Research on Performance Test of New Carbon Fiber Nano Antifouling Materials in Offshore Oil Field

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Abstract. Firstly, zinc dioxide and titanium dioxide were prepared from zinc acetate and butyl titanate. A nanometer ZnO/TiO2 film with different morphologies was prepared by doping the two materials. A new type of aluminum alloy base material which can be used in offshore oil exploitation was prepared by using a variety of proportioning methods. The results show that the modification agent can improve the corrosion resistance of the material. The results show that nano-ZnO composite titanium oxide coating has better antifouling and antifouling performance.

Keywords: Carbon fiber; nano antifouling materials; offshore oil field; performance testing; nano zinc oxide composite titanium oxide coating.

1. Introduction

With the continuous development of oil field exploration and development, oil field gradually from the land to the sea, and the offshore development work from the shallow water gradually to the deeper sea, in order to meet the increasing demand. The situation is very different on land and at sea, especially at sea, where seawater can cause extreme erosion of mining equipment, greatly reducing the life of mining equipment and increasing the cost of mining [1]. At present, most land mining equipment is mainly steel, but when using steel, it will encounter many technical difficulties such as ocean erosion and so on. This project intends to achieve this through nanomaterials /GFRP and nanomaterials/Aromatron base (CF/KFRP). The use of nanomaterial reinforced plastic materials in subsea oil development highlights five characteristics. The resulting complex has a density of 1.50 g /cm3 and about 1.60g /cm3, compared with 7.87g /cm3 for steel. Obviously, carbon fiber cloth weighs much less than steel. (2) High specific strength and modulus. Carbon fiber reinforced plastics have 7~12 steel and 3~5 modulus of elasticity. Therefore, carbon fiber cloth can be used to make a variety of products, such as: weight, strength, hardness and so on. (3) It has high fatigue resistance. Carbon fiber reinforced plastics have higher fatigue resistance and longer service life than steel. Especially in the reciprocating process of the pump, because of the non-uniformity between the external water pressure and the internal water pressure, it is easy to cause the material damage and even destruction of the pump. The sucker rod tube made of carbon fiber cloth can overcome this difficulty effectively. (4) It has good corrosion resistance. Nanomaterials reinforced plastics have high acid and alkali resistance, can resist a variety of environmental erosion, and does not rust, their service time in the ocean is much longer than steel products. (5) Excellent heat resistance. The ratio of thermal expansion and cold shrinkage of carbon fiber composites is lower. Axial thermal expansion coefficient is about $-0.1\times10^{-6}/℃$, and perpendicular to axial thermal expansion coefficient is about $+35\times10^{-6}/℃$. There is no obvious brittleness at low temperature, but it has good stability at high temperature. The high temperature resistance of carbon fiber reinforced plastics is mainly determined by the matrix material. According to the high temperature resistance of carbon fiber, it can work in the atmosphere below 300 degrees Celsius for a long time. The corrosion resistance and pollution resistance of aluminum

used in offshore oil exploration and exploitation were studied systematically. The aluminum plate was coated with a composite nano oxide film and then dried in an oven.

Zinc oxide sol with good stability was prepared by zinc acetate, and then it was leachate into film by pull-out method. Finally, TiO_2 sol was obtained by hydrolysis of butyl titanate. Zinc oxide-titanium dioxide nanocrystals were synthesized by using the above two types of solvents as raw materials and using the two solvents as precursor system, and the corrosion resistance of aluminum materials was tested.

2. Nanomaterials in oil drilling completion fluid for anti-fouling

The introduction of nanoparticles into drilling fluid can effectively improve the borehole stability and reservoir protection effect, so as to increase the drilling speed, shorten the drilling period, and reduce the formation instability caused by long-term immersion. In complex formations, extreme environments and superconducting drilling operations, working fluids are required to have multiple functions and adaptive capabilities under extreme conditions such as high temperature and high salt. Nano-substance can be a new substance in drilling and completion fluid when it is added to drilling and completion fluid. In the process of preparation, due to the interaction with metal ions, there is a large number of nanoparticles in the process of preparation [2]. In order to achieve efficient rheology, wetting, modification, disqualification, film formation, migration and other nano functions, it is necessary to study its distribution law in the drilling process from the perspective of nano, and combine its properties of filtration, anti-collapse, lubrication, rheology and so on in the drilling process to construct its internal connection with "Nano" and "nano" in the drilling process. In order to realize its "observation" function in the drilling process. For example, in new drilling systems combined with nonionic surfactants/lubrication, due to their super surface action, it is possible to prevent the loss of large amounts of surfactants due to pore migration, thus preventing the loss of surfactants resulting in damage and blockage of oil and gas flow lines; In the drilling fluid with the characteristics of anti-collapse, inhibition, inhibition and oil protection, nano-scale drilling fluid can effectively control the growth of fine paraffin crystals, and realize the multi-function that micro-paraffin crystals cannot achieve, so as to achieve the function that micro-paraffin crystals cannot achieve. Multi-level nanoparticles are introduced into the system to achieve formation repair, anti-collapse and protection based on the salt-resistance, heat-resistance and "turbidity point" effects of the polymer alcohol drilling fluid.

Among them, binary complex hydroxide (LDHs) and binary complex hydrotalcite montmorillonite (MMT) are the most representative nanostructures. Montmorillonite MMT is a new type of slurry mixing agent which has the functions of increasing viscosity, adjusting density and improving liquid viscosity. It has been widely used in oil drilling field. Since 1960s, Beijing Institute of Chemical Industry successfully prepared LDHs, Shandong University successfully developed the compound MMH positive adhesive with hydrotalc as the main component [3]. At present, the industrial production process of MG-Al hydrotalcite positive electric adhesive is mainly based on a certain material as raw material, adding an alkali metal co-sink, through aging, filtration, washing and other processes, to obtain LDHs positive electric adhesive. LDHs lamellae has a permanent positive charge, which can neutralize and peel off negative ions between layers to form a huge surface area and expose the positive charge components, thus forming a strong electric and contact retention effect with the negative geological environment, so that the drilling fluid can protect the wall well. Al-Fe-Mg complex positive colloid has an electrostatic field higher than +30 mV, high salt resistance, high viscosity and shear strength. It can be applied in reservoir rocks which are prone to hydration and collapse, such as Huaibei, Shenli, etc. to stabilize borehole wall, inhibit cuttings dispersion, cuttings carrying and protect reservoir rocks. In recent years, water soluble composite nanomaterials have been synthesized by in-situ block copolymerization using layered materials such as montmorillonite and hydrotalcite as raw materials. In recent years, some researchers have summarized the research progress of water-soluble (PVA, PEO, PVP)/MMTs composite systems

synthesized by solution using MMA and AM or N, n-dimethyl aminoethyl acrylamide as polymers. In this project, montmorillonite (MMT) is used as raw material to prepare composite Montmorillonite (MMT) with particle size ranging from 20 nm to 70 nm by NPP method. The composite montmorillonite has much greater influence on the viscosity of drilling fluid than the simple montmorillonite - PAM system, and it also has the ability to resist calcium corrosion. PAM polymer-silica nanocomposites, PAM reversed phase emulsion, PLS, etc., all show high temperature resistance, salt and alkali resistance, rapid dissolution characteristics.

3. Material preparation and results

3.1. Material preparation

A nanometer composite coating was formed on the surface of a new type of Marine aluminum plate by zinc acetate and butyl titanate. In order to prevent foreign substances from entering the aluminum, the aluminum is cleaned. A good water-soluble solution of zinc oxide was prepared with zinc acetate, and then a good water-soluble solution of zinc oxide was prepared with wire drawing and other processes. Titanium oxide was prepared by hydrolysis of butyl titanate. The ZnO and TiO_2 solution are completely stirred evenly, then sealed and placed. The clean and dry aluminum plate is soaked in the aging solution for 8 hours, and then slowly lifted at a constant speed [4]. After three coats, the coated aluminum plate is put in the oven to dry and set aside for use. The interaction between coated aluminum and coated aluminum was investigated by the experiment of copper sulfate dropping on coated aluminum and non-coated aluminum. The anticorrosive and antifouling abilities of nano-oxide films of different proportions were compared and analyzed, and their applications in aluminum alloy materials were discussed.

3.2. Experimental parameter Settings

In order to improve the anti-corrosion ability of the basic antifouling coating, it is necessary to modify the surface of the coating and regulate the ultrasonic wave to reduce the corrosion of the coating to the equipment to the maximum extent. When synthesizing a new type of nanocomposite material, it can be used to express the phase velocity and group velocity of each molecule of this substance in vibration, so it can be used to express the dispersion equation of this substance:

$$\omega = 2\sqrt{\frac{\beta}{m}}\left|\sin\frac{qa}{2}\right| \tag{1}$$

The corrosion resistant substance appears as a single molecular chain structure on the one-dimensional plane. For a molecule with an oscillating lattice structure, the phase velocity is:

$$v_p = \frac{\omega}{q} = a\sqrt{\frac{\beta}{m}}\left|\sin\frac{qa}{2}\right| / \frac{qa}{2} \tag{2}$$

The vibration velocity is

$$v_g = \frac{d\omega}{dq} = qa\sqrt{\frac{\beta}{m}}\cos\frac{qa}{2} \tag{3}$$

In order to achieve the best corrosion resistance, it is necessary to maintain the same temperature rise and oscillation rate as much as possible because the molecules are in different forms during the forming of corrosion resistant substances. Let's say that different atoms at different temperatures, atoms are the same distance away from each other, and atoms are the same distance away from each other. Figure 1 shows the curve of molecular mass change [5]. In A kinetic case, if one molecule has the magnitude of A, and the other has the magnitude of B, then both are compatible.

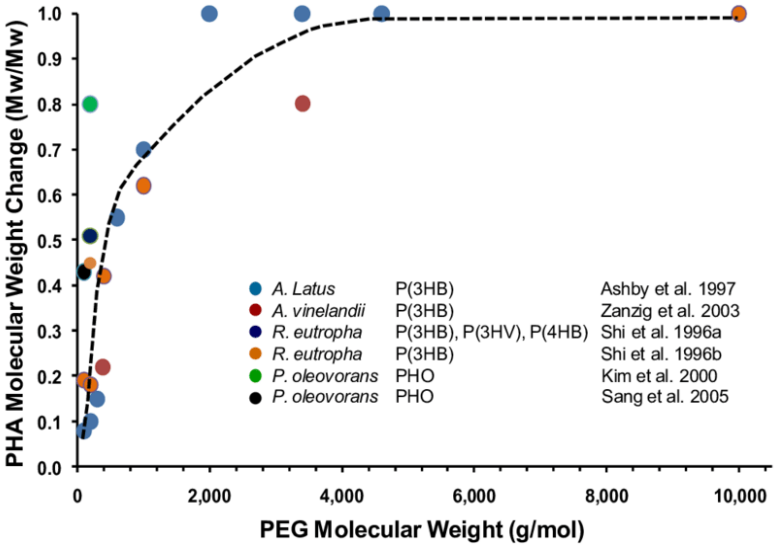


Figure 1. Molecular weight change curve

$$\frac{B}{A}=\frac{\beta_1+\beta_2-m\omega^2}{\beta_1+\beta_2 e^{-iqa}} \tag{4}$$

According to the characteristics of nanomaterials, the dispersion relationship formula between each molecule is established, and the frequencies in the two dimensions are respectively

$$\omega_A^2=\frac{(\beta_1+\beta_2)}{m}\left\{1-\left[1-\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\sin^2\left(\frac{qa}{2}\right)\right]^{1/2}\right\} \tag{5}$$

$$\omega_0^2=\frac{(\beta_1+\beta_2)}{m}\left\{1+\left[1-\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\sin^2\left(\frac{qa}{2}\right)\right]^{1/2}\right\} \tag{6}$$

The two dimensions described above describe acoustic and optical waves, respectively, and the ratio of their amplitudes is

$$\frac{B}{A}=\frac{(\beta_1+\beta_2)\left[1-\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\sin^2\left(\frac{qa}{2}\right)\right]^{1/2}}{\beta_1+\beta_2 e^{-iqa}} \tag{7}$$

Due to

$$\begin{aligned}&\left|\beta_1+\beta_2 e^{-iqa}\right|=\sqrt{(\beta_1+\beta_2\cos qa)^2+(\beta_2\sin qa)^2}=\\&\sqrt{(\beta_1+\beta_2)^2-2\beta_1\beta_2(1-\cos qa)}=\\&(\beta_1+\beta_2)\left[1-\frac{4\beta_1\beta_2}{(\beta_1+\beta_2)^2}\sin^2\left(\frac{qa}{2}\right)\right]^{1/2}\end{aligned} \tag{8}$$

When the above equation meets $\frac{B}{A}=1$, the diatomic molecular chain composed of different molecules in the nanomaterials can realize the tightest bond, ensuring the performance of Marine anticorrosive materials and maximizing the reduction of preparation errors [6]. The molecular spectrum is shown in Figure 2. The surface microstructure is shown in Figure 3.

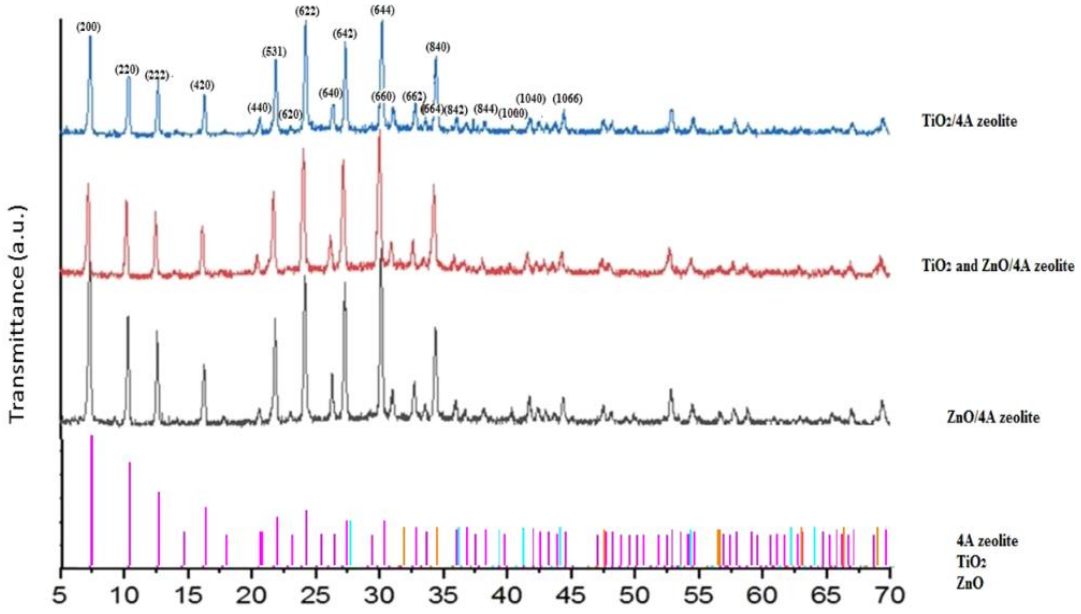


Figure 2. Molecular spectrogram

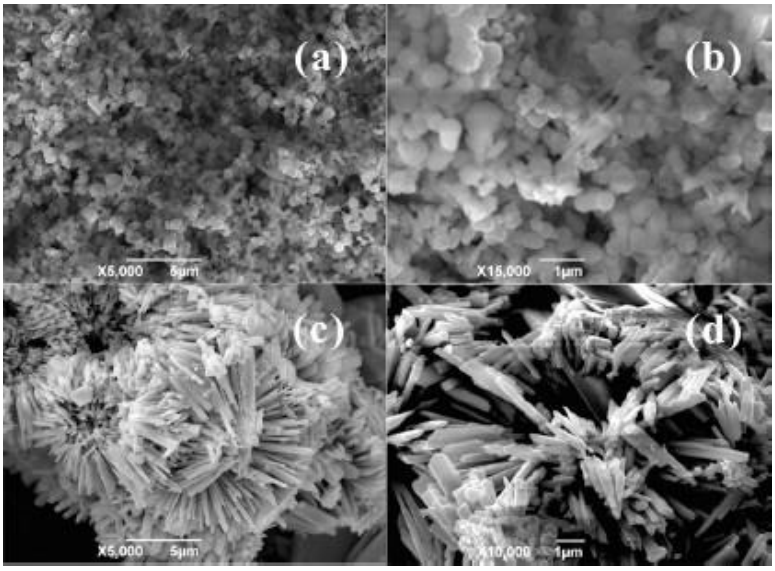


Figure 3. Microsurface structure of nano-zno composite titanium oxide

3.3. Experimental results

Compared with the conventional oxide film coating, the corrosion resistance of the coating is compared as shown in Figure 4 and 5. As can be seen from Figures 4 and 5, on day 15, the conventional oxide coating exhibits a double arc property, that is, the metal beneath the coating has been somewhat eroded, and the erosion subsequently intensifies [7]. However, during the coating process, the coating formed by ZnO and TiO_2 presents a single potential property, which remains unchanged throughout the coating process. Indicating that the metal material under the coating is well protected. The main reason is that nano ZnO/TiO_2 coatings with high density and low hydrolysable. It can be seen from the test results that the seawater antifouling paint developed has better corrosion resistance than the common oxide coating. After conventional oxidation treatment, the coating on the surface has taken on a "spot" shape, while the "spot" shape on the surface of the seawater corrosion antifouling paint of the invention is almost unchanged. The results show that the seawater antifouling paint has better corrosion resistance than the conventional coating.

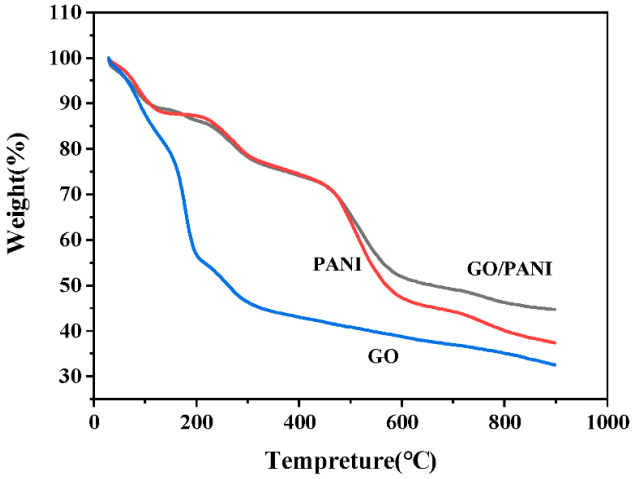


Figure 4. Corrosion resistance of traditional oxide coatings

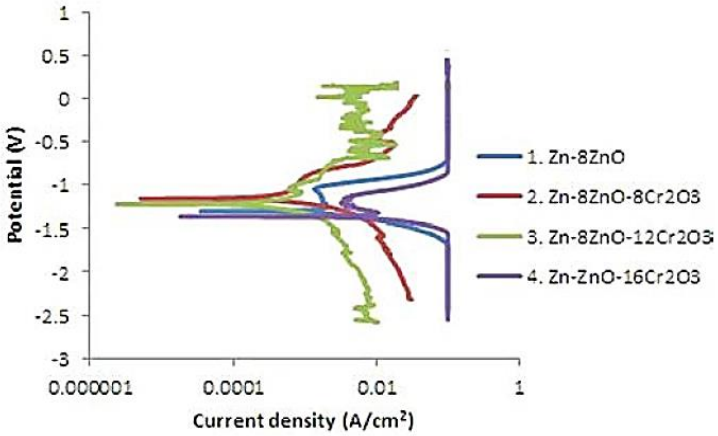


Figure 5. Corrosion resistance of nano-zno composite titanium oxide coating

Table 1 shows the fitting results of polarization characteristics of electrode materials at various composite ratios. By comparing the data in Table 1, it can be found that the oxides composed of zinc oxide and titanium oxide compound have great effects on the corrosion and antifouling properties of aluminum alloy. When W (butyl titanate) /W (zinc acetate) =8:1, aluminum alloy presents the best corrosion resistance at the same heat treatment temperature, and with the change of heat treatment temperature, the corrosion resistance of nano-oxide on aluminum alloy surface will also change [8]. When the ratio of W (butyl titanate) /W (zinc acetate) is 12:1,8:1,4:1, the optimum heat treatment temperature matching is 220℃, 160℃, 160℃, 190℃. As the corrosion strength decreases, so does the corrosion strength of the sample. The data in Table 1 show that under different heating conditions and at different incorporation ratios of ZnO and TiO_2, the erosion current intensity will also change.

When W (butyl titanate) W/ (zinc acetate) =8:1 and the heating temperature is 160℃, the corrosion current density reaches the lowest value of 3.450×10-7 A/cm2. When the heat treatment temperature continues to rise, the corrosion current density first decreases and then increases when W (butyl titanate) /W (zinc acetate) =8:1, and when W (butyl titanate) /W (zinc acetate) =12:1 and W (butyl titanate) /W (zinc acetate) =4:1, The current density will continue to decrease due to the high temperature of heat treatment. It is likely that the chemical reaction generated by the composite nano oxide coating during the heating process will lead to changes in the properties and structure of the oxide film. However, from the general trend of corrosion current density, low temperature heat treatment is not conducive to the realization of nano oxide film anticorrosion and antifouling [9]. But for nano composite materials, it is not necessarily the higher the better, because at high temperature, the composite nano oxide film will produce cracking and other phenomena, which greatly increases the probability of erosion in seawater, therefore, only under certain conditions, through appropriate

heating, can play the strongest corrosion resistance and pollution resistance. As can be seen from Figure 1, when W (butyl titanate) /W (zinc acetate) =12:1, W (butyl titanate) /W (zinc acetate) =8:1, and W (butyl titanate) /W (zinc acetate) =4:1, the corrosion current density is the minimum at the heat treatment temperatures of 220, 160 and 190℃. In this case, The corrosion resistance of nano-composite oxide is the highest, and this heat treatment temperature is the best heat treatment temperature under the corresponding recombination ratio.

Table 1. Polarization curve fitting data of nano-oxide undercoating under different recombination ratios

Temperature /℃	**W (butyl titanate)/W (zinc acetate) = 12:1**		**W (butyl titanate)/W (zinc acetate) = 8:1**		**W (butyl titanate)/W (zinc acetate) = 4:1**	
	E*corr*/V	Jcorr/(A·cm^{-2}) *10^{7}	E*corr*/V	Jcorr/(A·cm^{-2}) *10^{7}	E*corr*/V	Jcorr/(A·cm^{-2}) *10^{7}
100	-0.77	284.48	0.77	44.28	-0.82	192.92
130	-0.78	69.63	-0.76	41.28	-0.73	44.07
160	-0.76	21.48	-0.68	3.59	-0.70	41.19
190	-0.77	13.02	-0.75	5.56	-0.69	9.73
220	-0.74	10.04	-0.77	9.71	-0.80	10.33

4. Conclusion

Using ZnO/TiO_2 coating can improve the corrosion resistance and pollution resistance of ship materials used in offshore oil production. Reasonable proportion of these solvents can give full play to the best anti-corrosion and anti-pollution effect, so as to play a good protective effect for the service and maintenance of oil field mining ships.

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