The Influence of NaCl Concentration on Salt Spray Corrosion Behavior of P92 Steel

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Abstract—In the paper, the neutral salt spray with various NaCl concentration was carried out, and effect of NaCl concentration on P92 steel corrosion behaviour was studied by weight loss, macro-appearances and scanning electron microscope/energy dispersive spectrometer (SEM/EDS). The results showed the formation rate and amount of corrosion product would rise according with elevated chloride ion concentration which were composed of ferric oxide and chromic oxide.The corrosion process of P92 steel during neutral salt spray was mainly non-uniform corrosion, the compact corrosion product formed in early stage could hinder the diffusion of corrosive ion.

Keywords- P92 Steel; Neuter Salt Spray Tests; SEM; nonuniform corrosion

I. INTRODUCTION

Metal materials are widely used in industrial society, while metal failure resulted from atmospheric corrosion is the common phenomenon which account for more than half of the annual metal loss in the world. It is quite necessary to carry out the research concerning about metal corrosion and process in atmosphere environment[1]. The metal atmospheric corrosion highly depends on its surrounding environment factors, such as chloride ion concentration[2], humidity, temperature [5,6]. Now high performance materials are in urgent need, because the efficiency promotion of ultra supercritical power units are usually achieved by increasing temperature and pressure of main steam. Based on this situation, new types of heat-resistant steel are always choosed in design of superheater, superheater, main steam pipe and reheat steam pipe of power plant[7]. The P92 steel corrosion behaviour and mechanism in marine atmospheric environment were investigated by means of NaCl salt spray tests.

II. MATERIAL AND METHODS

The material used in this work is P92 pipe steel, two kinds of samples with different size (Sample A,30mm×20mm× 2mm, Sample B,10mm×10mm×2mm) were obtained by wire electrical discharge machining. The chemical composition of as-prepared specimens is shown in Table 1. Data from five parallel samples were collected in each experiment in which 3 samples for the weight loss analysis and the rest for the SEM/EDS analysis. The working surface of the specimens were cleaned successively in acetone and alcohol after being abraded mechanically with a series of abrasive papers (400#, 600#, 800#, and 1000#).

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Element	Content
С	0.12
Si	0.18
Mn	0.5
Cr	8.96
Nb	0.068
Мо	0.36
Ni	0.13
Р	0.013
S	0.005
Al	0.01
Ν	0.062
W	1.75
V	0.18
Fe	Bal.

Neuter salt spray tests were carried out in YWX/Q-150 salt spray machine with specimens exposed to different concentration NaCl solutions (0.5%, 1.0%, 5.0% and 10%) according to the national standards GB6458-86. After the neuter salt spray tests, the morphologies of both the corrosion products and the corroded surface were characterized successively using a scanning electron microscope (JSM-6360LV) which the corrosion products were removed by rust remover.

III. RESULTS AND DISCUSSION

A. Weight loss

The weight loss curves for P92 steel in the salt spray tests for different NaCl concentrations are shown in Fig. 1. It can be seen that the weight loss for the P92 steel increased rapidly at the early stage of experiment when in low concentration NaCl solution which only slightly rised after 25 h. When the NaCl concentration increases to 1.0% and 5.0%, the mass loss curve for the P92 steel gradually increased over time. However, except for the increase of mass loss, the slope of curve also showed a significant trend as the experiment went on implying that corrosion rate were speeding up.

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Figure 1. Mass loss from the P92 steel as a function of exposure time in the different NaCl solutions





Figure 2. Macro-appearance of corrosion products of P92 steel under salt spray with different NaCl solution: (a) 0.5%; (b) 1.0%; (c) 5.0%; (d) 10%

The macro-appearance of corrosion products of P92 steel under salt spray with different NaCl solution are shown in Fig. 2. After undergone a 100 h salt spray corrosion test with 0.5% NaCl solution, one fifth of the sample surface were covered by massive corrosion product, while rust spot emerged in the uncovered area. Compared with the salt spray corrosion test in 0.5% NaCl solution, the spotty corrosion region of P92 steel surface further expanded which accounting for 30 percent of total superficial area as the concentration of NaCl solution were increased to 1.0%. It indicated that the pitting corrosion generated and growed comparatively quickly during the experimental process, however, the growth rate of macroscopic rust layer was relatively slow. Therefore, it could be concluded that high concentration NaCl accelerated the formation of pitting corrosion in early stage of experiment, then boosted the growth rate as corrosion continued to develop. Once the concentration of NaCl solution was elevated to 5%, blocky corrosion product occupied one half of P92 steel surface. On the basis of 0.5% NaCl solution, the formation rate of rust layer on P92 steel surface further speeded up in this situation. Meanwhile, the quantity and diameter of pitting corrosion also increased. Then as the concentration of NaCl solution was set at 10%, the whole surface of P92 steel was covered with densely packed pitting corrosion and thin rust layer which interconnected with each other. Along with addition of rust layer thickness, 90 percent of sample surface were covered with blocky corrosion product.

In comparison with the macroscopic corrosion product of P92 steel in NaCl solution of different concentration, it revealed that surface corrosion product increased with the concentration enrichment of NaCl at the end of experiment which indicating the rust formation rate was positively correlated with NaCl concentration. In addition, comparative study of the corrosion weight loss of P92 steel in same conditions showed that there were significant positive correlations between the formation of macroscopic corrosion product and the corrosion weight loss of sample.

C. SEM/EDS analysis of corrosion product

The corrosion product and morphology change were investigated taking neuter salt spray test in 5.0% NaCl solution as an example, which uncovered the general law of salt spray corrosion behavior of P92 steel.



Figure 3. Corrosion surface morphologies for the P92 steel after a 25 h exposure in the 5.0% NaCl solution

The morphologies of corrosion product on P92 steel surface after a 25 h exposure in neuter salt spray test are shown in Fig.3, with the corresponding EDS analysis results listed in Table 2. The light corrosion product scattered their petals around the P92 steel surface. As can be seen from the enlarged figure and EDS analysis results that the sample surface were partly naked consisting of Fe and Cr which corresponded with the main components of P92 steel. Furthermore, the scattered corrosion product with the appearance of loose cotton wool were mainly composed of iron oxide.



Figure 4. Corrosion surface morphologies for the P92 steel after a 50 h exposure in the 5.0% NaCl solution

The morphologies of corrosion product on P92 steel surface after a 50 h exposure in neuter salt spray test are shown in Fig.4, with the corresponding EDS analysis results listed in Table 2. The corrosion product showed amarked increase which almost spread over the entire sample surface. The corrosion product still exhibited loose structure which containing mainly iron oxide and NaCl residue. Moreover, as shown in Fig. 4b, the forming internal corrosion product with dark appearance were composed of iron oxide and metal matrix.

The morphologies of corrosion product on P92 steel surface after a 75 h exposure in neuter salt spray test are shown in Fig.5, with the corresponding EDS analysis results listed in Table 2. The corrosion product quantity remained growing compared with the previous experiment which outer porous product were still iron oxide. In the meantime, the oxygen content of inner corrosion product increased along with the decrease of iron content. This illustrated the further oxidation of inner corrosion product during the process from 50h to 75h.

Table 2 EDS analysis results for the P92 steel exposed in the 5.0% NaCl solution(at.%)

Position	С	0	Fe	Cr	Si	Na	Cl
1	-	42.26	42.86	1.77	3.34	7.46	1.76
2	-	-	87.00	11.11	1.47	-	-
3	-	36.97	44.20	1.68	-	14.85	2.29
4	-	5.58	81.15	10.38	-	2.88	-
5	-	34.30	60.01	1.85	-	3.21	0.64
6	7.82	22.39	54.45	9.33	-	4.97	-
7	-	22.71	59.78	1.64	-	-	15.87



Figure 5. Corrosion surface morphologies for the P92 steel after a 75 h exposure in the 5.0% NaCl solution

The morphologies of corrosion product on P92 steel surface after a 100 h exposure in neuter salt spray test are shown in Fig.6, with the corresponding EDS analysis results listed in Table 2. As shown in the figure, P92 steel were thickly covered with corrosion product. It can be seen that the product layer were not tight with honeycomb intervals which mainly consisting of iron oxide and NaCl residue. In addition, we could reasonably assumed that the outer corrosion product coexisted with inner corrosion product after a 100 h test which played as major physical barriers in protecting metal matrix.



Figure 6. Corrosion surface morphologies for the P92 steel after a 100 h exposure in the 5.0% NaCl solution

Through the above analysis, the conclusion could be drawn that porous outer corrosion product gradually emerged on sample surface with the erosion time extending which were mainly iron oxide and NaCl residue. From the view of structure and chemical composition that the corrosion were incapable of isolating metal matrix form erosive ion. In early stage (25 h), there were no compact inner corrosion product until the neuter salt spray test lasted for 50 h. Hence we could speculate that the inner corrosion product started to appear during the process from 25h to 50h which were mostly made of iron oxide and chromium oxide. Hereafter, the corrosion layer developed gradually obstructing erosive ion from transferring towards metal matrix.

D. SEM analysis of corrosion morphology

The corrosion morphology for the P92 steel after a 25 h exposure in the 5.0% NaCl solution are shown in Fig.7. As seen in the figure that the mechanical scratch were quite apparent coexisting with massive corrosion pit about 20 μ m in diameter.



Figure 7. Corrosion surface morphologies for the P92 steel after a 25 h exposure in the 5.0% NaCl solution

The corrosion morphology for the P92 steel after a 50 h exposure in the 5.0% NaCl solution are shown in Fig.8. It turned out that the diameter of corrosion pit and surface area ratio sustained growing along with the extension of erosion time which indicating that the corrosion pit were constantly growing and developing during the process from 25h to 50h.





Figure 8. Corrosion surface morphologies for the P92 steel after a 50 h exposure in the 5.0% NaCl solution

The corrosion morphology for the P92 steel after a 75 h exposure in the 5.0% NaCl solution are shown in Fig.9. The corrosion pits on P92 steel surface interconnected with each other forming spot corrosion and pitting corrosion phenomenon also existed at the bottom of spot corrosion.



Figure 9. Corrosion surface morphologies for the P92 steel after a 75 h exposure in the 5.0% NaCl solution

The corrosion morphology for the P92 steel after a 100 h exposure in the 5.0% NaCl solution are shown in Fig.10. In this situation, sample surface were alomst fully covered by spot corrosion with absent of local corrosion at the bottom of spot corrosion. The results showed that the former pitting corrosion at the bottom of spot corrosion stopped growing eventually forming non-uniform corrosion appearance.



Figure 10. Corrosion surface morphologies for the P92 steel after a 100 h exposure in the 5.0% NaCl solution

E. Formation and development mechanism of corrosion pitting

During the entire corrosion process, the formation and development of corrosion pitting could be divided into two stages, nucleation and growth. In consideration of the Cr content of P92 is approximately 9%, it is inclined to form a passivation film on surface which was composed of iron oxides and chromium oxides. However, the chlorion was prone to infiltrate into interface of the solution/passive film taking advantages of weak spots of passive films (inclusions, dislocations, alloy phases etc.). As a result, the protective ability decreased due to destruction of passive film bringing about the unceasing invasion of chlorion. Afterwards, the core of corrosion pitting emrged on the basis of chlorion aggregating near one random weak spot. It turned out that the chlorion also made contribution to destruction process of passive film.

Subsequently, small corrosion pits started to nucleate and grow on the P92 steel surface. In this incubation period, solution was acidified by reason of hydrolysis of Fe3+/Fe2+ and Cr2+. The steel in the hole were maintained at activated state on account of the ion concentration and conductivity increasing in the holes as well as repassivation potential of the steel. Hence, agalvanic couple of a large cathode/small anode was produced on the surrounding of surface of the hole which accelerating the corrosion rate of P92 steel.

IV. CONCLUSIONS

The corrosion rate of P92 steel was influenced by chlorion concentration that formation rate and amount of corrosion product increased along with rise of chlorion concentration. Corrosion product of P92 steel in salt spray tests were mainly iron oxides and chromium oxides. Compact corrosion product generated in early stage provide protection for metal base via obstructing the transfering of erosive ion. The corrosion process of P92 steel could be devided into two stages, firstly forming scattered corrosion pits, and corrosion pits growed and developed interconnecting with each other. Finally, non-uniform corrosion morphologies were obtained owing to the arise of compact corrosion pits.

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