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Application of Fractal Dimension on Electrochemical Corrosion Behavior of Steel Wire

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In order to apply the fractal dimension to the research on the wire corrosion behavior, this paper observed fractal dimensions of the wire corrosion surfaces in different immersion mediums. The relationship between the fractal dimension and parameters of weight loss and electrochemical corrosion were studied, and the reliability of fractal dimension in the analysis of electrochemical corrosion behavior of steel wire was focused on. The results show that the weight loss rate in acidic solution has always been the largest during the whole soking, the effect of different solutions on wire corrosion characteristics was getting smaller and smaller with the increase in immersion time. The corrosion current density curve has the similar trends with the weight loss rate curve in the same solution, which reflecting the test reliability and the variation of the wire corrosion rate. And the fractal dimension curve also have a consistent variation with the first two curves, which indicating that the fractal dimension of corroded wire surface can well reflect the variation of the wire corrosion behavior.

Keywords: Steel wire; fractal dimension; weight loss rate; corrosion current density

1. INTRODUCTION

In 1975 , in order to express the complexity and nondifferentiable of the curve the American French mathematician Mandelbrot proposed the concept of fractal dimension ,which can solve the descriptors of those irregular rough shapes and can measure the irregularity of component surface. Fractal dimension D can reflect the intensity of the changes in the amplitude of the surface morphology, i.e. the large D value showed a large variation of the surface amplitude, and vice versa.

During the study of corrosion behavior, in addition to the measurement methods such as weight loss, electrochemical parameters and etc, fractal dimension, as a means of characterizing materials surface complexity and uneven morphology in corrosion, is more and more widely applied to the corrosion behavior. The morphology as one of the important characteristics in material corrosion, has been used to evaluate the extent and level of corrosion [1]. Therefore, the study on the corrosion morphology is of significance to analyze the extent of corrosion and to explore the corrosion law.

Since Mandelbrot's fractal geometry theory [2, 3] provided a new way to study irregular surfaces, the fractal dimension has been favored by more and more experts and scholars [4-8]. Falconer [9] made a detailed description of fractal in the mathematical view. A.P Pentland [10, 11] used the random fractal model - fractional Brownian motion model for the description of natural texture and got the FBRF model. E. Sarmiento [12] researched the corrosion inhibition of carbon steel in a bromide solution by fractal analysis. Masashi Kurose [13] studied the problem of metal corrosion in salt solution by fractal geometry, and observed that corrosion defects in the surface morphology have fractal characteristics. Jin [14] indicated that the fractal geometry was a non-destructive testing method, and calculated the fractal dimension of the aluminum alloy corrosion surface in two ways. Sarmiento [15] studied the corrosion characteristics of carbon steel in bromide solution with fractal method, and found that the electrochemical signal of carbon steel corrosion was closely related to surface morphology, corrosion inhibitors added amount and the corrosion mechanism. Park [16] have found that the formation and development of the 600 alloy pitting had fractal characteristics, and pitting fractal dimension increased with the increase in corrosive liquid temperature. DONG Yuan et al [17] analyzed and compared the amount of calculation and sphere of application of the commonly used image fractal dimension algorithm, and found BB Chaudhuri law and Peleg law were better. Weng Yongji et al introduced the application of fractal theory in describing the corrosion behavior and researching corrosion model. He alsocollected [18] the surface measurement data of the carbon steel specimen in the soil corrosion and observed that two-dimensional and three-dimensional fractal dimension values of corrosion images were linearly correlated to etch pit diameter and fractal dimension of pit depth distribution, respectively, and both were approximately equal in value .

Wire rope as a carrying device in coal mine greatly affects the safety and reliability in mine production. In order to apply the fractal dimension to the research on the wire corrosion behavior, we observed fractal dimensions of the wire corrosion surfaces in different immersion mediums. This paper mainly studies the relationship between the fractal dimension and parameters of weight loss and electrochemical corrosion, and focuses on its reliability in the analysis of electrochemical corrosion behavior of steel wire.

2. EXPERIMENTAL

The test specimens were steel wires used in coal mine. According to the statistic pH values of the typical water in coal mine in China, through the analogy of the composition of the water quality in coal mine, we prepared the acid corrosion solution with a pH value of about 3 using $CaSO_4$, $MgSO_4$, KCl, Na_2SO_4, dilute hydrochloric acid and other chemical raw materials, neutral corrosive solution with a PH value of about 7 using $CaSO_4$, $MgSO_4$, KCl, NaCl, Na_2SO_4 and $NaHCO_3$, and the alkaline corrosive solution with a pH value of about 10 by $CaSO_4$, $MgSO_4$, KCl, NaCl, $CaCl_2$, and NaOH. The specific parameters of those solutions are shown in Table 1.

Table 1. Typical water quality of coalmine in China

pH value	Content of ions / mg/L							
	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	D_0
2.97	11.73	92.42	676.55	364.74	28.36	3283.81	18.92	5.60
6.97	11.73	141.16	80.56	49.33	89.33	551.38		5.60
9.97	11.73	35.63	54.43	36.45	89.33	232.95		5.60

Corrosion tests used complete immersion mode, 1 month cycle, and corrosive solutions with three different pH values. Each solution contained seven groups of samples, which correspond to seven time periods. Before soaking accurately, the samples were weighed and the weight recorded using the electronic balance, and the corrosive solutions replaced regularly during tests.

Take out the specimens in corresponding groups in accordance with the corrosive time of 1d, 3d, 7d, 12d, 18d, 24d and 30d, clean the wire surface using alcohol ultrasonic, and wipe them with cotton. After weighing dried specimens accurately, corrosion weightlessness and corrosion weightlessness rate are calculated.

Using the average rate of weight loss to evaluate the specimen corrosion condition, weight loss rate is calculated as

$$v = \frac{\Delta w}{s \times t} \quad \text{..........} \quad (1)$$

Where Δw is the weight loss of the sample, mg, s is the exposed area of the sample, cm^2, and t is the soaking time, h.

The polarization curve of steel wire in different conditions was studied through the classic three-electrode system. To ensure that the sample surface area in the solution is $1cm^2$, the rest of the wire as the working electrode was sealed, with platinum wire as the counter electrode, and the saturated Ag/AgCl electrode as a reference electrode. Then we got the corrosion current density curve of steel wires in different solutions for different time using Tafel extrapolation.

In order to more accurately understand the corrosion morphology of the wire, we carried out another immersion tests. In each of three solutions, respectively, prepare 8 groups of samples, each group of two samples; remove surface rust after immersion using deionized water and alcohol ultrasonic cleaning, and observe the surface corrosion morphology of soked steel wires in three different solutions for 1d, 3d, 6d, 10d, 15d, 20d, 25d, 30d using L-2020A type optical microscope, and measure its fractal dimension.

3. RESULTS AND DISCUSSION

3.1 Weightlessness rate analysis

Figure 1 shows the variation curve of weight loss rate of steel wires immersed in the different solutions with the immersion time. It can be seen from the figure 1, in the acidic solution, the weight loss rate of steel wire gradually decreased with time (in addition to 7d). When soaked for 1d , wire weight loss rate was greater and up to 0.058mg•(cm^2•h)$^{-1}$, then followed by a rapid decrease , after 12d weight loss rate was lower than 0.0306mg•(cm^2•h)$^{-1}$, and during the immersion time of 12d-30d weight loss rate gradually stabilized. At the beginning of immersion, due to the highly corrosive effect of the acidic solution, steel wire surface generated more corrosion products, it is the reason of high weightlessness rate. Gradually, the corrosion product film on the surface of the steel wire played a protective role on steel matrix, whose generation speed and damage speed were consistent, so weight loss rate was maintained at a certain value.

In neutral solution , when soaked for 1d ,the weight loss rate of the wire was lower and only 0.005mg•(cm^2•h)$^{-1}$, but after 3d weight loss rate rapidly increased to 0.03 mg•(cm^2•h)$^{-1}$; when immersed for about 12d ,weight loss rate has been floating on the 0.025 mg•(cm^2•h)$^{-1}$; after immersed 12d , the wire weight loss rate decreased rapidly and stabilized at about 0.01 mg•(cm^2•h)$^{-1}$. The corrosion effect of neutral solution is weak, so at the beginning the weightlessness rate is low.

In alkaline solution, in the early immersion, wire weight loss rate is very small and close to 0. With increasing immersion time the wire weight loss rate slowly increased and up to 0.017mg•(cm^2•h)$^{-1}$ at 18d , then slowly decreased to about 0.01 mg•(cm^2•h)$^{-1}$ and stabilized. That is because of the protective effect of alkaline solution OH$^-$ on steel wire, corrosion was weak. The protective effect of the corrosion products formed on the steel matrix resulted in the lower weight loss rate in the later immersion.

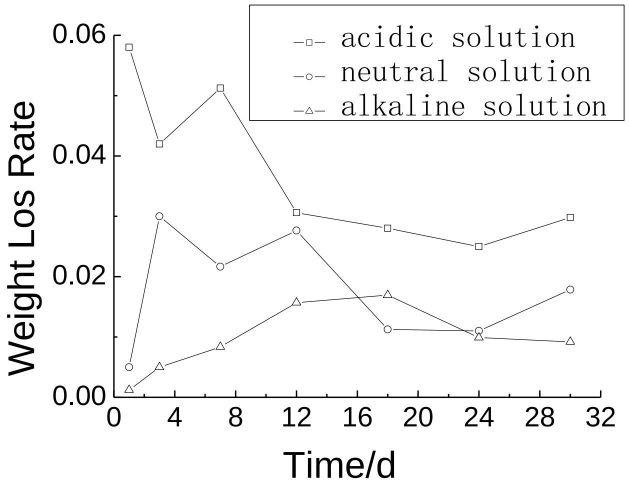


Figure 1. The weight loss rate variation curve of steel wires immersed in the different solutions with the immersion time.

Comparing three solutions , we found throughout the soaking process in acidic solution corrosion weight loss rate is the largest , followed by soaked in neutral solution , and in alkaline solution corrosion weight loss rate was the smallest. Especially at the beginning weight loss was quite different, which also reflect the impact of the different solutions on wire corrosion characteristics. But with the extension of soaking time, the difference of weight loss rate in three solutions is more and more smaller, reflecting that the corrosion product films formed on steel substrate played a certain degree of protection.

3.2 Polarization curve analysis

Different solutions present different corrosion characteristics, but with the immersion time increasing, the differences in corrosion characteristics of the wire in the three solutions were getting smaller and smaller. Figure 2 is the polarization curves of steel wires immersed in the different solutions for different time (1h，24h，96h，168h，240h，312h，432h，562h，720h). From the figure we found that in the acid solution [19], the current of cathode region slowly decreased with potential increasing, and when the potential reached about -0.45V, the current rapidly reduced. In the anode region, with further increase in potential, the current rapidly increased. However, while the potential rised to -0.3V, the current changed slowly, which suggested that at the initial of immersion wire surface didn’t form dense corrosion product film, and the anode reaction process mainly had the anode activation. With the increase in immersion time, the steel polarization curve change significantly. Through observing the cathodic polarization curve of steel wires immersed for 24h-240h, it is found that the current increased rapidly at first and then slowly decreased as the potential rising, which is because the cathode reaction is mainly the reduction of H, i.e. $2H^{+}+2e = H_2\uparrow$ [20]. It can be found from anodic polarization curve in this interval, when potentials from the wire corrosion potential risied, the current presented the rapid increase at first, then slow increase and finally rapid increase again; during this process, the anodic polarization curves showed a platform. Those indicated that when the current slowly increased, the wire surface gradually formed a relatively dense corrosion product film; the corrosion current kept constant and the corrosive rate was relatively slow due to the protective effect of the film on the substrate. When the electrode potential raised to a certain value, the polarization current was maintained stabilized, which is due to the occurrence of similar secondary passivation on the sample surface. We can find from the cathodic polarization curve of steel wires immersed for 312h-720h, the current gradually decreased with increasing potential, but there was no phenomenon that the current sharply reduced at specific potential. That may indicate that H^{+} concentration on the wire surface decreased with the increased immersion time, and the cathodic reaction at this time was: $O_2+4H^{+}+4e=2H_2O$ [20]. In this time interval, the polarization potential still presented a platform in the range of -0.9 to -0.7v and similar passivation phenomenon still existed due to the strong protective effect of the corrosion product film, constant corrosion current and the slow corrosion rate.

After soking for 1h in neutral solution, observing anodic polarization curves, the current density increased more slowly and the potential curvepresented the platform in the range of -0.5V to -0.4V. With the anode potential further increasing, the growth rate of current density became larger. That indicated when the wire was immersed for 1h , though the anodic process still mainly was anodic activation, the dissolution rate of corrosion product film was slower in neutral solution, which played a protective role on the matrix. With the increase in immersion time, the platform area of the anode curve increased; in the range of -0.5v to -0.7v, the growth rate of current density slowed down with increased immersion time, the protective effect of the corrosion product film on matrix gradually increased, and the anode activation gradually weakened. Observing cathode curve in the whole soking process, after soking for 1h, corrosion current density increased rapidly when the potential reduced to -1.0V. As the soaking time increased, the current density also increased rapidly when the potential reduced to a specific value, which indicated that the cathode reaction during the whole process was H restore: $2H^{+}+2e = H_2\uparrow$.

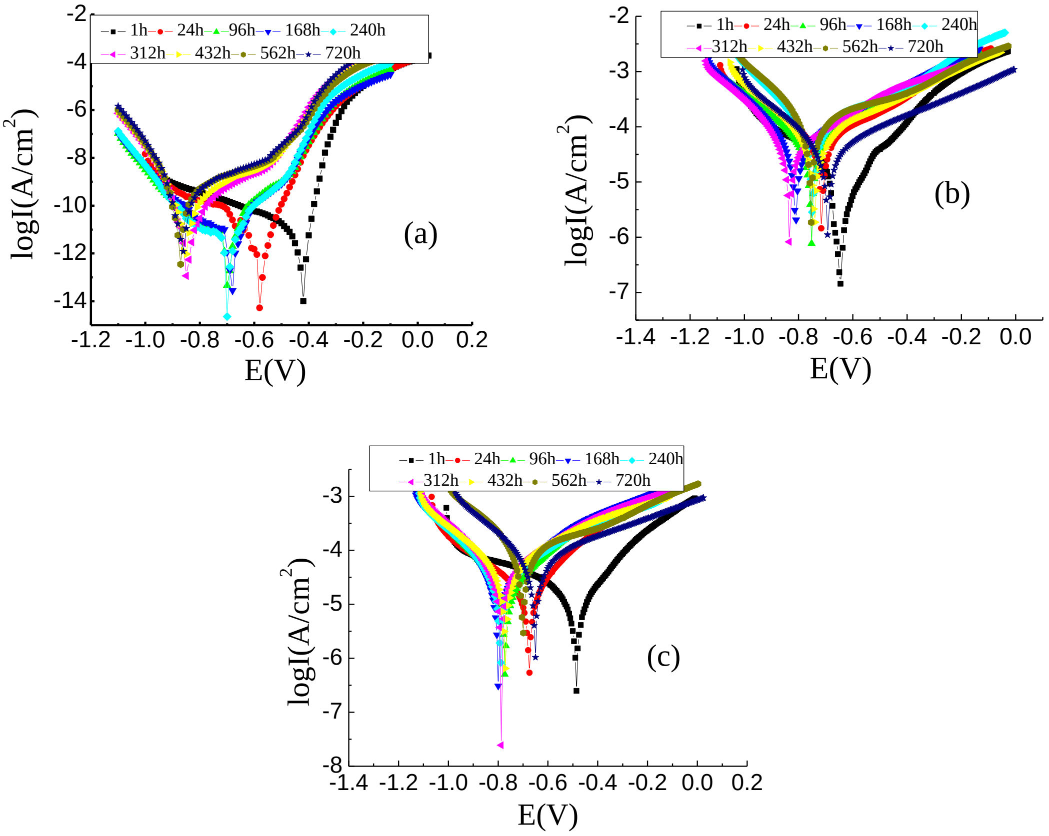


Figure 2. Polarization curves of steel wire soaked in three solutions with the immersion time changing (a) the acidic solution ; (b) the neutral solution ; (c) the alkaline solution .

In alkaline solution, when the wire was immersed for 1h, the anode area curves showed the anodic process mainly occurred anode activator dissolved. With the increase in immersion time, as the anode potential increases the growth rate of corrosion current density gradually reduced due to the protective effect of the corrosion product film on the substrate. During the process of soaking for 24h ~ 432h the open-circuit potential maintained between -0.8v and -0.7v, and during the process of soaking for 562h ~ 720h process the open circuit potential increased to -0.7v ~ -0.6 v .

Through using Tafel extrapolation [21] according to the above polarization curve, we got three variation curves of corrosion current density in different solutions with the increase in immersion time (Figure 3). The figure showed that Icorr rapidly reduced when wire was immersed for 24h in the acidic solution. At the beginning of soaking, the wire surface quickly corroded and formed corrosion products that played a protective effect on the wire surface, but due to the strong corrosive effect of acidic solution, the corrosion product film was very unstable in the solution, which was the significant reason that wire corrosion current density fluctuated largely during the initial 312h. As the soaking time further increased, the formation and decomposition of corrosion products achieved the stability, and corrosion rate gradually stabilized. The change trend of Icorr in neutral solution was similar to that in an acidic solution. However, due to the presence of OH^- in an alkaline solution, Icorr was lower and slowly increased with immersion time during the inhibit process.

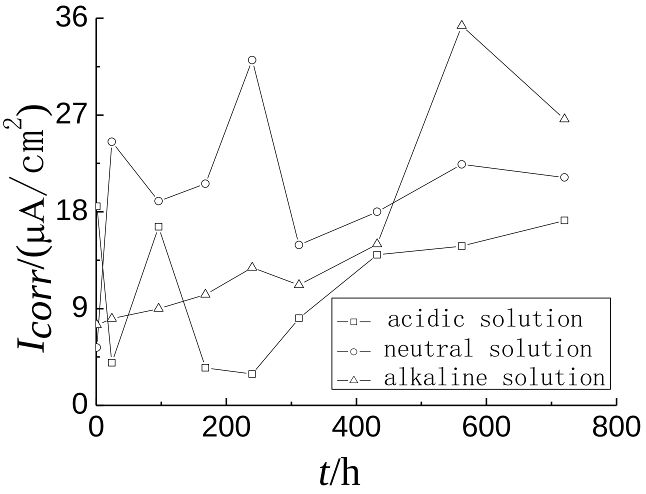


Figure 3. Corrosion current density of the wire immersed in three different solutions for different time

3.3 Fractal dimension calculation and analysis

Using an optical microscope observing the sample macro corrosion morphology, and photos were 640bit × 480bit × 8bit true color digital image. The true-color image was converted to grayscale images using matlab 7.0, then the gray-scale image was stored in a 480 × 640 matrix, where each value represented a gray scale value , and the so called gray value was the integer between 0 (black) and

255 (white). The size and distribution of the gray value in a certain extent reflected the unevenness of morphology of wire corrosion surface.

In this paper, Hausdorff fractal dimension was used to demonstrate the wire corrosion surface fractal dimension which is written as follows.

$$D = \lim_{\delta \to 0} \frac{\ln N(\delta)}{\ln(1/\delta)} \quad \ldots\ldots \; (2)$$

Wherein, N(δ) represents the measured value in scale δ, D is the Hausdorff dimension [22] .

Hausdorff dimension is only suitable for the derivation of the fractal theory and can not directly calculate fractal dimension in the practical application. There are several ways to solve the fractal dimension of the image. Differential box -counting method (DBC) was used to calculate the fractal dimension of the wire immersed in three different solutions for different time.

The principle of DBC method divided the size of M × M pixel image into a size of L × L lattice in accordance with the scale r (L is an integer, $1 < L \leq M/2$). The gray level of the image is as the third dimensional. Cover the entire image with a size of L × L × L' of the lattice in the vertical direction, wherein

$$L' = [L \times G / M] \quad \ldots\ldots\ldots \; (3)$$

G is the number of gray levels in the image. Investigated in each box the column number k of the box smallest gray scale value falled in and the column number l of the box biggest gray scale value fell in, and found it contained the number of boxes [22]:

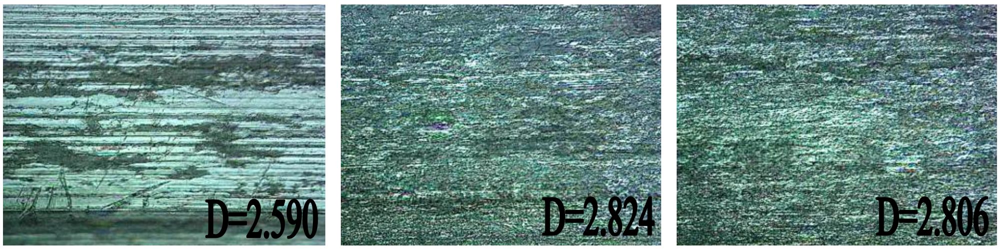
$$n_r(i, j) = l - k + 1 \quad \ldots\ldots\ldots \; (4)$$

All cartridge n_r (i, j) were summed as follows.

$$N_r = \sum_{i,j} n_r(i, j) \quad \ldots\ldots\ldots \; (5)$$

Wherein Nr is the number of boxes calculated by different scales r. Fit the curve of ln (1/r) to ln (Nr) by the least squares method, and the absolute value of the slope is the fractal dimension D of the image.

Figure 4 was the corrosion morphology of wire surface immersed in acid corrosion solution for different time (Using Matlab software process morphology). Figure 4 (a) was surface morphology of steel wire before soaking, from which we could see the wire surface was more bright and had very obvious drawing traces, and the fractal dimension was only 2.590. After soaking for 1 Day, as shown in Figure 4 (b), wire corroded rapidly, presenteda lot of corrosion pits and grown along the wire drawing direction, whose color was deeper than the surrounding part. The wire surface became rough, and the fractal dimension increased rapidly to 2.824. With the immersion time increasing, the fractal dimension didn't increase like the imagination, but there was a decreased trend. That was because wire surface occurred severe corrosion and became uneven in the acidic solution at the initial soking due to chloride ion strong corrosion effect. With the increase in immersion time, the wire surface changed from the serious pitting at the beginning to uniform corrosion.



(a) before immersion (b)1d (c) 3d

(d) 6d (e) 10d (f)15d

(g) 20d (h) 25d (i)30d

Figure 4. The surface corrosion morphology of steel wires immersed in acidic solution for different time (Matlab treatment)

Contrasted to the decreased start measurement value D value, it was still at a high level at a more stable stage.

It can be seen from figure 5,in neutral solution after soking for 1d, the fractal dimension was less (D = 2.763), and the wire surface roughness gradually increased in the process of soaking 1-10d. At the same time, due to the weak corrosion of neutral solution, pitting was less obvious when soaked for 1d, and with the immersion time increasing, pitting had the trend of spreading around. Then the D value maintained at around 2.77, and the morphology failed to large changes. When soaking for 30d, the steel wire surface became more rough and the D value reached 2.809.

(a) before immersion (b)1d (c) 3d

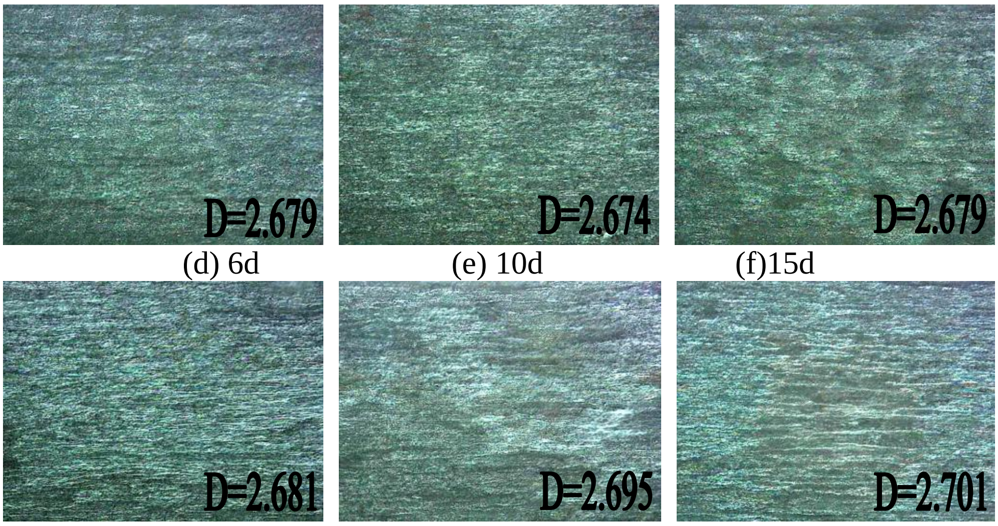
(d) 6d (e) 10d (f)15d

(g) 20d (h) 25d (i)30d

Figure 5. The surface corrosion morphology of steel wires immersed in neutral solution for different time (Matlab treatment)

Figure 6 was the surface morphologies of steel wires immersed in the alkaline solution during different periods, and the wire fractal dimension gradually increased. It can be seen from Figure 6 (b) that after immersion corrosion, there was no etch pits, and wire fractal dimension was lower and reached only 2.662 after soaking for 1d. With immersion time increasing, the surface became a concave-convex undulation and more rough. After soking for 3-15d, fractal dimension had smooth fluctuations. In the late soaking time, the corrosion degree increased, and the fractal dimension also showed an increasing trend.

(a) before immersion (b)1d (c) 3d



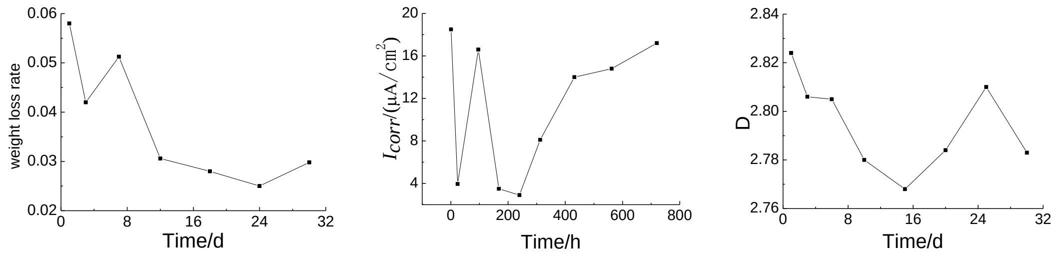
(d) 6d (e) 10d (f)15d

(g) 20d (h) 25d (i)30d

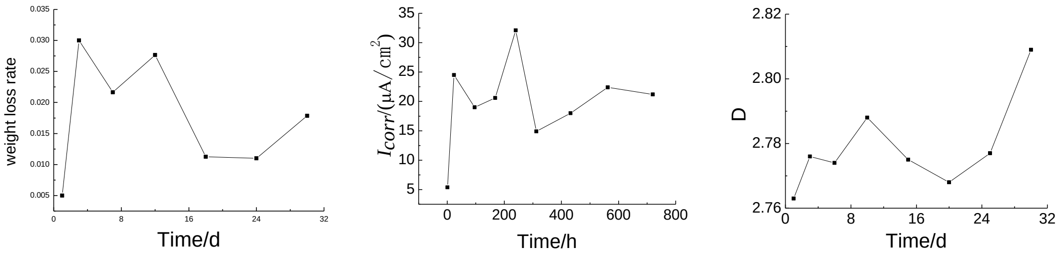
Figure 6. The surface corrosion morphology of steel wires immersed in alkaline solution for different time (Matlab treatment)

3.4 Comparative analysis of weightlessness rate, corrosion current density and fractal dimension

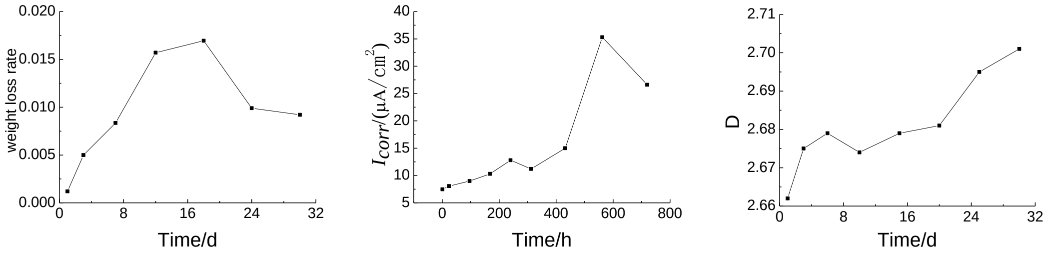
In order to analyze the reliability of the fractal dimension in the corrosion behavior of steel wire, we made the comparisions of the weight loss rate curve, the corrosion current density curve and fractal dimension curve, as shown in Figure 7. We found in different solutions, the wire weight loss rate and the change trend of Icorr were both different. But in the same solution, the weight loss rate and Icorr change trend had very high similarity. The weight loss rate and the corrosion current density curve could represent the corrosion rate at a certain extent, which could embody the test reliability and also reflected the variation of steel wire corrosion rate. Finally, we compared the fractal dimension with the weight loss rate and Icorr curve, and found in the same solution fractal dimension curve had a consistent variation trend with the other two curves, which showed that the fractal dimension of wire surface corrosion morphology could well reflect the variation of the corrosion rate of the steel wire. The literature [23] pointed out that the larger the fractal dimension, the more irregular and the more rough the surface of the image, and vice versa to flatten and smooth. The more serious corrosion, the greater the fractal dimension, but sometimes fractal dimensional didn't increase with the increase in corrosion degree. That was due to uniform corrosion the wire surface. Corrosion pits gradually became not obvious and the surface became "flat", whose corresponding fractal dimension reduced. That is the reason why in alkaline solution at the initial soking, the variation of fractal dimension and weightlessness rate can not be unified.



(a) acidic solution



(b) neutral solution



(c) alkaline solution

Figure 7. Variation curves of fractal dimension, weight loss rate and corrosion current density in different solutions for different time

4. CONCLUSIONS

(1)During the whole soking, in acidic solution corrosion weight loss rate has always been the largest, followed by in the neutral solution, and in alkaline solution the wire corrosion weight loss rate is the lowest. Corrosion product film formed at the beginning and middle term played a certain degree of protection on steel wire matrix. With the increase in immersion time, the effect of different solutions on wire corrosion characteristics was getting smaller and smaller.

(2) The acidic solution has strong corrosion, and the corrosion product film is very unstable in solutions. In neutral solution, Icorr trend of the wire is similar to that in the acidic solution. However, due to the presence of OH^- in the alkaline solution, anodic dissolution process is suppressed.

(3) In the same solution, the weight loss rate curve and Icorr curve had the similar trends, respectively, reflecting the test reliability and the variation of the wire corrosion rate. And the fractal

dimension curve with the first two curves also have a consistent variation, indicating that the fractal dimension of corroded wire surface can well reflect the variation of the wire corrosion rate.

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