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Microstructure Evolution and Element Redistribution in Carburizing Process of Ethylene Cracking Furnace Tube

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Abstract. Carburizing is the main damage form of ethylene cracking furnace tubes. In this process, the microstructure of the furnace tube would change and the element diffuses and redistributes. After serving for about 41000h, the radiation section of a plum blossom tube of SC-1 tubular cracking furnace from a petrochemical company was tested and analyzed in this article. Results show that the higher the service temperature, the more serious the carburizing of the furnace tube. In the inner-wall carburized zone of the middle temperature section of the furnace tube with an initial C content of 0.1wt%, the maximum C content reaches 1.83wt% and the number of carbides increases obviously as well as its organizational morphology changes from fine granular to coarse block or chain like and its organizational type changes from single $M_{23}C_6$ to the coexistence of $M_{23}C_6$, M_7C_3 and MC type carbides. The Cr and C elements in the carburized zone are mainly concentrated in the grain boundary area in the form of carbides. At the same time, the diffusion of alloy elements causes Cr deficiency in the matrix, and the carbide deficiency zone appears in the subsurface of the inner wall.

Keywords. Cracking furnace tube, carburizing, microstructure evolution, element redistribution

1. Introduction

In petrochemical industry, ethylene is the most important monomer and the basis of organic raw materials. As a leading product, it plays an exceeding significant role. Almost all the ethylene production facilities utilize tubular cracking furnace and the service environment of the ethylene cracking furnace tube is extremely bad. During the operation of the furnace tube, the outer wall of the tube in service is radiated by high temperature flame and its ambient temperature can reach 1100°C. The raw material inside the tube is a mixture of high carbon potential hydrocarbon gas and water vapor, therefore its inner wall is in the environment of circulating oxidation and carburizing, and its outer wall is in the environment of high-temperature oxidation and

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decarburization; besides, the ethylene cracking furnace tube is subject to additional stresses caused by internal pressure in the tube, body weight of the tube, temperature difference between the inner and outer walls and on/off process; working in such environment, carburizing, thermal fatigue, creep and other damages are quite easy to occur in the cracking furnace tube and its actual service life is often far lower than the design life [1-8]. Carburizing is the main damage form of ethylene cracking furnace tubes. As drawn in figure 1, domestic and international investigations on the damage of a large number of ethylene cracking units show that the failure directly caused by carburizing occupies a prominent position [9].

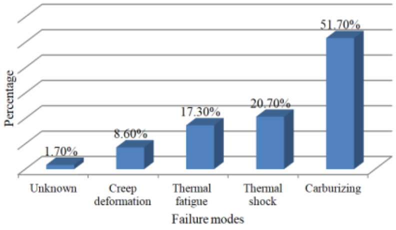


Figure 1. Statistics of failure modes of partial ethylene cracking furnace tubes.

2. Experimental Material and Methods

The furnace tube radiation section of a SC-1 tubular cracking furnace after serving for about 41000h from a petrochemical company was selected as the test material. The furnace tube belongs to rolled plum blossom type and contains 10 inner grooves. Its cross-sectional shape and size are shown in figure 2. The radiation section of the furnace tube was divided into upper, middle and lower three parts, respectively with ambient temperature of 1060℃, 1030℃ and 980℃. The design pressure is 0.34mpa and the medium in the tube is naphtha. Table 1 writes the original chemical composition of the furnace tube.

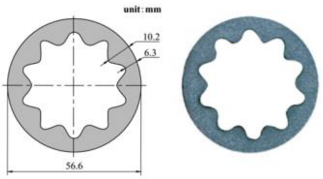


Figure 2. The cross sectional shape of the furnace tube.

Table 1. Standard chemical composition of the furnace tube (wt.%).

Element	C	Cr	Ni	Si	Mn	Mo	Ti	Zr
Wt.%	0.1~0.2	25.0~26.0	37.0~40.0	1.4~2.0	≤1.5	1.0~3.0	0.2~0.6	≤0.050

Without obvious bending and creep expansion, the furnace tube to be tested presents in good macroscopic condition. Its outer surface has a uniform oxide layer and an obvious damage layer can be also found in the inner wall. According to the results of penetrant flaw detection, no cracks exists on both the inner and outer surfaces of the furnace tube. Rings in thickness of 10mm were cut from the upper, middle and lower parts of the radiation section, respectively. After grinding and polishing of each tube part rings, their cross-sectional carburization after etched by aqua regia and ferric chloride; microstructure morphology seen from the light microscopy (MEF4) after electrolytic etching with 10% oxalic acid solution; cross-sectional carbon distribution tested through infrared carbon and sulfur analyzer (CS-8800); phase composition obtained using X-ray diffraction (XRD-6000); element distribution in the inner and outer surface damage layers and the carburized zone acquired utilizing electron probe (CS-8800); were holistically observed and analyzed in this work.

3. Experimental Results

3.1. Carburizing of the Furnace Tubes

The cross-sectional carburization distributions of the upper (I#), middle (2#) and lower (3#) parts of the radiation furnace tube are sketched in figure 3, respectively. It shows that the actual carburizing distributions of the three furnace tube parts are quite different, which is caused by their different service temperatures in service. The upper part of the furnace tube has high service temperature, rapid diffusion of elements and the most serious carburization with some areas almost infiltrated, while the lower part of the furnace tube has low temperature and only slight carburization. Furthermore, the cross-sectional carburization of every furnace tube part is not uniform and the carburization degree of the protruding sections of the inner grooves is more serious, which is induced by the large contact area between these sections and the high carbon potential atmosphere as well as the large carbon concentration gradient.

Figure 3. Schematic diagrams of the cross-sectional carburization distribution in different parts of furnace tube: I# upper part, II# middle part and III# lower part; 1 carburized zone, 2 transition zone and 3 non-carburized zone

3.2. Cross-sectional Carbon Distribution

Carburizing starts from the inner wall of the furnace tube, so the C content in the cross section of the furnace tube also changes gradually. Figure 4 draws the C content (in mass percent) distribution curve of the maximum section of the 3# furnace tube part. It can be seen that the C content is gradually reduced from the inner wall to the outer wall of the furnace tube, and in the highest inner wall it reaches 1.83wt%, while less than 0.1wt% in the lowest outer wall due to the oxidation and decarburization during high temperature service.

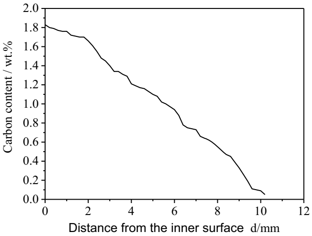


Figure 4. Cross-sectional distribution of carbon content in the furnace tube part of II#.

Composition test results of the carburizing zone 1 of the 3# furnace tube part indicate that the contents of Ni, Mo, Mn, P and S meet the requirement of the standard, but the content of Si decreased slightly and the content of Cr decreased dramatically to a number of 19wt%.

3.3. Cross-sectional Carbon Distribution

Figure 5 exhibits the microstructure morphology of different areas in the cross section of the II# furnace tube part. Obviously, in the non-carburized zone of the furnace tube, only a small amount of carbides exist at the grain boundary and in the grain, which are secondary carbides formed by aging precipitation of the carbon solidly dissolved in austenite. Meanwhile, in the carburized zone, not only the amount of carbides increases, but also the morphology changes from fine granular to coarse block in the grain as well as chain at the grain boundary. This is mainly resulted from the high content of C in the carburizing zone leading to the formation of a large number of secondary carbides in this region in the process of high temperature service, some of which gradually grow up in the grain, and some grow up to the grain boundary in the shape of chain.

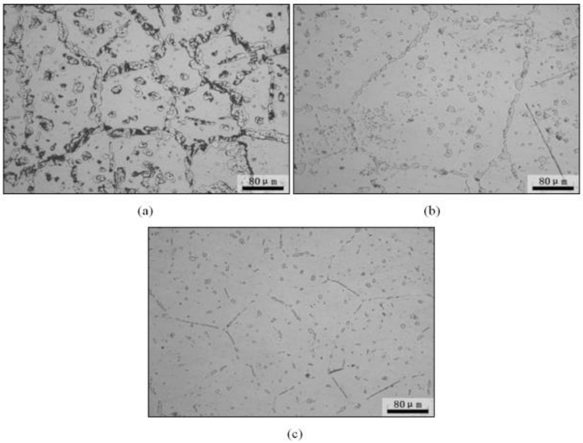


Figure 5. Microstructure of different regions in the furnace tube part of II#. (a) carburized zone, (b) transition zone, (c) non-carburized zone.

3.4. X-ray Diffraction Analysis

X-ray diffraction analysis was performed on different regions of the II# cross section and the diffraction pattern is shown in figure 6. Results show that M_7C_3, $M_{23}C_6$ and MC carbides coexist in the carburized and the transition zone, while only $M_{23}C_6$ carbide can be found in the non-carburized zone. Normally, the precipitated secondary carbide should be $M_{23}C_6$ under the right service temperature range of furnace tube. However, the higher C content in the carburizing and transition zone can promote the transformation of carbide type from $M_{23}C_6$ to M_7C_3. Since the C content in the carburizing zone is the highest, its number of M_7C_3 type carbides is also distinctly more than that in the transition zone.

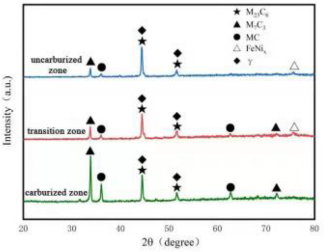
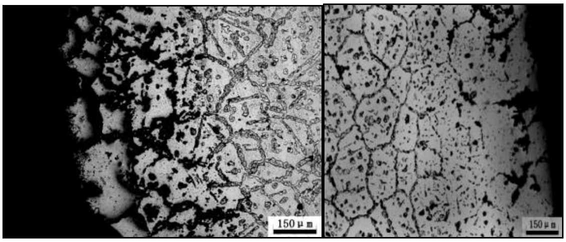


Figure 6. XRD diffraction patterns of different zones in the furnace tube part of II#.

3.5. Distribution of Elements

There are obvious damage layers on both the inner and outer surfaces of the II# furnace tube part, as shown in figure 7.



(a) (b)

Figure 7. OM images of the (a) inner and (b) outer surface damages in the furnace tube part of II#.

The analysis indicates that an obvious intergranular oxidation zone of Cr_2O_3 exists in the inner surface damage layer and a poor carbide zone locates right in its adjacent area followed by a carburizing zone. Meanwhile, only a small amount of SiO_2 appears in the damaged layer on the external surface and the loss of C element is obvious due to the decarburization environment of the external wall, and simultaneously, Cr element continuously diffuses to the interface and gets oxidized to form oxidation products in the service process, which finally results in the lack of Cr in the outer sub-surface of the furnace tube. The element distribution maps in the damaged area on the inner and outer surfaces are shown in figures 8 and 9, respectively.

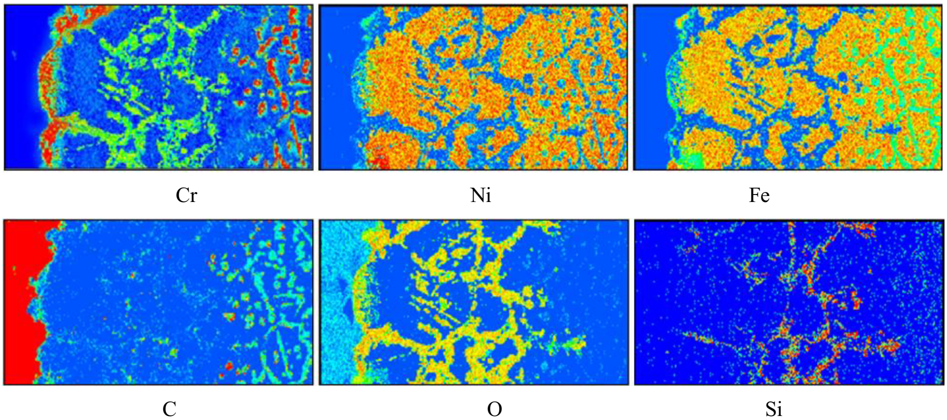


Figure 8. Distribution of alloying elements in the internal surface damage zone of the II# furnace tube by EPMA in mapping mode.

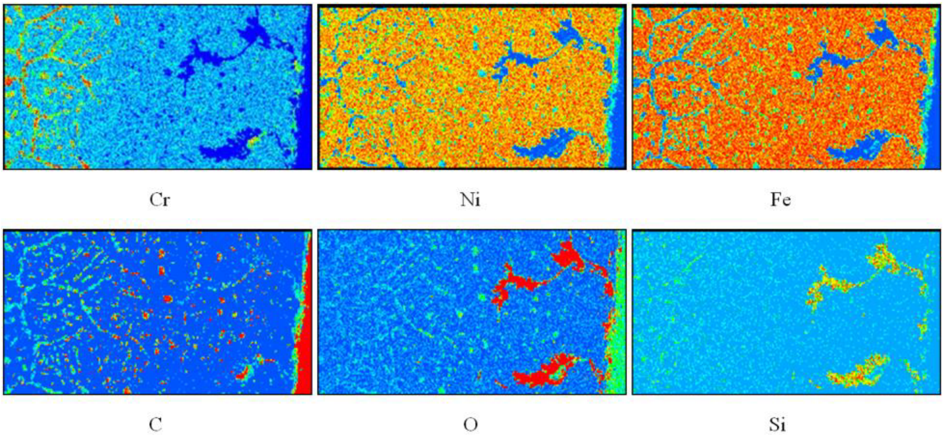


Figure 9. Distribution of alloying elements in the external surface damage zone of the II# furnace tube by EPMA in mapping mode.

As present in figure 10, electron probe was used to test the element distribution in the 1 carburizing zone of the II# furnace tube part. Seen from the images, Cr and C are mainly concentrated at the grain boundary in the form of carbides, while Ni is still solidly dissolved inside the austenite grain and the other elements of Si, Mo and Mn are less and evenly distributed inside the grain. In the service process of the furnace tube, carbides will gradually precipitate and grow up following the change of type and the diffusion to grain boundary, which will result in the lack of Cr in the matrix and consequently reduce the high temperature oxidation resistance of the furnace tube.

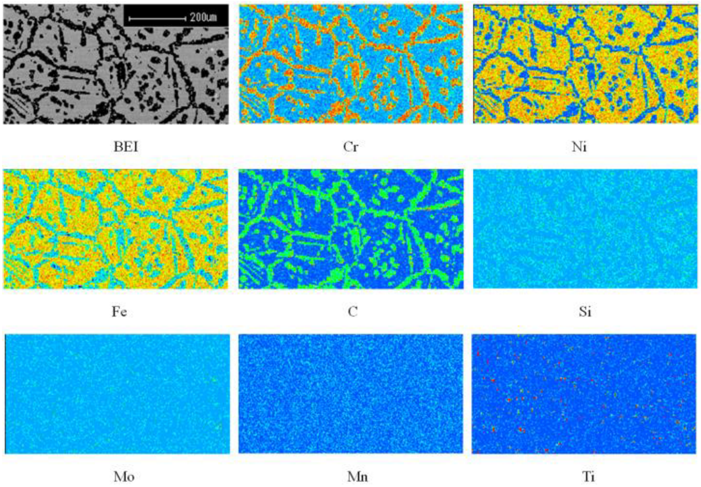


Figure 10. Distribution of alloying elements in the carburized zone of II# furnace tube by EPMA in mapping mode.

4. Analysis and Discussion

In the process of ethylene production, naphtha and LPG with high carbon potential atmosphere are the cracking materials that through the radiation section of furnace tube, and the main components are alkanes, cycloalkanes and aromatics. The carburizing process of ethylene cracking furnace tubes is essentially a chemical heat treatment process, but the existence of C is not the only factor in carburizing. Carburizing does not occur even at high temperatures when the C molecules in contact with metals are inactive. Only when the C molecules decompose into active C atoms, they can adsorb on the surface and then migrate to the interior of the metal, consequently forming a carburizing layer with certain thicknesses. The whole process includes:

(1) Contacting with the carburizing atmosphere

During the operation of the ethylene plant, a large number of alkanes, cycloalkanes, aromatics, olefins and other mixtures are produced in the cracking process of diesel oil or naphtha, which decompose and precipitate active C atoms at high temperatures [10].

$$CH_4 \leftrightarrow 2H_2 + [C]$$

$$C_nH_{2n} \leftrightarrow nH_2 + n[C]$$

(2) Adsorption of active C atoms on the surface

The adsorption process can be simple physical adsorption, that is, the formation of a single or multiple atomic adsorption layer on the metal surface due to van der Waals attraction. Also, chemical adsorption process may occur forming strong chemical bonding between the adsorbed atom and the surface atom of the metal.

(3) Diffusion of C atoms in the metal

Driven by the difference of C concentration between the surface of the furnace tube and the interior of the metal, the adsorbed active C atoms will diffuse into the metal and form carbides with the other elements. This process is controlled by the diffusion coefficient and the concentration difference of C atoms.

The reaction rate in step (1) is related to the transfer coefficient and the difference of C potential between the carburizing atmosphere and the surface of the furnace tube, and the reaction rate in step (3) is determined by the C diffusion coefficient.

In the early service stage of the furnace tube, coking layer and oxide layer will appear on its inner surface gradually. The C content in the coking layer is more than 95 wt%, forming a large C concentration gradient between the inner surface and the matrix metal. The diffusion of C into the matrix metal can be inhibited by Cr_2O_3 which is the main content in the oxide layer [11], but the Cr_2O_3 oxide layer cannot always exist stably. Firstly, the oxide layer would be broken in case of improperly removing the coking layer. Secondly, the partial temperature of the furnace tube increases and the partial pressure of oxygen decreases with the formation of the coking layer. When the temperature is above 1050 ℃ and the C in the environment reaches a certain level of activity, oxygen partial pressure is not enough to keep the stabilization of Cr_2O_3, and thus on one hand, Cr_2O_3 would react with C and generate brittle Cr_xC_y phase, on the hand, Cr_2O_3 would also react with S in the cracked gas and form loose and brittle Cr_xS_y phase. Thirdly, the density of the oxide layer can be degraded due to carbonization, brittleness and other factors during service, then when the temperature exceeds 950 ℃, Cr_2O_3 would react with O and form volatile CrO_3 [12]:

$$\frac{1}{2}Cr_2O_3(s) + \frac{3}{4}O_2(g) = CrO_3(g)$$

All the above reasons will lead to the loss of protective effect of the Cr_2O_3 oxide layer.

Due to the loss of the protective effect from Cr_2O_3 layer, the cracking gas in the furnace tube and C atoms in the coking layer diffuse into the inner of the furnace tube through cracks and holes in the oxide layer. The oxidizing atmosphere in the cracking gas is consumed because of the formation of oxide layer, and only hydrocarbon gas remains in the cavity and crack area of the oxide layer. Under the catalysis of the base metal, the hydrocarbon gas breaks down to form active C atoms and further diffuses into the substrate of the furnace tube. Then, the carburizing zone is formed in the inner wall of the furnace tube due to carbide precipitation, which is a nonlinear and unsteady process. On one hand, the thickness of the coking layer gradually increases as the service time increased. The existence of the coking layer with poor heat conduction increases the thermal resistance of the tube wall and reduces the thermal conductivity, consequently increasing the furnace tube local temperature and the C atom diffusion coefficient [13.14]. On the other hand, because Cr can effectively inhibit the diffusion of C atoms, Cr deficiency in the matrix will lead to the increase of the C diffusion coefficient. The above two reasons make the carburizing process a gradually accelerated process.

The structure of the unserved furnace tube is composed of austenite and a small amount of eutectic carbide. During the service process, $M_{23}C_6$ secondary carbide precipitates gradually from the saturated austenite matrix. With the proceeding of the carburizing process, the C content in carburized zone increases gradually while the Cr content decreases slowly. Seen from the projection of Fe-Cr-C ternary phase diagram at 850 °C in figure 11, the carbide type will convert from $M_{23}C_6$ to M_7C_3. With the increase of service time, Cr deficiency becomes more severe on the surface of the furnace tube, especially at the interface between the oxide layer and matrix metal, consequently increasing the critical C concentration of carbide formation. Therefore, the carbides of Cr in this region are unstable and finally decompose to form the carbide deficiency zone. Meanwhile, the decomposition of carbide leads to the increase of carbon concentration at the interface between the oxide layer and the matrix metal, generating a C concentration gradient between the interface and the matrix metal, which results in the C diffusion into the matrix metal and further leads to the formation of carburizing zone in the vicinity of the carbide deficiency zone [15].

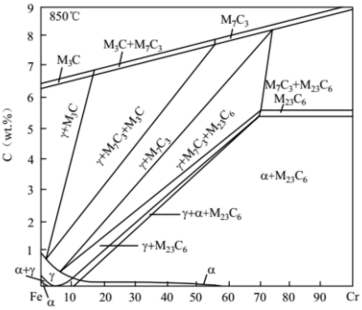


Figure 11. Projection diagram of Fe-Cr-C ternary phase diagram at 850 °C.

5. Conclusion

The testing results and analysis on the radiation section of a plum blossom tube of SC-1 tubular cracking furnace after serving for about 41000h, illustrate that the carburizing of ethylene cracking furnace tubes is a alternating process of oxidation and carburizing. Carburizing occurs on the inner wall of the furnace tube in contact with cracking gas, and the degree of carburization increases gradually with the rising of temperature. The maximum C content in the carburized zone reaches 1.83 wt% and the diffusion of C atoms causes the Cr deficiency in the matrix. The number of carbides increases as well as its organizational morphology changes from fine granular to coarse block or chain and type changes from single $M_{23}C_6$ in the non-carburized zone to the coexistence of $M_{23}C_6$, M_7C_3 and MC carbides in the carburized zone. The migration and redistribution of alloying elements happen during carburizing, i.e., the Cr and C elements in the carburized zone are mainly concentrated in the grain boundary area in the form of carbides and the Ni element is still solidly dissolved inside the austenite crystal. Moreover, there are obvious damage layers on both the inner and outer surfaces of the furnace tube. The damage layer on the inner surface mainly belongs to intergranular oxidation and the carbide deficiency zone appears in the subsurface of the inner wall; while the decarbonization of the sub-surface and the deficiency carbide zone are the main damage to the outer surface.

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