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Bonding strength of graded anti-corrosive coatings of fluoroethylenepropylene (FEP)/polyphenylene sulfide (PPS)

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Abstract: Fluororesin-based anti-corrosive coatings including graded FEP/PPS were prepared on carbon steel by melt powder coating, the bonding strength of all coating systems was determined by the pull-off test. It is found that the poor adhesion of fluororesin coatings to metallic substrates is improved obviously by the graded coating structure of FEP/PPS, and the bonding strength reaches up to 11.8 MPa for the five-layer system. Examination by electron probe microanalysis (EPMA) verifies that the distribution of main components is graded in the five-layer system, which is responsible for the enhancement of the interfacial bonding.

Key words: fluororesin; anti-corrosive coating; graded coating structure; polyphenylene sulfide (PPS); bonding strength

1 Introduction

Fluororesin-based coatings show such remarkable properties as highly anti-corrosive, temperature-resistant, incoherent and weather-resistant [1-3], so they can be used as corrosion-resistant coatings under harsh terms. Of all fluoropolymers, FEP (fluoroethylenepropylene) has the same highest level of chemical resistance as PTFE (polytetrafluoroethylene). It is much easier to make FEP to pin hold free coating because of the low melt viscosity. However, the poor adhesion of this fluororesin reduces the bonding strength of fluororesin coatings to metallic substrates and the anti-corrosion effect. PPS (polyphenylene sulfide) is a high-temperature thermoplastic resin with good comprehensive performance and particularly excellent adhesion to metallic substrates [4-7], which can form a solid coating on the metal surface.

Graded materials are new inhomogeneous composites, whose performances change continuously with the components and structure along a certain direction. Graded materials have a lot of properties including dynamic, chemical, optical, electromagnetic and biological, which can be combined together and used under different conditions [8]. Based on the concept of graded materials, FEP and PPS can be selected as the main component in surface and bottom layers of anti-corrosive coating system, respectively. Between the surface and bottom layers, FEP/PPS blend coatings are filled in, with transition in proportion, thus forms FEP/PPS graded anti-corrosive coatings. This coating system can give full play to the advantages of high adhesion in bottom layer and excellent corrosion-resistance in surface layer.

In this paper, fluororesin-based anti-corrosive coatings including the graded FEP/PPS were prepared on carbon steel by powder hot melting, the bonding strength of these coatings to steel substrates and the distribution of components in the graded coatings were investigated.

2 Experimental procedures

2.1 Experimental materials

The substrate used in the experiment was common mild steel Q235-A (Φ20 mm×30 mm). The coating materials were FEP (white powder; melting point, 250-280°C; provided by Shanghai Organic Fluorin Research Institute) and PPS (yellow powder; melting point, 280-290°C; provided by Dupont). The filling was TiO_2 (chemically pure); the dispersion mediums were deionized water, industrial spirit and n-butyl alcohol.

2.2 Preparation of coatings

In order to eliminate the effect of surface pretreatment on the bonding strength of coatings, oil and rust removal were carried out for all the samples followed by coarsening with 30# emery cloth before the coating processes.

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The following 6 coating systems were designed for the experiment (the components of each layer is shown in **table 1):**

(1) Pure FEP coating (surface layer);

(2) PPS coating (bottom layer);

(3) FEP/PPS blend coating (intermediate layer 1);

(4) Bottom layer + surface layer;

(5) Bottom layer + intermediate layer 2 + surface layer;

(6) Bottom layer + intermediate layer 1-3 + surface layer.

Table 1 Components of each coating wt%

Coating	FEP	PPS	TiO_2
Surface layer	100	0	0
Bottom layer	0	75	25
Intermediate layer 1	35	50	15
Intermediate layer 2	60	30	10
Intermediate layer 3	85	10	5

First, FEP, PPS, TiO_2 and the dispersion medium were mixed in proportion according to the components of each coating, then ground in a ball grinder for 48 h to ensure that all the components were mixed uniformly. The prepared suspension liquid was dried to obtain powders.

The step for preparing coating with FEP and FEP/PPS powder is as follows.

Samples (pretreated)→preheating→powder coating →melting and curing→quenching

In order to obtain multilayer composite coatings, powder coating, melting and curing must be repeated several times.

2.3 Measurements

Tensile test was used to measure the bonding strength of the coatings in a Digital Tensile Testing Machine LYS-50000. Because it is difficult to find proper adhesive for fluororesin coating, the tensile test was conducted with reference to the relevant reference [9], *i.e.* butt-jointing 2 samples during the coating process when the coating material was melting; after quenching the coupled samples were formed and tested (see **figure 1).** The bonding strength of coatings to the steel substrates was determined based on the specific failure load between the coating/samples interface. For the samples after pull-off, features of the section were observed and photographed with a digital camera Nikon COOLPIX995.

The coating system 6 (5-layer graded FEP/PPS coating) was examined with EPMA JXA-8800R and energy dispersive spectrometer (EDS). The distribution of components on the cross-section was analyzed for this composite coating.

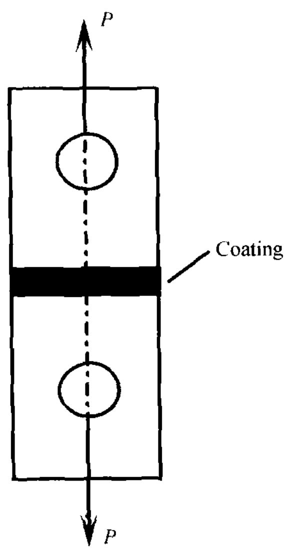

Figure 1 Coupled samples for tensile test.

3 Results and discussion

The bonding strength and failure styles of the coating systems tested are shown in **table 2.**

Table 2 Bonding strength and failure style of the tested coating systems

Coating system	Average thickness / mm	Average bonding strength / MPa	Failure style
1	0.17	3.62	Smooth failure of coating/substrate
2	0.18	38.3	Cohesive failure of coating
3	0.15	8.31	Failure of coating/substrate
4	0.26	2.72	Interlayer failure of bottom/surface layers
5	0.32	4.34	Interlayer failure of bottom/intermediate layer 2
6	0.51	11.8	Failure of coating/substrate

3.1 Bonding strength of the single-layer coating

For comparison, tests were conducted on the bonding strength of a single layer, including surface layer (pure FEP coating), bottom layer (PPS coating) and intermediate layer 1 to the substrates. As shown in table 2, the bonding strength of the surface layer to the substrates is only 3.62 MPa with a smooth interfacial failure (see **figure** 2), which proves that fluororesin molecules are nonpolar with only a bad mechanical adhesion. The main component of the bottom layer is PPS with an appropriate amount of fillings, cohesive failure occurs for this coating under a load of 12.025 kN (see **figure 3),** and the bonding strength to the metallic substrates is over 38.3 MPa. It was reported in reference [10] that the interface-bonding mechanism of PPS to the metallic substrates is due to some multinuclear macromolecular coordinates formed after the coordination of lone pair electrons of S atoms in PPS with Fe^{+3} in the metallic substrates.

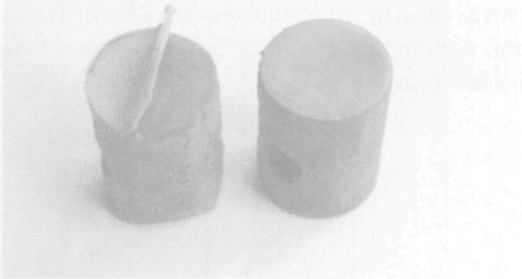

Figure 2 Adhesive failure of FEP coating to the substrate.

Figure 3 Cohesive failure of PPS coating.

As compared with the surface layer, the bonding strength of the modified intermediate layer 1, which was prepared by blending 50wt% PPS, 35wt% FEP and appropriate fillings, increases from 3.62 to 8.31 MPa. The introduction of the blend component PPS obviously improves the adhesion between the coatings and the substrates. However, the blend coating still shows limited adhesion because of the FEP component, so the failure style is interfacial failure between the coating and the substrates. It can be estimated that with the increase of PPS component, the bonding strength of the FEP/PPS modified coating would be further improved. But PPS cannot resist strong oxidation medium during application [11]. If the coatings are used as corrosion-resistant ones in serious conditions, the increase of PPS component will reduce the anti-corrosive performance of fluororesin coatings to some degree. For these reasons, researches were conducted on multilayer FEP/PPS composite coating systems to improve the bonding strength without reducing the corrosion resistance of fluororesin coatings.

3.2 Bonding strength of FEP/PPS composite coatings

The adhesion of PPS to substrates and the corrosion resistance of FEP of the 2-layer (bottom layer + surface layer) composite coating were tested and analyzed in this experiment. It shows that this composite coating always has interface failure between bottom/surface layers under a small load, and that their bonding strength is only 2.7 MPa, lower than that of pure FEP coating to substrates. Obviously, in this 2-layer coating, sudden change of the composition and performance from bottom to surface is the weak point.

Coating systems 5 and 6 are graded coatings designed for this test. The former has a transition layer (intermediate layer 2) between the bottom and the surface. As seen from table 2, the introduction of this intermediate layer gives rise to the improvement of the bonding strength from 2.72 to 4.34 MPa, the failure style is the interfacial failure between the bottom layer/intermediate layer 2, verifying that the composition is still quite different between these two coatings.

Then, on the basis of the 3-layer coating system, a 5-layer graded coating system, *i.e.* bottom layer + intermediate layers 1-3+surface layer, was designed (coating system 6). It can be seen from table 2 that these graded coatings have a bonding strength of 11.8 MPa, obviously higher than that of the above 2-layer and 3-layer coatings. The main failure style of this 6-layer coating is adhesive failure between the coating/substrate, accompanying with a little cohesive failure, as shown in **figure 4.**

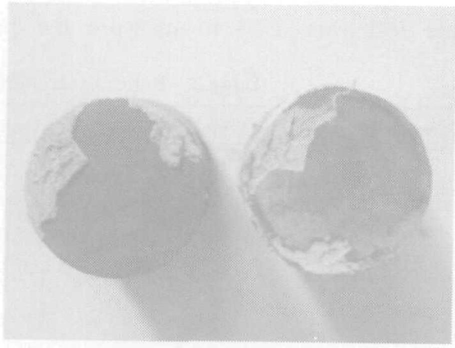

Figure 4 Failure style of the 5-layer FEP/PPS graded coating.

To find out the actual distribution of the main components in this 5-layer coating system, composition microanalysis was performed by using EPMA JXA-

8800R and EDS.

3.3 Microstructure and component distribution in the 5-layer graded FEP/PPS composite coating

Figure 5 shows the EPMA result of a 5-layer graded FEP/PPS composite coating. Figure 5(a) is the cross-section micrograph of the coating (the light color area at right was the substrate), from which it can be seen clearly that the coating has 3 zones, bottom, transition and surface layers. From the coating/substrate interface, the bottom layer bonds tightly with the substrate, and no defects such as foreign substances and air holes can be observed, indicating that the bottom layer melts and flats well during the coating process. This contributes to the improvement of the bonding strength to some degree.

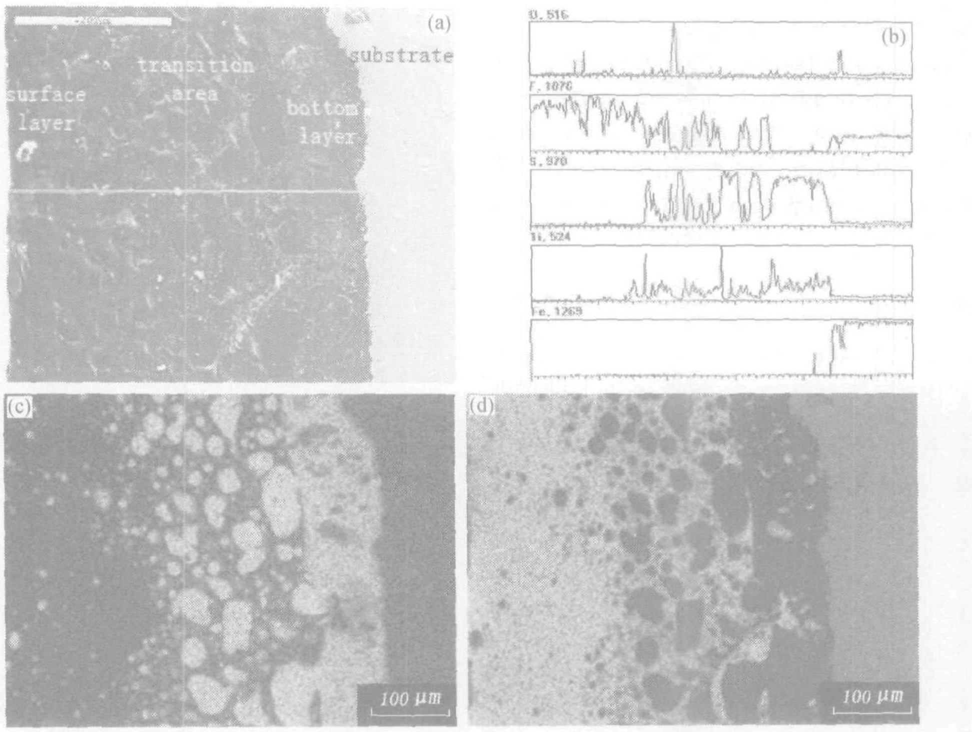

Figure 5 EPMA images: (a) cross-section micrograph of the graded FEP/PPS coating (five layers); (b) linear scan microanalysis profiles of main elements; (c), (d) planar scan microanalysis profiles of S, F.

Figure 5(b) is the linear scan microanalysis profiles of the main elements across the coating shown in figure 5(a). The distributions of S and F are opposite from the substrate to the left. The content of S, representing the PPS component in the coating, is higher in the bottom layer, implying that PPS is the main component. In the transition layer, PPS decreases gradually to zero in the surface layer. The change of F content represents the distribution of FEP component in the coating. The content of F increases gradually in the transition layer till the surface layer made fully of FEP. The distribution of element Ti representing fillings in the coatings is approximately graded.

Figures 5(c) and (d) are planar scan microanalysis profiles of S and F, respectively. From 5(a), (c) and (d), the structure of the graded transition layers can be obviously observed in the 5-layer composite coating. The transition layer is the FEP/PPS blend coating. These pictures clearly illustrate the biphase structure of the blend, in which PPS is the dispersive phase and FEP is the continuous phase. Granular PPS, with the size decreasing from right to left, distributes uniformly in FEP.

The EPMA results demonstrate that the introduction of 3 intermediate layers bring about the graded coating structure from bottom to surface in the composite coating system, resulting in the effective decrease of the difference between the neighbor layers and the promotion of the bonding strength.

As stated above, the graded FEP/PPS composite coatings, on one hand, effectively improve the adhesion of fluororesin coatings owing to the increase of transition layers, on the other hand, the failure style is adhesive failure between the bottom layer and the substrate with a bonding strength of 11.8 MPa for the 5-layer coating system in this experiment. This can be explained that every coating should melt and cure at high temperature for multilayer coatings. Long time curing the bottom layer might result in the excessive crosslink and the reduction of the bonding strength to metallic substrates.

4 Conclusion

The poor adhesion of fluororesin coatings to metallic substrates was improved effectively by introducing the blend component PPS. The FEP/PPS blend single-layer coating with 50wt% PPS has a bonding strength of 8.31 MPa. In graded FEP/PPS anti-corrosive coatings, the bonding strength improves gradually with increasing the intermediate layers and the continuous change of the components from bottom to surface. For the 5-layer coating, the bonding strength may reach 11.8 MPa. However, more coating layers cause more coating process and more difficulties in application. Meanwhile, the multilayer-coating process also has negative effect on the bond between the coatings and the substrates.

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