistance of the coating is not high enough. Adding various additives and nano fillers to the coating is a promising method to improve the barrier effect of the coating¹. In the concept of sustainable materials management, the effect of mixing inorganic materials on wood hardness and flame resistance is explored. The pyrolysis performance of
Pinus sylvestris L. (Pinus sylvestris L.) is enhanced with sodium silicate and TiO$_2$ nanoparticles through vacuum pressure technology. To develop a method for preparing porous iron oxide nanomaterials, and to study its applicability as a smart self-healing protective coating for steel. In this regard, iron oxide nanoparticles doped with iodine and end-capped with a naturally modified rosin surfactant were prepared and used as a self-healing material to repair cracks in epoxy coatings. Organic coatings have been widely used to protect carbon steel pipelines from external corrosion; synthetic lanthanide double phthalocyanine complex LnPc2 (Ln= lanthanide metal, Pc=C32H16N8 represents phthalocyanine ligand) can be used to form a new nanocomposite coating to provide corrosion protection of basic carbon steel pipes. Surface modified silver nanoparticles are used to protect the epoxy coating on low carbon steel. Organosilane (3-methoxyxilpropyl methacrylate) is used as a surface modifier to improve the dispersion of inorganic nanoparticles in the organic epoxy coating matrix. A new dual-phase PDMS/CrN coating was developed and the corrosion resistance of the system under seawater conditions was studied. In order to avoid fire hazards and prolong its service life, it is necessary to improve and maintain the protection function of ethylene-vinyl acetate copolymer (EVA) cable materials from aging degradation caused by unstable weather. These studies related to the content type and number of experiments experimental methods, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) used to characterize the nanoparticles. Differential scanning colorimetry (DSC) was used to study the effects of curing heat and glass transition temperature. Salt spray and electrochemical impedance spectroscopy (EIS) are used to evaluate corrosion resistance. Check the dispersion of the filler in the matrix by scanning electron microscope (SEM). These studies are very instructive for the research of this article.

It is required that the protective coating can ensure the stability of its own performance while reducing the impact of adverse environmental factors on the hull, which requires a series of material performance tests to verify. The ZS series of protective coatings were selected for related performance tests, and the test schemes for physical and mechanical properties and endurance properties. The physical and mechanical performance test program includes: the appearance quality, hardness, adhesion and thermal properties; the endurance performance test program includes: salt spray, TG test. Discuss coatings with different fillers and different proportions, and at the same time explore the pros and cons of protective coatings by comparing and analyzing performance test results.

2. Materials and methods

2.1. Materials
In response to the requirements of the ship's navigation environment at sea, through the preliminary research work and the comparison of actual product performance indicators, the selected test material is the ZS series of fire-resistant and heat-insulating coatings produced by Zhisheng Weihua Technology Co., Ltd. as the raw material, which is compounded into test samples.

2.2. Methods
By visual method, macro-morphology was observed applied coating on the glass. Determine the appearance quality of the coating according to the surface morphology of the coating.

In order to characterize the hardness of the coating, according to the test method specified in GB/T6739-2006, pencils with hardness of B-9H from low to high are used to test the ZS2000, ZS1000 and ZS hybrid coating samples applied on the glass plate hardness.

In order to characterize the hardness of the coating, according to the test method specified in GB/T6739-2006, pencils with hardness ranging from low to high B-9H are used, and the hardness of the ZS2000, ZS1000 and ZS hybrid coating sample was tested by a QHQ-A scratch hardness tester (Dongguan Huaguo Precision Instrument, China).

Adhesion refers to the firmness of the bond between the coating and the coated surface. Select the pulling method to test the adhesion of the coating. The test is based on GB/T5210-2006. Use a CMT4203 universal testing machine (Mitsubishi Industrial Systems, USA) to test the adhesion and
failure mode of the coating as it is and after the damp heat cycle and normal temperature salt corrosion treatment.

In order to characterize the thermal insulation performance of the coating, the test refers to the international standard IOS22007-2.2008, and the thermal constant of the coating samples are analyzed using the Hot Disk thermal constant analyzer (Hot Disk Company, Sweden).

Since ships are often in a salt spray environment while sailing at sea, the salt spray test can well characterize the protective ability of the coating. The test is carried out in accordance with the relevant regulations of GJB/T150.11A-2009, and the YWX/Q-010 salt spray box (Beijing North Lihui Instrument, China) is used to simulate the neutral salt spray environment at sea.

In order to characterize the fire and high temperature resistance of the coating, a thermogravimetric (TG) analyzer was used to set the temperature in the range of 30-800°C to determine the thermal decomposition and thermal decomposition rate of the components in the coating, and analyze the sample at a certain temperature The lower decomposition rate and the final remaining margin can explain the resistance of the coating to high temperature environment to a certain extent.

3. Results & Discussion

3.1. Physical and mechanical properties of the test results and analysis

3.1.1, Analysis of appearance & quality observation results

As shown in Figure 1, (a), (b) and (c) are the fireproof and thermal insulation ZS-2000, hybrid and 1000 coating samples after curing and molding respectively.

![Fig.1 The appearance of the fireproof and thermal insulation coating, it can be observed that the surface flatness becomes better from right to left.](image)

As can be seen in Figure 1, the macroscopic morphology of the fully cured coating has no cracks, smoothness, and no bubbles on the surface. After long-term exposure to the external environment, the coating does not change color and does not chalk. At the same time, it can be seen that due to the difference in particle size, the surface smoothness is 2000 type, hybrid type and 1000 type in order.

3.1.2, Analysis of coating hardness test results

In order to characterize the ability of the coating to resist deformation such as local collisions, a scratch hardness tester was used to test the coating hardness according to the test plan.

Three kinds of coating scratch test graphs are shown in Figure 2. It can be seen from the figure that when the pencil hardness is 9H, 8H and 4H, respectively, the ZS2000, ZS hybrid and ZS1000 coatings have plastic deformation and cohesive failure. It can be clearly seen from the enlarged figure that the pencil leaves dent. It can be concluded that the hardness of ZS2000 type coating is the highest, and that of ZS1000 type is the lowest. The hardness of the three coatings is ≥8H, ≥7H, ≥3H respectively.
Fig. 2 Coating hardness scratch test results. As can be seen, hardness of (a) ≥8H, hardness of (b) ≥7H, hardness of (c) ≥3H.

3.1.3. Analysis of adhesion test results
The adhesion test of the original sample, after damp heat cycle, and after salt corrosion at room temperature were carried out through the pull-off adhesion test. The tensile force-displacement curve of the coating is shown in Figure 3.

![Image](a)ZS 2000  (b)ZS hybrid  (c)ZS 1000

Fig. 3 The tensile force-displacement curves of the three coatings after different environmental impacts. It can be clearly seen that the adhesion has decreased, with ZS2000 having the highest tensile force and ZS1000 having the lowest.

The figure shows three coatings of tension value rises with increasing displacement, ZS2000 type displacement changes linearly with the force, and the ZS1000 type ZS hybrid with the displacement rate of rise of the tension gradually increases. In addition, the tensile value of the coating after damp heat cycle and room temperature salt corrosion has decreased. Among them, the tensile values of ZS2000 type original, damp heat aging and room temperature salt corrosion are respectively 499.1N, 326.1N, 255.3N; ZS1000 type original, damp heat aging and room temperature The salt erosion tensile values are 150.2N, 110.2N, 89.0N, respectively; the ZS hybrid type original, damp heat aging and normal temperature salt erosion tensile values are 258.7N, 174.0N, 144.4N, respectively. The cross-sectional area of the test samples is 400mm. The adhesion forces of the three types of specimens of ZS2000 are 1.247MPa, 0.815MPa, and 0.638MPa; the adhesion forces of the three types of specimens of ZS1000 are 0.375MPa, 0.275MPa, 0.222MPa; the adhesion of the three types of ZS hybrid samples is 0.647MPa, 0.435Mpa, 0.361Mpa. It can be seen that the adhesion strength is ZS2000 type>ZS hybrid type>ZS1000 type. Among them, the coating adhesion decreased by 34.6% and 48.8% after ZS2000 damp heat cycle and room temperature salt etching, respectively, and the coating adhesion decreased by 26.6% and 40.8% after ZS1000 damp heat cycle and room temperature salt corrosion; ZS hybrid type damp heat cycle and The coating adhesion decreased by 32.7% and 44.2% after salt corrosion at room temperature. It can be seen that the degree of adhesion reduction is ZS2000 type>ZS hybrid type>ZS1000 type.

3.2. Endurance test results and analysis

3.2.1. Analysis of salt spray test results
The salt spray resistance and protection performance of the coating were tested through a 15d salt spray test. The protective effect of the sample with or without coating after the test is shown in Fig. 4.
Fig. 4 The results of the salt spray resistance test found that the uncoated metal substrate has serious corrosion, while the coated metal substrate has no corrosion.

It can be clearly observed from the figure that after the 15-day salt spray test, the surface of the uncoated specimen is severely rusted, and there is salt deposition on the surface; after washing and drying, it is observed that the ZS2000 and ZS1000 coatings have good surface morphology without salt corrosion or cracks. Bubbling and other defects, observe the salt corrosion depression on the surface of the ZS hybrid coating, and the salt spray resistance of ZS2000 and ZS1000 is better than ZS hybrid. Analyzing the reason, due to the different particle size of the hybrid coating filler, after being washed by the water film formed by the salt spray, the structure is destroyed, and part of the filler is washed away to form a depression. Moreover, it can be seen from the figure that the three kinds of coatings have the same protective effect on the substrate without rust and other phenomena.

3.2.2. Analysis of TG test results
The coating samples of ZS2000, ZS1000 and ZS hybrid type were subjected to thermogravimetric test by thermogravimetry. The test results are shown in Fig. 5.

Fig. 5 The thermal weight loss curve shows the weightlessness ratio of the coating sample, and the relationship between Weightlessness speed and temperature.

It can be seen from figure (a) that after the temperature rises to 600°C, the residual margin values of the three tend to stabilize, and the final residual margin percentages of ZS1000, ZS2000, and ZS hybrid are 85.29%, 80.72% and 77.90%, respectively. The thermal stability of ZS1000 is the best, and the difference in the final remaining margin of the three is not big, so the three have good thermal stability; from Figure (b), it can be seen that the three have weightlessness before 100 °C The reason is the evaporation of bound water, which leads to the increase in weight loss rate. The reason for the increased degradation rate of ZS hybrid type at 150°C is that silicic acid (H₂SiO₃) decomposes into H₂O and SiO₂. The reason for the increased weight loss rate of ZS2000 at 520°C is the sample There is a small amount of carbonate (limestone) in it, and CO₂ is liberated at this temperature. From an overall point of view, the weight loss rate of the three is always at a low value, indicating that their thermal stability is excellent.

4. Conclusions
After a series of experimental studies, the conclusions are as follows:
(1) The coating has certain water absorption problems. Applying a thin layer of waterproof coating on
the outer surface to solve such problems, and the effect is good.

(2) The thermal conductivity of the three coatings is at a very low value, which can meet the requirements of the engine in an unexpected flame environment.

(3) The coatings are proven to have good salt spray resistance, and have obvious protective effect on the steel substrate.

(4) The thermal stability of ZS1000 is the best, but the final remaining margin of the three coatings is not much different. So all three have good thermal stability.

Acknowledgments
This article is one of the phased achievements of the “Research on the Storage Failure Mode and Failure Mechanism of the Russian Ship Missile” project of Marine Ordnance Support Department.

References
[1] Ahmadi, A., Ramezanzadeh, B., & Mahdavian, M. (2016). Hybrid silane coating reinforced with silanized graphene oxide nanosheets with improved corrosion protective performance. Rsc Advances, 6(59), 54102-54112.
[2] Garskaite, E., Karlsson, O., Stankeviciute, Z., Kareiva, A., Jones, D., & Sandberg, D. (2019). Surface hardness and flammability of Na2SiO3 and nano-TiO2 reinforced wood composites. RSC Advances, 9(48), 27973-27986.
[3] Atta, A. M., El-Saeed, A. M., El-Mahdy, G. M., & Al-Lohedan, H. A. (2015). Application of magnetite nano-hybrid epoxy as protective marine coatings for steel. RSC advances, 5(123), 101923-101931.
[4] Deyab, M. A., Slota, R., Bloise, E., & Mele, G. (2018). Exploring corrosion protection properties of alkyd@ lanthanide bis-phthalocyanine nanocomposite coatings. RSC advances, 8(4), 1909-1916.
[5] Ghazizadeh, A., Haddadi, S. A., & Mahdavian, M. (2016). The effect of sol–gel surface modified silver nanoparticles on the protective properties of the epoxy coating. RSC advances, 6(23), 18996-19006.
[6] Guan, X., Wang, Y., Zhang, G., Xin, J., Wang, L., & Xue, Q. (2016). A novel duplex PDMS/CrN coating with superior corrosion resistance for marine applications. RSC advances, 6(90), 87003-87012.
[7] Zhang, Y., Wang, B., Sheng, H., Yuan, B., Yu, B., Tang, G., ... & Hu, Y. (2016). Enhanced fire-retardancy of poly (ethylene vinyl acetate) electrical cable coatings containing microencapsulated ammonium polyphosphate as intumescent flame retardant. RSC advances, 6(88), 85564-85573.
[8] Soares, C. G., Garbatov, Y., Zayed, A., & Wang, G. (2009). Influence of environmental factors on corrosion of ship structures in marine atmosphere. Corrosion Science, 51(9), 2014-2026.
[9] ZHANG, Y., TAN, Z. D., WANG, G. D., & HE, C. (2009). Application of fireproof and heatproof materials upon ships. Ocean Technology, 1.
[10] Liu, S. Y., & Yang, C. S. (2004). Anticorrosive and Fireproof Coating for Ultrathin and Swelling Steel Structures. MATERIALS PROTECTION-WUHAN-, 37(7), 1-3.