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Microstructural analysis of Cr35Ni45Nb heat-resistant steel after a five-year service in pyrolysis furnace

Jingfeng Guo, Congqian Cheng, Huifang Li, Jie Zhao*, Xiaohua Min

School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China

A R T I C L E I N F O

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A B S T R A C T

To analyze the microstructure across thickness exposed to various environment of the pyrolysis furnace tubes, the sample of Cr35Ni45Nb heat-resistant steel from a five-year service tube was sliced into slices from inner to outer wall. Moreover, microhardness was examined to investigate the influence of the microstructure on the property of the heat-resistant steel. The results show that the primary carbides Cr_7C_3 and NbC have transformed into chromium-rich $Cr_{23}C_6$ and niobium-rich carbides G phase in the middle section of the aged pyrolysis furnace tube. The Cr_2O_3 and SiO_2 layer covered the outer and inner surfaces, and the Cr-depleted zones were formed under the oxide layer of the inner and outer walls. The carbides of $M_{23}C_6$ were transformed into M_7C_3 type carbides in the carburization zone under the Cr-depleted zone of inner surface, while the M_7C_3 type carbides also existed under the Cr-depleted zone of outer wall.

1. Introduction

Pyrolysis furnaces are the critical component in petrochemical systems which are welded by heat-resistant cast steel tubes. The pyrolysis furnace tubes are produced via centrifugal casting process which has excellent high temperature creep strength, good oxidation and carburization resistance. Due to prolonged exposure to high temperature (950–1100 °C), the microstructure of the heat-resistant cast steel is subjected to degradation. The heat-resistant cast steel consists of the primary eutectic carbides of M_7C_3 and NbC and will be transformed into $M_{23}C_6$ and G phase during service, respectively [1–3]. Due to the burning of the burner in the pyrolysis furnace, the outer surface of the pyrolysis furnace tube is oxidized and the thickness of the tube is reduced, so the oxidation is one of the factors which are contributed to the premature failure [4].

In the ethylene cracking process, coke deposition occurs at the inner walls of the pyrolysis furnace tubes, which blocks heat transfer and results in the furnace tube over temperature. The coke also accelerates the carburization rate as well as creep damage [5,6]. In order to remove the coke, a decoking process is carried out at regular intervals, the steam and water are passed through pyrolysis furnace tubes. Some of the coke is burned away and some is cracked off the surface and blown away. So the inner surface is in a cycling oxidation and carburization environment [7,8].Because of prolonged exposure to the carbon-rich environment, the heat-resistant steels tend to degrade primarily by carburization [9]. And the carburization results in precipitation of various types of Cr-rich carbides, which can degrade both the environmental resistance and mechanical strength of the component [8,10]. Due to the regular decoking, the inner surface oxidation of the alloy occurs leading to a two-layered oxide morphology. The outer layer is a spinel, consisting mainly of Fe, Ni, and Cr in the metallic sub-lattice. Beneath this is an oxide layer, which is predominantly Cr_2O_3 [7,8].Many papers focused on the microstructural evolution and the degradation mechanism of the HP heat-resistant steel [5,11–14].

The Cr35Ni45Nb heat-resistant steel as one of the most important alloy used in pyrolysis furnace, it is necessary and urgent to

* Corresponding author.
E-mail address: jiezhao@dlut.edu.cn (J. Zhao).

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Table 1
Chemical composition of the Cr35Ni45Nb heat-resistant steel (wt%).

Designation	C	Si	Mn	P	S	Cr	Ni	Nb
Cr35Ni45Nb	0.35/0.45	1.50/2.00	1.00/1.50	0.040	0.030	32.50/37.50	42.00/46.00	1.50/2.00

investigate the microstructure change [1,15]. Due to the pyrolysis furnace tubes from inner to outer wall are used in different environment, the microstructure is also different across the thickness. A few of studies have been report in the microstructure evolution of ageing for this Cr35Ni45Nb heat-resistant steel [2,16,17]. While these investigations introduced the microstructure evolution and the carbides transformation of the carburization zone in inner wall, the microstructure and carbides change in outer wall cannot be interpreted in these studies. Not only the inner wall damage, but also the damage of the outer wall has a great influence on the service life of the pyrolysis furnace tube. The profound understanding of the microstructure and property across the thickness of the tube will contribute to analyze of the service life and predict the remnant lifetime of these pyrolysis furnace tubes. This present work focused on the microstructure change across the thickness of the pyrolysis furnace tube and the relationship between the microhardness change and microstructure degeneration.

2. Materials and methods

Samples of the Cr35Ni45 heat-resistant steel were cut from an ethylene pyrolysis furnace tube. Table 1 shows the chemical composition of the as-cast Cr35Ni45Nb heat-resistant steel. The tube was from the ethylene pyrolysis furnace of the ethane as feedstock after a five-year service, and selected from the area in the central of the pyrolysis furnace with a maximum working temperature about 1100 °C. Inner and outer surfaces of the aged pyrolysis furnace tubes were dark grey in colour and the thickness of oxide scales was uniform.

Fig1 shows the macrostructure of the aged pyrolysis furnace tube. The macroscope of the sample shows that the structure type is columnar crystal in outer wall and equiaxed crystal in inner wall. The volume fraction of the columnar crystal is about 80%. There is no defect across longitudinal section of the pyrolysis furnace tube.

In order to investigate the second phases across the thickness of the aged furnace tube, the sample was sliced into seven thin slices by wire electrical-discharge machining (WEDM) from inner wall to outer wall as shown in Fig. 1(b). In order to remove the WEDM marks away, the slice thickness would be polished away 0.2–0.3 mm.

The investigation was performed on the longitudinal section of the pyrolysis furnace tube. In order to investigate the metallographic, the specimens were ground with silicon carbides papers from 200 to 2000 grit. Polishing was done on woollen cloth with 0.1 μm diamond paste. The specimens for observation of the microstructure were electrolytical etched in a solution of oxalic acid (10%). The composition of precipitates was characterized by scanning electron microscopy (SEM) and using energy dispersive spectroscopy (EDS). For a thorough recognition of the structure and precipitations, X-ray analysis was conducted in the slices. Microhardness was carried out by vickers hardness tester.

3. Results and discussion

3.1. Microstructure

Generally, the pyrolysis furnace tube exposed to a complicated environment, the outer surface was oxidized, while the inner surface was oxidized and carburized. Fig. 2 shows the X-ray diffraction analysis of every slice of the aged pyrolysis furnace tube. The second phase types and their volume fraction changed from inner to outer surface. Due to the inner surface was in the cycling

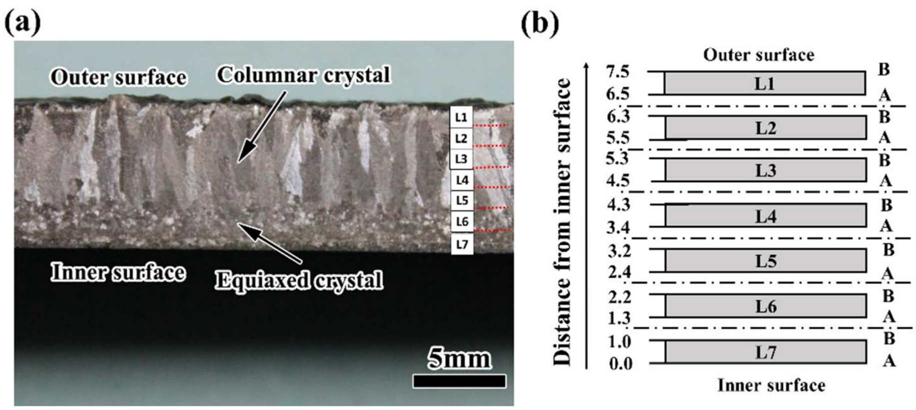

Fig. 1. Macroscopic view of a longitudinal section of the aged pyrolysis furnace tube and the schematic of specimen processing.