The corrosion behavior of T/P91 steel under the atmosphere environment in Hunan province

Feng Chao1, Xie Yi1, Wang Jun1, Long Yi1, Chen Wei1 and Xia Dahai2

1 State Grid Hunan Electric Power Company Limited Research Institute, Changsha 410007, China
2 School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

Abstract. The research of corrosion behavior of T/P91 steel was investigated taking the case for the T/P91 steel corrosions existed during the construction process of a thermal power plant in Hunan province. The morphology change, product component and mechanical properties change were studied during the corrosion process of SO4\(^{2-}\). The results indicated that the surface oxide layer are mainly composed of iron and chromium oxide. As the thickness of oxide layer increased, the ability of blocking the erosive ions diffusion also come into effect, thus slow down the corrosion rate.

1 Introduction

As the energy demand is ever-growing, the newly-built power plant aims to develop large capacity, high parameter units. The new martensitic heat-resistant steel which represented by T/P91 steel are widely used in the main steam pipe, reheater tube, superheater tube and so on due to its high strength and good chemical stability at high temperature. However, it is of great importance to study the corrosion behavior as T/P91 steel suffered relatively serious corrosion under Hunan atmosphere environment[1]. The atmospheric corrosion of steel depends largely on the environmental factors, such as corrosive ion concentration[2], relative humidity[3], temperature[5,6]. Except for the distinct character of hot rainy season, Hunan area is also affected by acid rain. The sulfate radical concentration holds dominant position in acid rain which is far beyond the nitrate concentration and chloride concentration. It is owing to the coal serving as the main consumption about 70 percent of the primary energy in Hunan. During process of power plant construction, mass metal parts are often stored in open field on account of project delay. As a result, these important components will inevitably be affected by sulfate radical in acid rain which derived from the oxidation of sulfur dioxide gas[2,7,8]. We devoted ourselves to the research of corrosion behavior of T/P91 steel under Hunan atmosphere environment, so as to provide theoretical guidance to material corrosion protection during infrastructure installation and operating maintenance of power plant.

2 Materials and Methods

The T/P91 steel used for test were obtained from main steam pipe of a certain power plant of Hunan province.

The chemical composition of samples were listed in Table 1.

| Element | C   | Mn  | Si  | Cr  | Mo  | Nb  |
|---------|-----|-----|-----|-----|-----|-----|
| Content(Wt%) | 0.11 | 0.49 | 0.31 | 9.12 | 0.93 | 0.07 |

| Element | V   | P   | S   | N   | Al  | Ni  |
|---------|-----|-----|-----|-----|-----|-----|
| Content(Wt%) | 0.23 | 0.015 | 0.007 | 0.065 | 0.03 | 0.27 |

The T/P91 steel samples were divided into two groups, one group was for natural corrosion test in air under Hunan province from May to September with the size of 20mm×20mm×2mm. And the other group were machined to the same size for netural salt spray test with the concentration of Na\(_2\)SO\(_4\) solution was set at 0.1% and the solution temperature was 35±2℃. The working surface of the samples was abraded mechanically with a a series of grit papers (400#, 600#, 800#, and 1000#). The corrosion product on samples were investigated by Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) successively for morphology characterization and component analysis.

3 Results and Discussion

3.1 Macro morphology analysis

The macro morphology of T/P91 steel surface during various stages of natural corrosion exposed to Hunan atmosphere environment were shown in Fig.1. From Fig. 1a to Fig.1f corresponds to the exposure time of 15 days, 30 days, 60 days, 90 days, 120 days and 150 days, respectively.
It can be seen from the pictures that localized corrosion took place on the sample surface during the atmospheric corrosion test of 150 days. At the early stage, spotted corrosion pit emerged randomly on the sample surface covering 30% of the total area. Corrosion product increased as time went on. The compact corrosion product occupied further more sample surface as Natural exposure experiment lasted for 90 days. On this basis, the cover area and thickness of corrosion product gradually increased until the formation of complete dense corrosion product layer at the end of test.

The corrosion products of T/P91 sample during various stages under salt spray corrosion of 0.1 % Na$_2$SO$_4$ solution were displayed in Fig.2. Macro morphologies of sample undergone 15h, 30h, 60h, 90h, 120h and 150h were shown successively. Atmospheric corrosion behavior could be explored by accelerated simulating corrosion test[10,11].

Large pieces of rust layer emerged on the surface of sample when corrosion test lasted for 15h. As the experiment went on, surface rust layer expanded to 70% of the whole surface area after 60h. When it came to 90h, the rust block accounted for 90% of sample surface area. The whole sample surface were covered by thick corrosion product at the end of test.

The EDS analysis result showed that the corrosion products of early stage were ferric oxides and chromium suboxides which the oxygen content was relatively low. As the experiment went on, corrosion developed towards the inner part of sample and corrosion product became more dense and thicker. And the oxygen content also rise as the previous suboxide were oxidized constantly forming a compact oxide layer which was shown in Fig.4. In general, dense oxide layer would protect the sample matrix from corrosive solution. The distribution of corrosion product was not not very uniform observing in a comparatively wide range, cracks appeared on local area of corrosion product surface. The chloridion ion in previous natural corrosion in atmospheric conditions, emergence and development of rust layer followed the same law as localized corrosion occurred on the surface of T/P91 sample. However, the rust layer under salt spray corrosion of 0.1 % Na$_2$SO$_4$ solution showed faster growing velocity and thicker thickness at the end of test.

### 3.2 Analysis of corrosion product

The compositions of corrosion product under two different experiment conditions were analyzed. Fig.3 and Fig 4 showed the SEM images of surface rust layer under natural corrosion in Hunan atmospheric conditions for 60 days and 150 days, respectively.

It is shown in Fig. 3 that most of sample surface were covered by rust layer after 60 days of natural corrosion. The ulcer-like corrosion product were evenly distributed with loose appearance which the EDS analysis result was displayed in Table 2.

### Table 2 The main component contents of T/P91 corrosion product under different corrosion conditions (at.%)

| Sample status                    | O    | Fe   | Cr   | S    | Cl  |
|----------------------------------|------|------|------|------|-----|
| 60 days of natural corrosion     | 28.17| 51.13| 10.06| 3.29 | 0.46|
| 150 days of natural corrosion    | 53.29| 39.64| 15.51| 2.26 | 0.75|
| 60h of accelerated corrosion     | 30.44| 49.14| 9.46 | 4.82 | -   |
| 150h of accelerated corrosion    | 48.59| 25.48| 13.16| 3.55 | -   |

The EDS analysis result showed that the corrosion products of early stage were ferric oxides and chromium suboxides which the oxygen content was relatively low. As the experiment went on, corrosion developed towards the inner part of sample and corrosion product became more dense and thicker. And the oxygen content also rise as the previous suboxide were oxidized constantly forming a compact oxide layer which was shown in Fig.4. In general, dense oxide layer would protect the sample matrix from corrosive solution. The distribution of corrosion product was not not very uniform observing in a comparatively wide range, cracks appeared on local area of corrosion product surface. The chloridion ion in
rust layer also came from air pollutants under atmosphere environment which accelerated the corrosion process by absorbing and diffusing into T/P91 steel matrix.

Figure 4. SEM images of rust layer on T/P91 steel after 150 days of natural corrosion under atmosphere environment.

SEM images of corrosion product after 60h of salt spray test in 0.1% Na\textsubscript{2}SO\textsubscript{4} solution were shown in Fig.5. As is seen that most of sample surface was already covered by porous rust layer. It could be observed from the Fig.5b that corrosion pits almost with the same size scattered over the surface of rust layer with uniform thickness. The EDS analysis results in Table 2 illustrated that the oxygen content was low while iron and sulfur content were relatively high.

Figure 5. SEM images of rust layer on T/P91 steel after 60h of salt spray test in 0.1% Na\textsubscript{2}SO\textsubscript{4} solution.

Once the salt spray test of T/P91 steel in 0.1% Na\textsubscript{2}SO\textsubscript{4} solution lasted for 150h, sample surface were entirely covered by dense corrosion product which was shown in Fig.6. The apparent cracks on the surface were caused by dehydration of corrosion product. The major ingredients of corrosion product were ferroferric oxide and chromium oxide. Compared to earlier period, the iron content declined and the oxygen content rised which were ascribed to the free oxygen diffusing towards inner part of T/P91 steel. At this moment, the chromium content of sample surface already towered over the average content of T/P91 steel and sulfur content was also comparatively high.

Figure 6. SEM images of rust layer on T/P91 steel after 60h of salt spray corrosion of 0.1% Na\textsubscript{2}SO\textsubscript{4} solution.

Combining with the corrosion product morphology and EDS analysis result of T/P91 steel under atmosphere environment and salt spray corrosion of 0.1% Na\textsubscript{2}SO\textsubscript{4} solution, a conclusion could be drawn that the main influence factor of T/P91 steel corrosion in Hunan province was sulfate ion. Under the influence of sulfate ion, the ulcer-like corrosion product developed and expanded until totally covering the whole surface in the first stage. During the second stage, the rust layer became thicker forming compact corrosion product layer[14]. In initial period, the rust layer were composed of ferric oxide, chromium oxide and sulfide[9,14,15]. With the development of corrosion process, the corrosion product transformed into compact ferroferric oxide and chromium trioxide which would provide physical isolation preventing the diffusion of corrosive ion.

4 Conclusions

1. Comparing the experiment results of T/P91 steel under atmosphere environment with salt spray test results of 0.1% Na\textsubscript{2}SO\textsubscript{4} solution, the conclusion has been verified that T/P91 steel mainly suffered from influence of sulfate ion under Hunan atmosphere environment.

2. The morphology change and product composition of T/P91 steel suffering from sulfate ion corrosion were thoroughly studied. Firstly, the ulcer-like corrosion product emerged on the sample surface, then the pitting corrosion developed and connected with each other forming a compact oxidation film. The corrosion product were mainly composed of ferroferric oxide and chromium trioxide.

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