

# Structure Degradation of 25Cr35Ni Heat-Resistant Tube Associated with Surface Coking and Internal Carburization

X.Q. Wu, Y.S. Yang, Q. Zhan, and Z.Q. Hu

(Submitted 15 May 1998; in revised form 28 May 1998)

Microstructures of 25Cr35Ni heat-resistant cracking tube after service were investigated and degradation mechanism of tube material was discussed. Results reveal that three distinguished zones, that is, internal oxide, carbide free, and internally carburized zones, will gradually develop in the inner wall of a cracking tube during service. Carbide free and internally carburized zones are formed primarily in relation to the periodic spalling and regeneration of surface oxide scale, and diffusion velocity of carbon and carbide forming elements in matrix and the solubility limit of carbon in alloy. The formation and growth of filament coke can aggravate structure degradation of the inner wall of the cracking tube, while deposition of lamellar and spheroidal coke may slow structure degradation to some extent. Surface coking and decoking cycles strongly aggravate the structure degradation of tube material and damage the service life of the cracking tube.

**Keywords** carburization, coking, heat-resistant alloy

## 1. Introduction

Cracking tube is an important component in petrochemical plants and is usually made of heat-resistant alloy. In cracking operations, the tube serves in elevated temperature (approximately 1100 °C in hottest section) and carbonaceous environment (Ref 1-3). Therefore, it is important for tube materials to inhere excellent elevated temperature properties and good resistance to surface coking and internal carburization.

In the past three decades, much interest has focused on improvement of high temperature properties of cracking tube. The main ways are composition adjustment of tube materials and improvement of tube fabrication processing. Consequently, the new generation of tube materials such as niobium-modified HP, KHR35CW, 36XT, and PG28485 heat-resistant austenitic alloys have been developed and extensively applied in the petrochemical industry. Due to a raised nickel content and incorporation of an amount of additive carbide formers such as niobium, titanium, zirconium, and tungsten, the creep rupture strength and structure stability of elevated-temperature tube in long-term service have been improved satisfactorily (Ref 4-11). Moreover, some new fabrication processing, such as two-layer tube-casting skill and electromagnetic-centrifugal casting method, were invented and applied in industry practice, promoting improvement of elevated temperature properties of cracking tube (Ref 12-15).

However, with rapid development of the petrochemical industry, surface coking and internal carburization of cracking tube gradually have become prominent. The coke deposited on the inner wall of the tube gives rise to loss of cracking produc-

tion, decreases the effective cross section of tube and thermal efficiency, and blocks cracking reaction, all of which greatly increase production cost. Moreover, coke can promote carburization, especially during the period of decoking (Ref 1). Carburized metal in the inner wall of the cracking tube tends to increase in volume and has a higher thermal expansion coefficient. This results in tensile stresses on the outer uncarburized layer, making the tube more susceptible to creep rupture failure.

In past work, little progress had been made on the aspects of retarding coking and carburization of cracking tube. The only ways to improve resistance to coking and carburization were to increase silicon, tungsten, and molybdenum contents in tube material (Ref 16-21). As a result, HK and HP alloys with higher silicon contents were developed. But it has been confirmed by long-term service that only increasing the silicon content is not a lasting way to prevent coking and carburization in cracking tube. In addition, the experimental result obtained by Shinohara et al. (Ref 12) has indicated that increasing nickel content strongly promotes surface coking of heat-resistant alloy. So, it seems that the traditional tendency to increase nickel content of tube material does not tally with its application demands.

To develop a new type of tube material both resistant to coking and carburization and with sufficient creep-rupture strength, a series of investigations on coking and carburizing mechanisms and their relation to cracking tube materials were carried out. As part of this study, this paper reports the testing and analysis results of structure degradation of 25Cr35Ni HP heat-resistant alloy associated with surface coking and internal carburization.

## 2. Experimental Procedure

All specimens were cut from HP cracking tube after service. The chemical compositions are listed in Table 1. The coke tested was separated from the inner walls of the cracking tube. Because the inner wall (the original interface with coke) is the

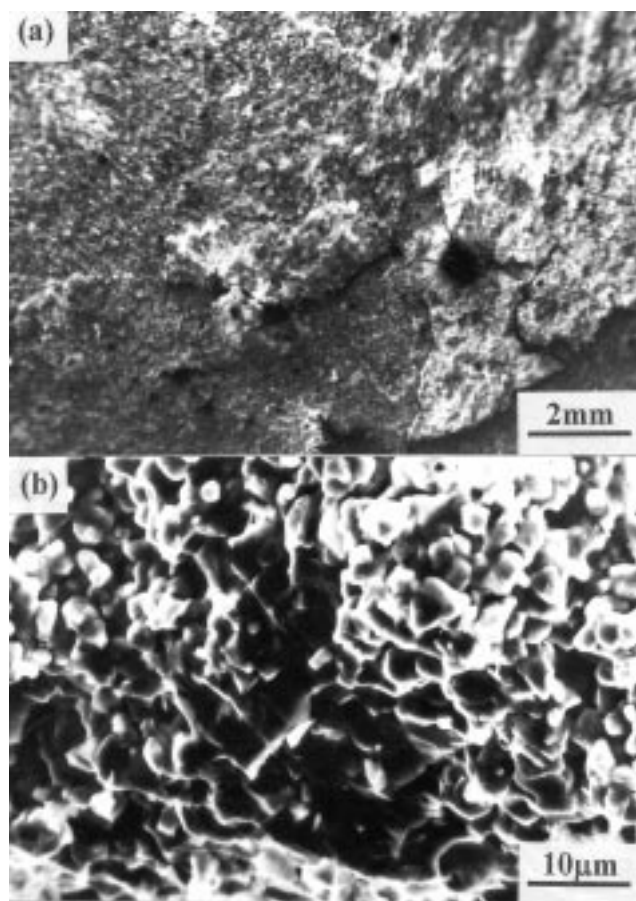
X.Q. Wu, Y.S. Yang, Q. Zhan, and Z.Q. Hu, Department of Superalloy and Special Casting, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110015, P.R. China.

major place where coke is deposited, investigations focused on the inner surface and wall of the cracking tube. Also the outer surface (the original interface with the inner wall of cracking tube) and cross sections of coke were investigated in detail. Metallographic specimens were prepared in accordance with standard metallography methods and etched with a 20% CuSO<sub>4</sub>, 40% HCl, and H<sub>2</sub>O solution. Both an optical microscope and a JSM-6301F (JEOL USA, Peabody, MA) scanning electron microscope (SEM) with a ISIS300 Series energy-dispersive x-ray analyzer (EDAX; Oxford Instruments Microanalysis, Concord, MA) were used in structure morphology observation and qualitative chemical analyses.

### 3. Experimental Results

Figure 1 is the scanning micrographs of the inner surface of HP cracking tube after long exposure to service environment. At (a) lower magnification, the local cracking and spalling morphology is clear, while at (b) higher magnification, the inner surface shows as flaky.

The cross section of the inner wall of the tube consists of three distinguished zones, depicted respectively by A, B, and C in Fig. 2. Layer A, typically the internal oxide zone, is approximately 10 to 33 μm thick; layer B, the carbide free zone, is



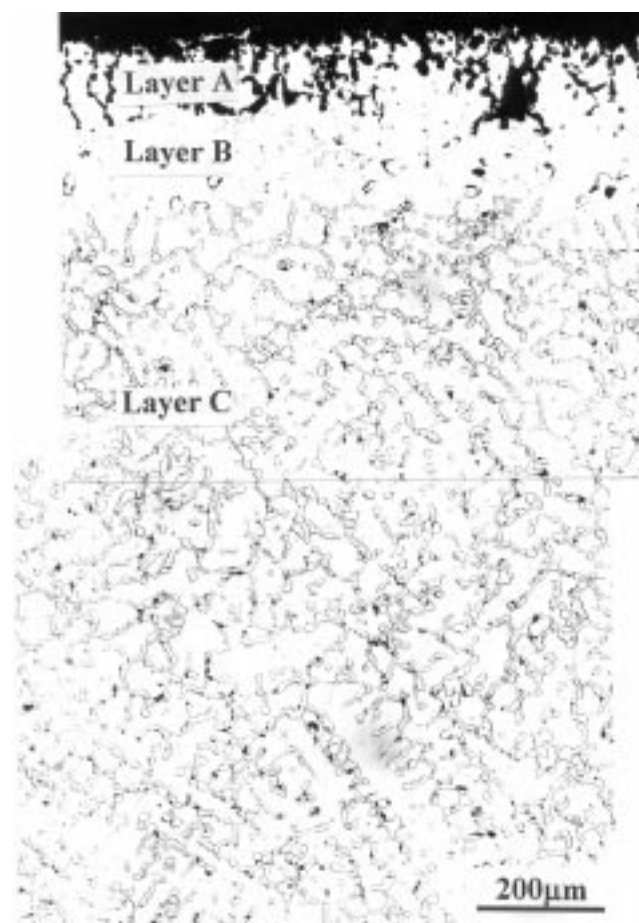
**Fig. 1** Scanning micrographs of the inner surface of the HP cracking tube after long service at (a) lower magnification and (b) higher magnification

about 30 μm thick, and the rest, layer C, is the internally carburized zone. Clearly, the inner wall of HP cracking tube was subjected to inhomogeneous oxidation during service. At the local region, A, one can clearly identify some heavier oxide protrusions into the carbide free zone. In B, small dispersive carbide particles exist. Layer C is primarily made up of coarser blocky carbide network, distributed throughout the inner wall of the tube. The initial lamellar eutectic carbides distributed at grain boundaries in as-received condition have disappeared, and the boundary carbides have thickened and become more blocky in nature.

Figure 3 is the result of linear scanning of EDAX of the elements oxygen, silicon, chromium, iron, and nickel. Clearly, the internal oxide layer A is rich in silicon, while layer B is obviously rich in iron and nickel. The cross-section morphology of the outer wall of the tube is shown in Fig. 4. Except for the thinner carbide-free zone and denser carbides randomly distributed in the carburized zone, the primary morphology is similar to the

**Table 1** Chemical compositions of HP cracking tube

Alloy	Composition, wt%								
	Ni	Cr	C	Nb	Si	Mn	S	P	Fe
HP	33.8	24.3	0.43	0.69	1.71	1.11	<0.03	<0.03	bal



**Fig. 2** Structure morphology on the cross section of the inner wall of the HP cracking tube

cross section of the inner wall of the tube. In addition, after long running, many microcracks and microvoids caused by carburization appear at the boundaries between carbides and austenitic matrix extensively, either in the inner wall or in the outer wall of HP cracking tube.

Figure 5 shows the scanning micrographs of coke separated from the inner wall of the HP cracking tube. According to morphology, coke can be divided into three types, that is, filament coke distributed on the local region of outer surface of coke, lamellar coke in the center region of coke, and spheroidal coke dispersed on the inner surface of coke (the original interface with the gas). The results of EDAX of coke are shown in Fig. 6. It is clear that filament coke contains some metal particles. Nickel and iron are predominant in these particles. However, no detectable amounts of iron and nickel exist in two other types of coke. This indicates that only the formation of filament coke is closely related to the chemical compositions of the inner surface of 25Cr35Ni cracking tube, which coincides with the points of view in the literatures (Ref 22-24).

#### 4. Discussion

Cracking tube usually serves in an elevated temperature and carbonaceous environment. Since cracking gas primarily consists of hydrocarbon and steam, a mixed carburizing and oxi-

dizing atmosphere, silicon and chromium oxide scale easily builds up on both surfaces of 25Cr35Ni cracking tube. Moreover, superheating steam or a mixture gas of air and steam is commonly used as decoking gas in petrochemical plants, which can promote formation of surface oxide scale of cracking tube. In coking and decoking cycles, the cracking tube is subjected to cold/heat fatigue and coke is deposited on its inner wall and swept away by decoking gas repeatedly. This easily results in periodic spalling and regeneration of the oxide scale and gives rise to the etched morphology of the inner surface of the tube (Fig. 1). So after long-term service, only internal oxide trace (layer A in Fig. 2) is kept in the inner wall of the cracking tube. Silicon is well known to tend to aggregate beneath the surface oxide scale and exist in the form of internal silicon oxide (Ref 19), which conforms to the result of linear scanning of EDAX (Fig. 3).

The more complicated carburization process of the inner wall of the cracking tube is closely associated with the oxidizing process. In accordance with the argument of Bennett and Price (Ref 22), cracking gas diffuses into the wall interior through the microvoids and microcracks distributed in the surface oxide scale of the tube. Once oxidants in cracking gas are consumed by internal oxidation, the carbonaceous gases re-

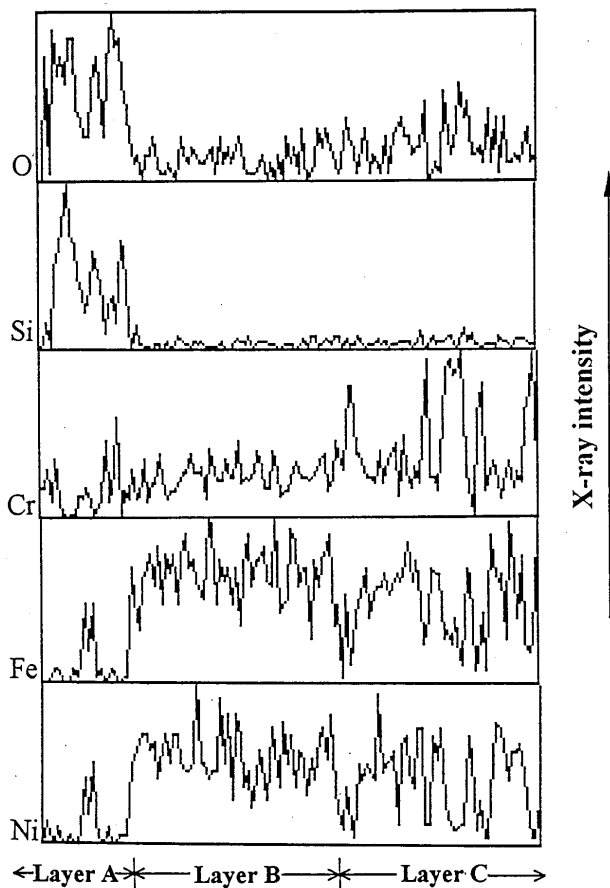


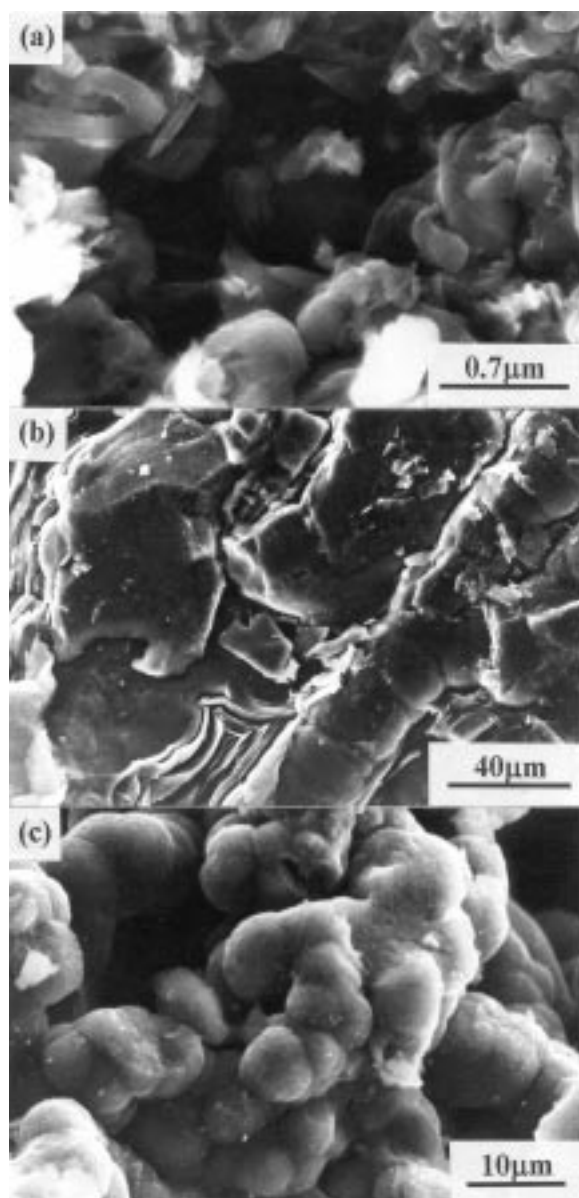
Fig. 3 EDAX linear scanning of the cross section of the inner wall of the HP cracking tube



Fig. 4 Structure morphology on the cross section of the outer wall of the HP cracking tube

maining in defects of scale are dissolved into activated carbon under the catalysis of substrate metal, accessing to the alloy along the intergranular regions and strongly promoting internal carburization. In terms of the above crevice mechanism, the internal carburization of the tube should start where intergranular oxidation ends. In the present work, this is true in the inner wall of the cracking tube after short-term service (Fig. 7). However, Fig. 2 clearly shows that the carbide-free zone in the cracking tube after long-term service is far beyond the internal oxide zone. Thus, relying only on the crevice mechanism proposed by Bennett and Price, it is difficult to completely explain the formation of such a wider, carbide-free zone.

In substance, carbon has higher solubility and diffusivity in Fe-Cr-Ni alloy and carbon more rapidly diffuses inward while metal elements diffuse outward, that is,  $C_C D_C \gg C_M D_M$  (where M primarily denotes chromium and partly iron). When



**Fig. 5** Scanning micrographs of coke. (a) Outer surface. (b) Center cross section. (c) Inner surface

the carbon content in alloy reaches the solubility limit, excess carbon will be precipitated in the form of carbides combining with metal elements. If the precipitated carbide is expressed as  $M_n C_m$ , consider the equilibrium:



The equilibrium constant is given by:

$$K_1 = a_M^n a_C^m \quad (\text{Eq 2})$$

where  $a_M$  and  $a_C$  are the activity of alloy element M and carbon, respectively. Substituting the  $a_M$  and  $a_C$  with:

$$\begin{aligned} a_M &= \gamma_M C_M \\ a_C &= \gamma_C C_C \end{aligned} \quad (\text{Eq 3})$$

one can obtain the solubility limit of carbon in alloy as:

$$C_{\max} = K^{1/m} \gamma_M^{-n/m} \gamma_C^{-1} C_M^{n/m} \quad (\text{Eq 4})$$

where  $\gamma_M$  and  $\gamma_C$  are the activity coefficient and  $C_M$  and  $C_C$  are the respective mole concentrations of alloy elements and carbon.

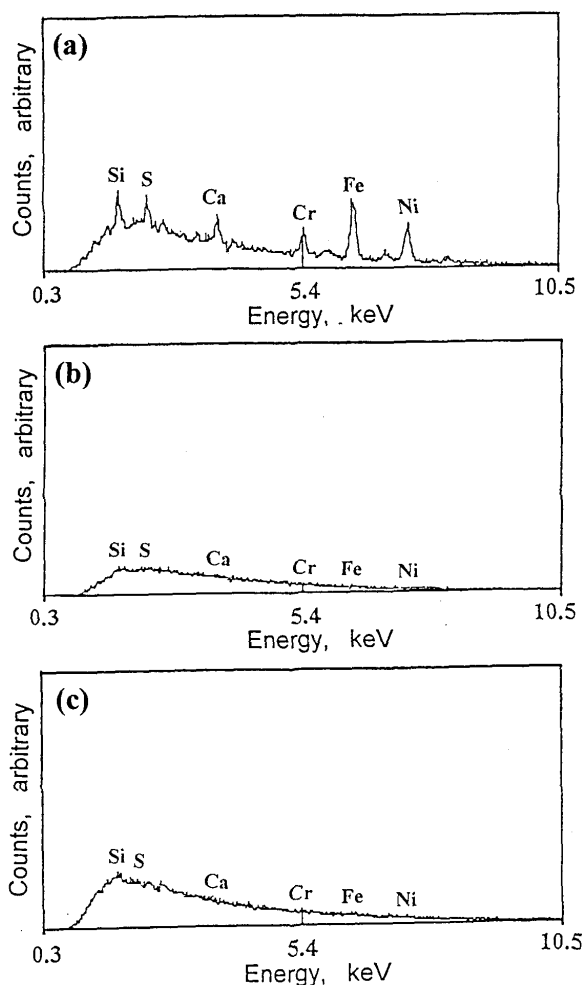
Therefore, the necessary critical carbon concentration to precipitate carbide in alloy increases with the concentration of carbide forming elements, according to Eq 4. For the HP cracking tube, periodic spalling and regeneration of external oxide scale and the formation of the internal oxide zone have consumed a part of chromium in matrix beneath the surface, and the outward diffusion of chromium in alloy is slower because of lower diffusivity, both of which will result in a chromium-depleted zone and, in turn, an increase of  $C_{\max}$  in the subsurface layer of tube.

Thus, it becomes difficult to maintain the carbon concentration levels required to keep the carbides stable. As a result, the carbides tend to dissolve and a carbide-free zone develops gradually. From Fig. 2, one can obviously identify some residual traces of incompletely dissolving carbides in layer B. The dissolution of the carbides increases the carbon content of the surrounding matrix and gives rise to the concentration gradient of carbon from the subsurface to the interior of the tube. Simultaneously, the activated carbon resulted from external cracking gas or incomplete combustion of coke during the decoking operation can further improve the driving force of diffusion of carbon, so carbon atoms inhering higher diffusivity will diffuse into the interior of tube where the chromium content is high enough to precipitate carbides. The combination of processes leads to the formation of a carbide-free zone and an internally carburized zone of cracking tube in service. With prolonged service time of cracking tube, the degradation of surface structures is more serious, the chromium-depleted zone in subsurface gradually widens, and the depleting-degree of chromium becomes more serious. Consequently, the carbides at the denuded zone/carburized zone interface become unstable and be-

gin to dissociate and the carbide-free zone in the subsurface gradually deepens inward.

The structure degradation mentioned above is also strongly influenced by the coking/decoking processes of cracking tube during service. Of three types of coke shown in Fig. 3, only the filament coke is closely associated with the inner wall of the cracking tube. The formation and growth of filament coke need the participation of catalysts such as elemental iron, nickel, and cobalt (Ref 25, 26). Thus the outer layer of coke separated from the inner wall of the cracking tube contains some metal particles. If the inner surface of the cracking tube is completely covered by protective oxide scale, the filament coke may be inhibited because of lack of the catalyst.

However, during service, the cracking tube is often subjected to periodic cold/heat fatigue or heat vibration, and this results in some microcracks or microvoids formed in oxide scale where filament coke is easy to nucleate and grow. The growth of filament coke further disrupts the oxide scale and makes it susceptible to spall. Once the oxide scale spalls off, the naked substrate metal, which is rich in iron and nickel, will be exposed in cracking gas directly. As a result, more heavy filament coke is continuously deposited on the inner wall of the tube under the catalysis of substrate metal.



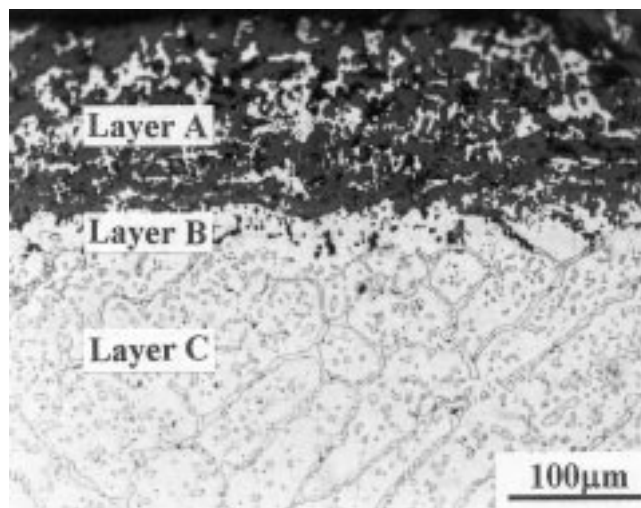
**Fig. 6** EDAX analysis of coke. (a) Outer surface. (b) Center cross section. (c) Inner surface

Moreover, activated carbon more easily diffuses inward by way of the defects distributed in oxide scale. Thus, formation and growth of catalyzed filament coke can accelerate the structure degradation of the inner wall of the cracking tube.

Other types of coke (i.e., lamellar coke in the center region of coke and spheroidal coke dispersed on the inner surface of coke) are deposited by gas reactive without participation of catalyst and bear no relation to tube material in nature. However, their deposition on the inner surface of the tube or on the filament coke can retard the nucleation and continuous growth of filament coke and prevent the inner wall of the tube from direct exposure to cracking gas. So the deposition of noncatalyzed gas coke can slow down the structure degradation of the cracking tube to some extent. But on the other hand, either for catalyzed filament coke or noncatalyzed gas coke, the decoking operation may give rise to spalling or protective oxide scale and aggravate the structure degradation of the inner wall of the tube.

Undoubtedly, the degraded structure caused by surface coking and internal carburization has great influence on mechanical properties of tube materials. The different structures in each layer (A, B, and C in Fig. 2) result in inhomogeneous material properties along the radius direction of the cracking tube and make the cracking tube susceptible to failure due to cold/heat fatigue or heat vibration. Thus, after long-term service, there are a great number of microcracks and microvoids nucleated and propagated along the interfaces between carbides and matrix (Fig. 4 and 5).

Moreover, once the carbide-free zone rich in iron and nickel is exposed in the cracking gas directly because of spalling of the oxide scale, the coking and carburization of the inner wall of the cracking tube is aggravated, seriously damaging the service life of the cracking tube. Therefore, either retardation of a carbide-free zone in the subsurface layer or a continuous, stable, and tight oxide scale formed in advance is an effective way to inhibit the deposition of catalyzed coke, alleviate the carburization of the inner wall of the cracking tube, and prevent cracking tube from premature failure.



**Fig. 7** Structure morphology on the cross section of the inner wall of the HP cracking tube after short-term service

## 5. Conclusions

During service, three distinguished zones, that is, internal oxide, carbide-free, and internally carburized zones, will gradually develop in the inner wall of the 25Cr35Ni cracking tube. The formation of carbide-free and internally carburized zones is primarily associated with the periodic spalling and regeneration of surface oxide scale, the diffusion velocity of carbon and carbide forming elements in matrix and the solubility limit of carbon in alloy.

The formation and growth of filament coke can aggravate the structure degradation of the inner wall of the cracking tube, while the deposition of lamellar and spheroidal coke may slow structure degradation to some extent. The coking and decoking cycles seriously disrupt the perfection of the oxide scale on the inner wall of the cracking tube and promote the internal carburization of the tube, thus strongly aggravating structure degradation and damaging service life of the cracking tube.

## Acknowledgments

The financial support received from Sinopec Technology Company of China and Science and Technology Foundation of Liaoning is gratefully acknowledged.

## References

1. S. Ibarra, Material Challenges in Ethylene Pyrolysis Furnace Heater Service, *Met. Prog.*, (No. 2), 1980, p 62-66
2. D.J. Hall, M.K. Hossain, and R.F. Atkinson, Carburization Behavior of HK40 Steel in Furnaces Used for Ethylene Production, *High Temp.-High Press.*, Vol 14, 1982, p 527-539
3. M.W. Mucek, Laboratory Detection of Degree of Carburization in Ethylene Pyrolysis Furnace Tubing, *Mater. Perform.*, Vol 22 (No. 9), 1983, p 25-28
4. L.T. Shinoda, M.B. Zaghoul, Y. Kondo, and R. Tanaka, The Effect of Single and Combined Additions of Ti and Nb on the Structure and Strength of the Centrifugally Cast HK40 Steel, *Trans. Iron Steel Inst. Jpn.*, Vol 18, 1978, p 139-148
5. H. Wen-Tai and R.W.K. Honeycombe, Structure of Centrifugally Cast Austenitic Stainless Steels, Part 1: HK40 As Cast and After Creep between 750 and 1000 °C; Part 2: Effects of Nb, Ti, and Zr, *Mater. Sci. Technol.*, Vol 1 (No. 5), 1985, p 385-397
6. G.D. Barbabela, L.H. Almeida, T.L. Silveira, and I. May, Phase Characterization in Two Centrifugally Cast HK Stainless Steel Tubes, *Mater. Charact.*, Vol 26 (No. 1), 1991, p 1-7
7. G.D. Barbabela, L.H. Almeida, T.L. Silveira, and I. May, Role of Nb in Modifying the Microstructure of Heat-Resistant Cast HP Steel, *Mater. Charact.*, Vol 26 (No. 1), 1991, p 193-197
8. G.D.A. Soares, L.H. Almeida, T.L. Silveira, and I. May, Niobium Additions in HP Heat-Resistant Cast Stainless Steels, *Mater. Charact.*, Vol 29 (No. 4), 1992, p 387-396
9. C.W. Thomas, M. Borshevsky, and A.N. Marshall, Assessment of Thermal History of Niobium Modified HP50 Reformer Tubes by Microstructural Methods, *Mater. Sci. Technol.*, Vol 8 (No. 10), 1992, p 855-861
10. J. Kelly, Industrial Heating, New High Strength High Temperature Microalloy Particularly Suited for Service in Carburizing and Oxidizing Atmospheres, *Ind. Heating*, No. 10, 1995, p 42-46
11. C.W. Thomas, K.J. Stevens, and M.J. Ryan, Microstructure and Properties of Alloy HP50-Nb: Comparison of As Cast and Service Exposed Materials, *Mater. Sci. Technol.*, Vol 12 (No. 5), 1996, p 469-475
12. T. Shinohara, I. Kohchi, K. Shibata, J. Sugitani, and K. Tsuchida, Development of Nondestructive Technique for Measuring Carburization Thickness and of a New Carburization-Resistant Alloy, *Werkst. Korros.*, Vol 37, 1986, p 410-418
13. Y. Yang, Q. Liu, Y. Jiao, Z. Hu, G. Jia, G. Zhang, Y. Gao, and J. Zhang, Solidification Structure of 25Cr-20Ni-Fe-C Alloy by Electromagnetic Centrifugally Casting, *Proc. of Int. Symposium on Electromagnetic Processing of Materials*, (Nagoya, Japan), ISIJ, Oct 1994, p 420-425
14. Y. Yang, Q. Liu, Y. Jiao, Z. Hu, J. Zhang, and Y. Gao, Effect of Fluid Flow on Eutectic Carbide of Steel HK40, *Proc. of the 2nd Pacific Rim Int. Conf. on Advanced Materials and Processing*, (Kyongju, Korea), Korea Institute of Metals and Materials, June 1995, p 149-153
15. Y. Yang, Q. Liu, Y. Jiao, Y. Ge, Z. Hu, Y. Gao, G. Jia, and J. Zhang, Application of Steady Magnetic Field for Refining Solidification Structure and Enhancing Mechanical Properties of 25Cr-20Ni-Fe-C Alloy in Centrifugal Casting, *ISIJ International*, Vol 35 (No. 4), 1995, p 389-392
16. J.A. Thuillier, Better Tube Life in Ethylene Pyrolysis Furnaces, *Mater. Perform.*, Vol 15 (No. 6), 1976, p 9-14
17. J. Blackburn, Current Status of Carburization Testing and Assessment, *Mater. Perform.*, Vol 16 (No. 12), 1997, p 24-29
18. L. Wolfe, Laboratory Investigations of High Temperature Alloy Corrosion and Failures, *Mater. Perform.*, Vol 17 (No. 4), 1978, p 38-44
19. R.H. Kane, Effects of Silicon Content and Oxidation Potential on the Carburization of Centrifugally Cast HK40, *Corrosion*, Vol 37 (No. 4), 1981, p 187-199
20. R.A.P. Ibanez, G.D.A. Soares, L.H. Almeida, and I. May, Effects of Si Content on the Microstructure of Modified-HP Austenitic Steels, *Mater. Charact.*, Vol 30 (No. 4), 1993, p 243-249
21. D.R.G. Mitchell and D.J. Young, The Effect of Molybdenum and Aluminium Additions on the Carburization Behavior of High Temperature Steel, *J. Mater. Sci. Lett.*, Vol 12, 1993, p 1076-1079
22. M.J. Bennett and J.B. Price, A Physical and Chemical Examination of an Ethylene Steam Cracker Coke and of the Underlying Pyrolysis Tube, *J. Mater. Sci.*, Vol 16, 1981, p 170-188
23. P. Tomaszewicz, P.R.S. Jackson, D.L. Trimm, and D.J. Young, Morphological Studies of Coking on Heat-Resistant Alloys, *J. Mater. Sci.*, Vol 20, 1985, p 4035-4044
24. D.R.G. Mitchell and D.J. Young, A Kinetic and Morphological Study of the Coking of Some Heat-Resistant Steels, *J. Mater. Sci.*, Vol 29, 1994, p 4357-4370
25. M.J. Graff and L.F. Albright, Coke Deposition from Acetylene, Butadiene and Benzene Decompositions at 500-900 °C, *Carbon*, Vol 20 (No. 4), 1982, p 319-330
26. P.R.S. Jackson, D.J. Young, and D.L. Trimm, Coke Deposition on and Removal from Metals and Heat-Resistant Alloys under Steam-Cracking Conditions, *J. Mater. Sci.*, Vol 21, 1986, p 4376-4384