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Study and prediction for the fire resistance of acid corroded intumescent coating

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Abstract

Acid corrosion may cause the deterioration of the fire resistance of the intumescent fire retardant coatings, especially for the coatings used in the acid polluted environment. This paper reported the results of an experimental study of degradation in fire protection performance of intumescent coating for steel elements after different times of immersion in the hydrochloric acid solution. After acid erosion, the thickness of the coating thinned, the surface became rough and had cracks and broken holes. The size of the pores in the char layer was larger and uneven, and some 'cement' parts were formed in the char layer. The TG/DTG results showed in the low temperature stage the curve was relatively flat. In the medium temperature stage, the number of the weight loss troughs decreased; the shape of the troughs simplified; and the top weight loss rate increased. In the high temperature stage, the troughs near 593 °C flattened gradually, and the top weight loss rate became smaller, while the top weight loss rate became larger around 674 °C. And there were significant changes in the thermal dynamic parameters. A prediction method of remained fire resistance property for the acid erosion coatings was proposed, by comprehensively considering the physical and chemical characteristics change trends of the corroded coating. And this method can be a reference for the fire safety evaluation of the built protected steel structure.
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Keywords: acid corrosion; intumescent fire retardant coating; fire resistant performance; thermogravimetry analysis; prediction method

1. Introduction

Steel elements are widely used in the industrial and civil buildings due to their unique advantages, such as high

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strength, good plasticity and toughness characteristics, light weight, simple manufacturing process, short construction time and good economic benefit. However, the high temperature performance of the steel elements is not ably poor. The strength and the elastic modulus decrease rapidly at 400 ℃, and the yield strength is less than 30% of the strength at room temperature. In addition, because of the low thermal conductivity, the heating speed of the steel elements is notably fast under the conditions of fire. All of the above causes lead to only approximately15 min of fire resistance of the steel elements if they are not protected by protection measures [1].

To enhance the fire resistance of the steel elements buildings and guarantee the safety of personnel, property and buildings, fire protection measures are required. Using a certain thickness of fire retardant coating is one of the commonly used methods, and intumescent coating is preferred due to the use of only a thin layer and its good decoration characteristics. Whereas the occurrence of fire is random, it may occur after one year of the application of the coating, or even ten years and longer. Whether the performance of the fire retardant coating remains as the original coating must be considered.

There are many reported research studies in the open literature concerning the durability of coatings [2−7]. However, the studies on the long-term fireproofing of fire retardant coatings are relatively few. Sakumoto et al. conducted some accelerated tests and small-scale heat tests, and based on their results they proposed a new testing method for evaluating the durability of intumescent coatings by considering the high-temperature and high-humidity weather conditions in Japan [8]. In the work of Roberts et al., Shell UK performed a long-term passive fire protection weathering program at a maritime test site using furnace tests to assess the fire performance of the materials [9]. Ling-ling Wang reported the results of an experimental study of degradation in the fire protection performance of two types of intumescent coatings after different cycles of accelerated hydrothermal aging tests and were proposed an aging mechanism according to the experiment results [10]. Jimenez et al. studied the fire performance deterioration of an intumescent coating(which contains epoxy resin, ammonium polyphosphate, melamine and titanium dioxide) in three different accelerated aging conditions (80% moisture atmosphere at 70 °C for 2 months and a static immersion bath with and without NaCl (5 g/L) at 20 °C for 1 month) [11].

With the development of industrialization of human society, an acidic atmospheric environment has become one of the problems of greatest concern. Acid atmospheric precipitation is formed when specific pollutants combine with water or dust particles in the atmosphere. By far the largest contribution to this problem arises from sulfur dioxide (SO_2), a by-product of fossil fuel combustion. Sulfur dioxide becomes oxidized to H_2SO_4, which accounts for 62−79% of the acidity of rain. Most of the remaining acid is from the nitrogen oxides (NO_x), produced mainly in automobile exhaust gas, that are oxidized to HNO_3 (15−32%). In addition to these two main species, HCl (2−16%), produced by burning coal, is also found in the atmosphere [12]. In the actual projects, the main acid media that corrode the fire retardant coatings for outdoor use are acid rain, dew, fog and dust. In particular, for petrochemical enterprises, the acid corrosive effects are much more significant due to the emission of a large amount of acidic gases. For example, in the summer of Jacksonville, a port city in the U.S., the pH of the rain was in the range of 3.5 to 5.5 [13]. Therefore, in this paper, a study of the acid durability of the intumescent fire retardant coating is presented, and a method for predicting the residual fire resistance is proposed. The results of this paper serve as a reference for the correct use of the fire coating in a heavily corrosive environment.

2. Experiment

2.1. Specimen preparation

The fire retardant coating used in this study was a solvent intumescent coating for outdoor steel structure. The base material of the coating was acrylic resin, and the functional pigments of the retardant system were ammonium polyphosphate (APP), melamine (MEL) and pentaerythritol (PER).The specimen substrate was Q235 steel plate of 80 mm×40 mm×1.2 mm. Before brushing the coating, the steel substrates were cleaned thoroughly. The interval between the coating layer and the whole thickness were according to the instructions of the product. The thickness of the dry coating layer was 0.7 mm. The specimens were in held for 30 days in the condition of 20±5 ℃ and RH60%±10% after the coating was applied. Next, the edge and back sides of the specimens were sealed by a mixture of rosin and paraffin (1:1 in weight).Under the same conditions mentioned above, the sealed specimens were held for 24 hours. Subsequently, two-thirds of the specimens were immersed vertically in a hydrochloric acid

solution (3% in weight) [14] for 8 h, 16 h, 24 h, and 72 h. All the specimens were dried in the laboratory conditions before testing.

2.2. Testing equipment and conditions

To investigate the acid erosion mechanism of the intumescent fire retardant coating, the fire resistance, the morphologies of the coating and char layer, the composition of the elements, and the thermal stability of the different erosion time specimens were tested.

The fire resistance of the intumescent coatings of the acid treated samples was tested by a small-scale fireproof testing furnace [15]. Fig. 1 shows the sections of the furnace used. During testing, the uncoated sides of two specimens were attached at the lower end of the respective sides of a cooling chip, which was made of steel or heat-resistant alloy. Wire was used to combine the cooling chip and the two samples covering the sides of the cooling chip together. The cooling chip and the two samples were placed onto the bracket in the furnace vertically. One thermocouple was placed in the groove of the cooling chip to measure the back-side temperature of the specimens, and another thermocouple was placed in the furnace to monitor the temperature of the furnace. The time-temperature curve in the furnace is in accordance with the ISO 834 standard curve. The time when the back side temperature of the samples reaches 538 ℃ is defined as the fire-resistance time.
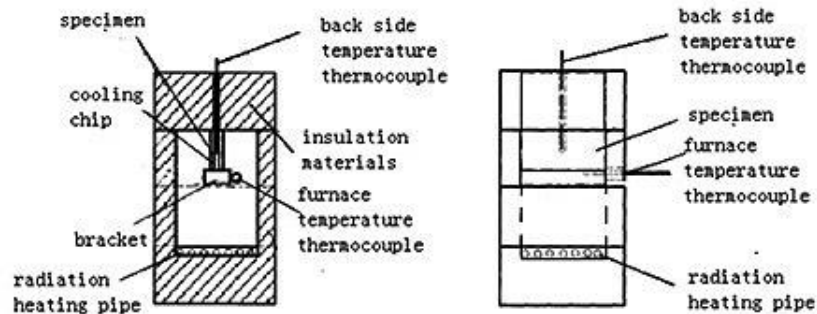

Fig. 1. Sections of the fire retardant coating testing furnace.

After emission in the acid solution for some hours, the apparent morphology of the specimens differs from that of the original ones. To observe the morphology clearly, a scanning electron microscope (SEM) was used at a magnification of 500 ×. The fire performance of the intumescent coating is not only determined by the composition, thickness, and strength of the foamed char but also the morphology of the char. The alteration of the char morphology could be one of the main causes leading to the deterioration of the coating fire resistance. In this study, the morphology of the foamed char layer was investigated using the stereo microscope at a magnification of 100 ×.

The elements and groups contained on the surface of the samples were measured using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy to understand the changes of the molecular structure in the process of erosion. The thermal stability and kinetic parameters of the thermal decomposition of the erosion samples were studied using thermogravimetry, in which the reaction gas was air, the test temperature range was from room temperature to 800 ℃ and the heating ratio was 10 ℃/min.

3. Experimental results

3.1. The surface morphology of the coating after erosion

Compared with the original coating sample, the surface of the specimens following acid erosion appeared rougher and thinner. Measuring the thicknesses of the two points that were near the dent, the difference was the thinning of

the coating. Five pairs of points were measured, and the average of the differences was used as the final thickness measured. Table 1 shows the thickness of the coatings after different periods of acid erosion. The loss rate of the coating is the amount of thinning of the coating per hour.

Table 1. The thickness of the coating after different periods of acid erosion.

Erosion time (h)	8	16	24	72
Thinning thickness of the coating (μm)	63.3	79.6	103.8	195.1
Loss rate of the coating (μm/h)	7.9	5.0	4.3	2.7

To investigate the changes of the surface morphology, the coating surface after different acid treatment times were observed using the SEM. Fig. 2 shows the surface morphology at a magnification of 500 ×. From the data shown in Fig. 3 indicate that the surface of the untreated coating is relatively smoother compared to the acid treated surfaces. The base resin covered and bonded the surface of the pigments and fillers continuously in the untreated coating. However, the corroded specimen surface was no longer flat and some particles appeared. After 24 h of corrosion, the particles became smaller and were fewer in number. In addition, some cracks and broken holes could be observed in the corroded samples surface.

Analysis of the data suggested that the particles in the coating surface were the fillers of the retardant system, mainly ammonium polyphosphate (APP), melamine (MEL) and pentaerythritol (PER). The APP is hydrolytic and produces ammonium ions (NH_4^+) and pyrophosphate in a corrosive environment [16]. The process of the hydrolysis would be catalyzed by the action of the NH_4^+ and Cl^- in the hydrochloric acid solution, leading to the production of ammonium chloride. The process of hydrochloric acid penetrating into the coating and the process of ammonium polyphosphate migrating to the surface occurred simultaneously. With increasing corrosion time, the consumption of the ammonium polyphosphate increased gradually, while the migration speed decreased. As a result, in the final period of long time erosion, the action was mainly between the hydrochloric acid and the APP in the coating surface, which caused the particles of APP to become smaller.

In the meantime, ammelid, ammeline and cyanuric acids are produced due to the action of MEL and hydrochloric acid. All the new products are water-soluble, which reduced the content of the MEL in the coating. PER also exhibits a degree of water-solubility, so as with the other two fillers, the migration to the surface and the consumption occur during the immersion process. In the immersion process, the hydrochloric acid and water would penetrate into the coating through the gap between the coating compositions; in addition, the coating fillers migrated to the surface, so that the coating swelled and became soft and the volume became larger. After the specimens were removed from the solution, during the period of the drying of the specimens, the absorbed water evaporates and the coating layer shrinks and becomes hard, eventually forming cracks. Broken holes would form after the drying process if spherical bubbles were produced during the coating swelling and softening. The coating surface is no longer continuous and integrated due to the presence of the cracks and holes, which affect the mechanical properties of the coating.

3.2. The fire resistance of the coating after erosion

When the specimens met the prescribed corrosion time, they were moved from the hydrochloric acid solution and then dried under laboratory conditions. Before conducting the fire resistance test, the mixture layer of rosin and paraffin was removed. Fig. 3 shows the back side temperature of the samples with testing time. For different erosion time samples, the trends of the temperature rising was found to be similar in the early 400 seconds, but the behaviors became quite different in the later stage.

a. Untreated coating surface

b. Coating surface after 8h erosion

c. Coating surface after 16h erosion

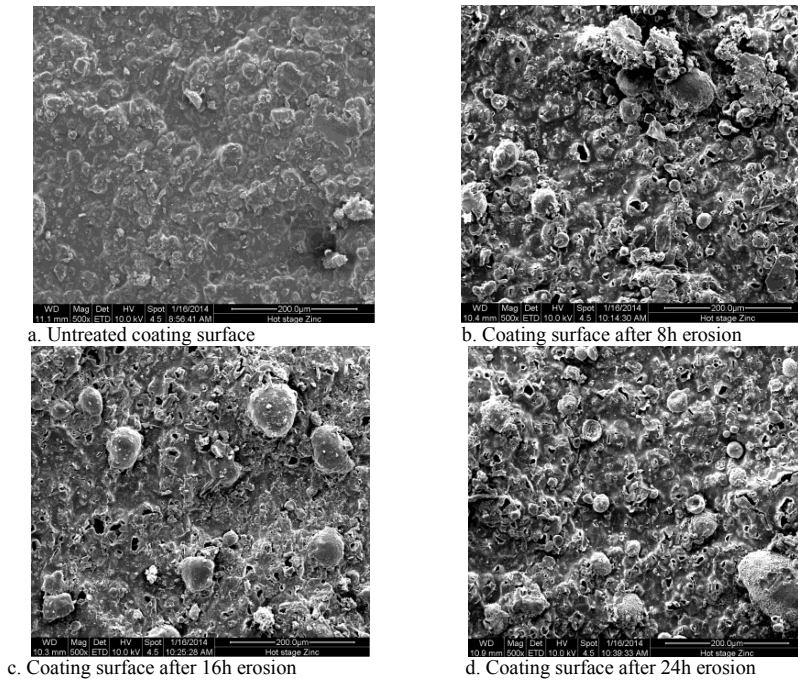d. Coating surface after 24h erosion

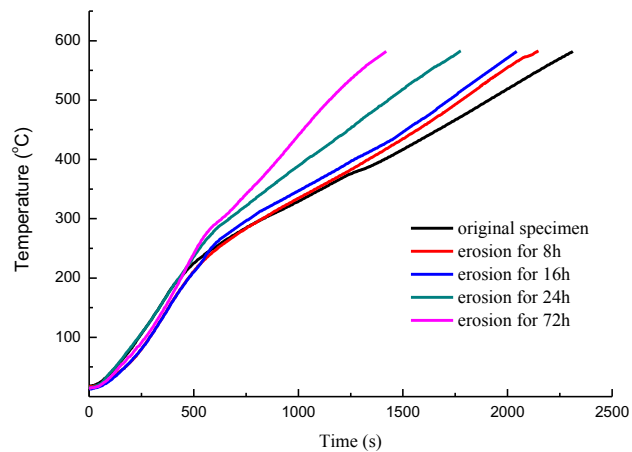Fig. 2. The surface morphology after different times of erosion.

Fig. 3. The back side temperature of specimens vs. time.

The fire resistance performance of the intumescent coating is affected by the thickness and the morphology of the char layer. The thicker, more compact, and stronger is the char layer, the longer is the fire resistance time. As a result, to investigate the alteration of the fire property of the coating due to acid corrosion, in addition to testing the fire resistance time, the thickness and the morphology of the char layer must be measured. Table 2 presents the fire resistance time and char thickness of the coating after different times of acid erosion.

Table 2. The fire resistance time and char thickness of the coating after different times of acid erosion.

Erosion time (h)	Fire resistance time	Aging rate (%)	Untreated layer		Erosion layer	
			Thickness of the char (mm)	Expansion rate	Thickness of the char (mm)	Expansion rate
0	39′25″	-	29.2	39.6	-	-
8	35′46″	9.3	27.5	37.2	23.6	31.8
16	33′27″	15.1	27.2	36.8	16.6	24.8
24	29′43″	24.6	26.8	36.2	13.6	20.9
72	24′06″	38.4	22.4	30.1	Not expansion	-

The aging rate reflects the fire resistance time variation amplitude of the samples after acid corrosion. From Table 2, along with the immersion time in hydrochloric acid solution prolonged, the fire resistance times of the coatings are found to gradually shorten and the aging rates are found to increase. The fire resistance time of 39′25″ of the original sample was shortened to 24′06″ for the sample after erosion for 72 h, with an aging rate of 38.4%. Because, in this study, the samples were not immersed in the acid solution completely, only two thirds of the length of each sample was corroded; therefore, the fire resistance times listed in the table are longer than the times for samples whose lengths are entirely corroded and the aging times are smaller.

In the same initial thickness of the coating, the higher the expansion rate, the thicker the char layer is and the slower the heating rate of the protected substrate is; correspondingly, the fire resistance performance is improved. The initial thickness of the untreated coating is the coating thickness before erosion and the initial thickness of the corroded coating is the reduced thickness of the sample after erosion.

3.3. The thermal analysis of the acid corroded coatings

3.3.1. The thermal gravity analysis of the acid corroded coatings

For the fire retardant coating, studied in this paper, has nearly dozens of effective components, the thermal decomposition process of the coating is very complex. As can be seen from its TG/DTG figure (Fig. 4), there were six stages in the decomposition process, which fully reflected the variety of physical and chemical changes in the heating process. In the weightlessness stages of 206−242 ℃ and 242−272 ℃, the decomposition occurred mainly in the APP, MEL, PER and chlorinated paraffin, and little amount of water, ammonia, methane and hydrogen chloride gas were released. The top weight loss rate temperature was 226 ℃ and 248 ℃ respectively, and the cumulative weight loss of the two stages was 5.06%. In the range of 272−380 ℃, the main chemical reaction was between the APP and PER, in which much of water, ammonia gas were produced. What is more, in this stage, the MEL, base resin and chlorinated paraffin decomposed too. Therefore, besides the relatively big trough at 291 ℃, there were four small troughs in the period of 300−380 ℃. The whole weight loss of the stage was 23%. The further decomposition and oxidation of base resin and chlorinated paraffin, in addition with the further reaction between the decomposition products of APP and PER, were occurred in the stage of 380−556 ℃. The top weight loss rate temperature was 389℃, and the cumulative weight loss of the stage was 17.9%. In the stage of 556−641 ℃, the phosphate, generated in the former stage, decomposed continually. The top weight loss rate temperature was 593 ℃, and the weight loss was 12.9%. In the last stage of 641−804 ℃, the C element contained in resin and PER was oxidized to CO_2, and the top weight loss rate was at 674 ℃, the weight loss was 8.61%

As mentioned above, some active components were lost when immersed in the hydrochloric acid solution. For example, the APP had a hydrochloric acid catalyzed hydrolysis; the MEL was corroded by the hydrochloric acid and chemical changes were taken place; some amount of PER was dissolved in the solution. All of these phenomenons would cause the deterioration of the fire resistance of the coating. By the thermal analysis of the samples with different time of erosion and comparing the changes, not only the internal reasons can be found, but also the evaluation method for the coating erosion degree could be established.

Fig. 4 shows the TG/DTG curves of samples with different erosion time. For the TG curves, looked from the

whole, the corrosion time had little effect on the thermal decomposition processes of the coatings. Especially lower than 400 ℃, there were little difference between the curves. Although there were slightly differences in the stage of 400−600 ℃, the overall trends were consistent. But for DTG curves, the corroded coating samples were quite different from the untreated one in trough number and size. In order to facilitate the analysis of changes at various stages, the DTG curve were divided into three temperature stages, which were low temperature stage (30−260 ℃), medium temperature stage (260−420 ℃) and the high temperature stage (420−800 ℃), as shown in Fig. 5, 6 and 7. The following for each temperature section is analyzed. The comparing analysis for each of the stage was conducted in the following sections.

In the low temperature stage, there were two main differences between the corroded samples and the original sample. One was that, before 175 ℃, there was an obvious weight loss trough, and the peak temperature was about 100 ℃. This difference was caused by the adsorbed moisture of the coating during immersion in the acid solution. The other difference was that, between 175−260 ℃, the untreated sample had two fast weight loss trough, while the weight loss rate of the corroded ones in this stage was slow, and the trough was not clear or even without trough. This change illustrated that, after the erosion of the acid, the APP, PER and MEL were lost in certain amount.
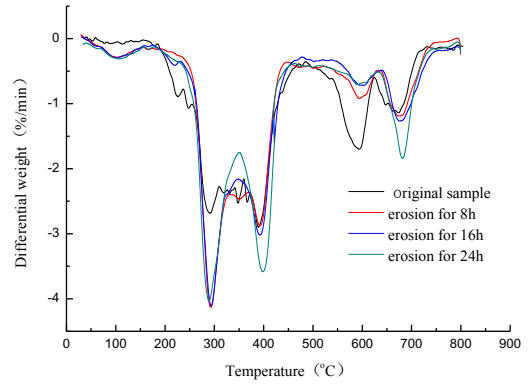
In the medium temperature stage, the coatings, with different corrosion degree, varied in the number and size of weight loss trough. The virgin sample had four weight loss troughs because of its complex reaction process. The sample, corroded for 8h, contained three weight loss troughs, and the middle trough was not obvious. There were only two troughs in the DTG curves of samples corroded for 16h and 24 h. This demonstrated that in this stage, with the immersion time prolonged, the reaction between each component simplified, and had the trend of single component decomposed. The four top weight loss rates were between -2.5−-2.9 %/min; the two obvious top weight loss rates of the sample for 8h erosion were -4.1 %/min and -2.9%/min respectively; the two top weight loss rates of the sample for 16 h erosion were -4.1 %/min and -3.0 %/min respectively; and the two for 24 h erosion were -4.0 %/min and -3.6 %/min respectively. At this stage, due to the loss of the fire retardant system during the corrosion, the reaction process was relatively simple and concentrated. Besides the decomposition of the residual APP, PER, MEL and their reaction products with acid (corresponding to the trough at 290 ℃), the main reaction materials were acrylic resin and chlorinated paraffin (corresponding to the trough at 390 ℃). Because of the loss the APP, PER and MEL, the relative content of acrylic resin and chlorinated paraffin increased, and the rate of weight loss had an increasing tendency. The phenomenon that with the erosion time prolonged the top weight loss increased, also showed that the relative content of the resin and chlorinated paraffin increased.

In the high temperature stage, the weight loss rate trough number was consistent for different corrosion degree of coatings, that all samples had two obvious weight loss rate troughs. However, the corresponding value of the troughs changed regularly with the erosion time prolonged. The weight loss rate trough value (absolute value) around 593 ℃ became smaller with the erosion time increasing, but became larger near 674 ℃. The top weight loss rate of the untreated sample around 593 ℃ was -1.7 %/min, while the top weight loss rates of the samples were -0.92%/min, -0.71 %/min and -0.72 %/min respectively for the erosion time of 8 h, 16 h, 24 h. The top weight loss rates of the samples were -1.14 %/min, -1.19 %/min, -1.27 %/min and -1.84%/min respectively for the original, 8h, 16h, 24h acid erosion specimens. The weight loss trough at 593 ℃ was generated by the decomposition of the phosphate, which produced by the reaction of APP and PER in the former stage. With the erosion time increasing, the contents of the APP and PER were decreased; the produced phosphate decreased correspondingly, and resulted in the lower top weight loss rate in this temperature. The oxidization of the C element contained in resin and PER to CO_2 generated the trough at 674 ℃. After the acid erosion, some active components lost, and the relative content of the base resin increased, which led the higher top weight loss rate at this temperature.

To sum up, with the acid erosion time increasing, the DTG curves changed significantly, which including: in the low temperature stage, the adsorbed water evaporated, and the loss weight was not obvious when the temperature was higher than 200 ℃, and the curve was relatively flat. In the medium temperature stage, the number of the weight loss troughs decreased; the shape of the troughs simplified; and the top weight loss rate increased. In the high temperature stage, the troughs near 593 ℃ flattened gradually, and the top weight loss rate became smaller, while the top weight loss rate became larger around 674 ℃. Thus by compared with the DTG curves of experimental samples, the resistant performance of the unknown coating samples can be roughly predicted.
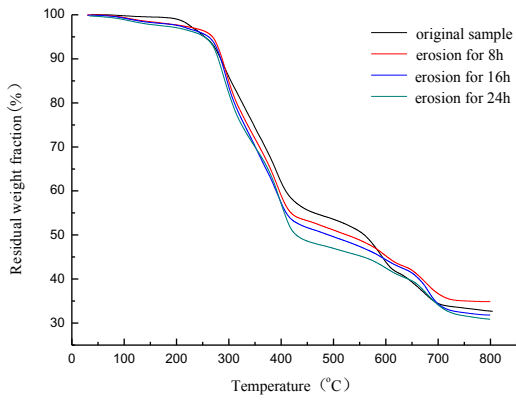
a. TG curves

b. DTG curves

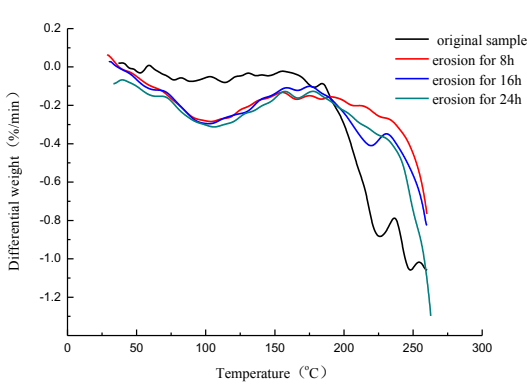Fig. 4. TG/DTG curves of samples for different erosion time.

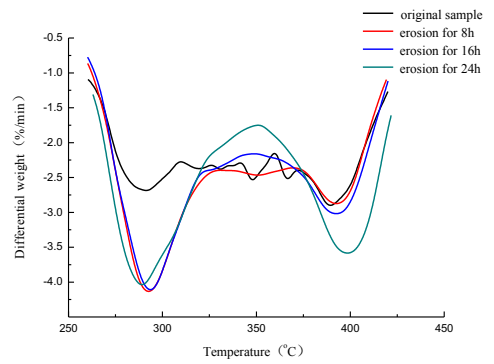Fig. 5. The DTG curves in the low temperature stage.

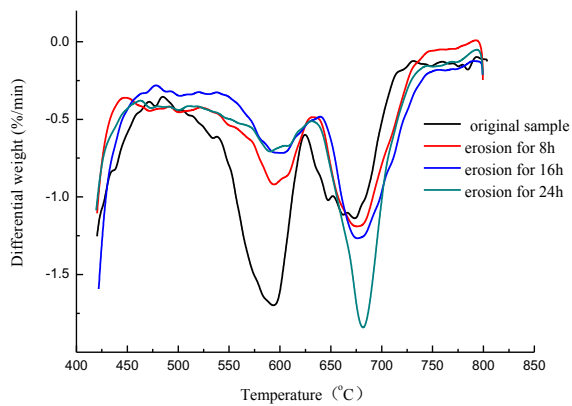Fig. 6. The DTG curves in the medium temperature stage.

Fig. 7. The DTG curves in the high temperature stage.

3.3.2. The thermal dynamics calculation of the acid corroded coatings

According to the data of the TGA curves, the thermal dynamic parameters of the coating during heated can be calculated. As the thermal decomposition of the coating was complex and had multi stages, the MacCallum-Tanner method was used to calculate the thermal dynamic parameters of the coating samples [17]. Table 3 showed the thermal dynamic parameters of the samples with different time of erosion.

Table 3. The thermal dynamic parameters of the samples for different erosion time.

Erosion time (h)	Decomposition stage	Reaction order	Related factors	Activation energy ((kJ/mol)
	low	1	0.93	27.7
0	medium	3	0.99	10.6
	high	3	0.98	14.1
	low	1	0.97	22.4
8	medium	3	0.99	13.6
	high	1	0.97	41.8
	low	1	0.98	14.7
16	medium	3	0.995	14.6
	high	1	0.99	43.4
	low	1	0.99	8.9
24	medium	3	0.99	14.1
	high	1	0.98	39.6

As can be seen from the Table 3, that the reaction orders of the different erosion degree samples were almost the same in the same decomposition stage. In the low temperature stage all the reaction orders of the samples were 1, and 3 in the medium stage. In the high temperature stage except for the original sample was 3 order reaction, all the others were 1. As for the activation energy in different temperature stage, in low temperature stage, the activation energy decreased with the erosion time prolonged. The loss of the APP, PER, MEL during the corrosion process, and the material amount decomposed in this stage decreased, could explain this change. There were not significant changes in the activation energy in the medium stage. But the corroded samples were slightly higher than the untreated one. This was caused by the more content of the materials, which decomposed in this temperature stage, contained in the erosion samples. The activation energy changes were the most remarkable in the high temperature stage. The activation energies of the corroded samples were much higher than the original one, which indicated that the reaction of the corroded samples were significantly different from the untreated sample. Thus by the calculation of the unknown sample, and comparing with the results in this study, the probable fire resistant performance of the sample can be predicted.

4. The prediction of the remaining fire resistance property of the coatings

If the coating type and initial layer thickness were similar to the studied one in this paper, according to the thinning of the coating, the remaining fire resistance property of the coating for certain time acid erosion can be predicted roughly and directly by the data in the Table 2. However, in practical engineering, the fire retardant coating type and thickness are usually determined by the demand of the fire protecting design and are often different. In addition, in this research, the specimens were not completely soaked in the acid solution, which would lead a deviation from the actual situation. Thus, to obtain the fire resistance performance of the fire coating used in the acid corrosion environment over some years, the coating samples extracted from the substrate should be tested by examining the surface morphology and TG/DTG, and the test results should be compared comprehensively with the case studied in this paper. The accelerated acid corrosion time can be determined under the laboratory conditions. The samples, with the same coating thickness as the pro-erosion thickness of the engineering coating, should be completely immersed in the acid solution. The bench scale fire resistance test can be used to determine the

remaining fire resistance time of the fire coating in the actual engineering practice.

Note that, in the testing process, the temperature-time curve in the test furnace should be calibrated according to the possible fire scenario in which the coating engineering may encounter. For example, the fires that occur in the petrochemical enterprises correspond to hydrocarbon fires (UL 1709), and the fire in common buildings correspond to fiber fire (ISO 834).

5. Conclusions

During the process of the acid corrosion, some components (especially the pigments of APP, PER and MEL) of the intumenscent fire retardant coating lost due to the dissolution, acid catalyzed hydrolysis and chemical reaction with the acid, which resulted in the deterioration of the fire resistance property. Meanwhile the proportion changes of the pigments, caused by the migration of the concentration gradient, could also affect the fire resistance performance of the coating.

When the coating surface and char layer morphology were concerned, after the acid erosion, the thickness of the coating thinned, the surface became rough and had cracks and broken holes.

The thermogravimetry and differential thermogravimetry were conducted for the samples scraped from the coating surface. And found that in the low temperature stage the curve was relatively flat. In the medium temperature stage, the number of the weight loss troughs decreased; the shape of the troughs simplified; and the top weight loss rate increased. In the high temperature stage, the troughs near 593 ℃ flattened gradually, and the top weight loss rate became smaller, while the top weight loss rate became larger around 674 ℃. And there were significant changes in the thermal dynamic parameters.

A prediction method of remained fire resistance property for the acid erosion coatings was proposed, by comprehensively considering the physical and chemical characteristics change trends of the corroded coating. And this method can be a reference for the fire safety evaluation of the built protected steel structure.

Acknowledgements

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