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ETHYLENE PYROLYSIS FURNACE TUBE DAMAGE INSPECTION

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Abstract: This aim of this study is to identify failure mechanism of ethylene pyrolysis furnace tube after five year of operation. The tubes were manufactured from centrifugally cast heat resistant steel HK 40. Failure analysis of the radiant tubes was performed by careful visual inspection of the failed tubes, scanning electron microscopy observation of crack region samples, hardness and micro-hardness measurements. Selected specimens were prepared from the four samples, measurements was carried out at inner, middle and outer sides of the samples. The experimental results showed that the mode of tube failure was a combination of high temperature carburization attack and creep damage leading to intergranular cracking. Maximum hardness is associated with internally carburized zone where the amount of carbides is maximum in this region. The hardness of the radiant tubes decreases as the distance moves from the inner surface to the middle section. The metallurgical background of the combined action of carburization and creep ductility exhaustion have been investigated and are explained. Pyrolysis tube failures can be prevented by a combination of proper furnace operation, materials choice, regular inspections and good design.
Keywords: ethylene pyrolysis; furnace; tube; damage; inspection

INTRODUCTION

Ethylene is a key product in the petrochemical industry, and it is produced by the thermal cracking of complex hydrocarbons in pyrolysis furnaces. The furnace coils are formed from the tubes by welding. The tubes used in thermal cracking furnaces in an ethylene manufacturing process are usually made of HP and HK grades of heat resistant stainless steel. These alloys exhibit excellent properties in terms of oxidation resistance, carburization resistance, high temperature creep and thermal expansion. These tubes are exposed to high temperature (approximately 1100 °C and internal pressure of about 1 bar). Normal service life of these coiled tubes is approximately 100.000 h, but does depends on the service condition and could vary from 30.000 to 180.000 h [4].

Ethylene pyrolysis furnace tubes which are made of high Cr-Ni alloys often become difficult to weld after few years in service due to carburization and creep damage. The presence of carburization, often attempted to detect by magnetic permeability, can escape detection due to high Cr-Ni content of the alloy. Based on optical microstructural analysis and supported by scanning electron microscopy, this paper establishes that carburized material becomes difficult to weld due to carburized internal layers of the tube and cause hot shortness. To provide a practical way out for ethylene furnace operators, a solution annealing heat treatment is recommended to have a successful weld.

Pyrolysis coils in ethylene cracking furnaces (Fig. 1) are exposed to very severe conditions, e. g. high temperatures up to 1150 °C, severe start/stop and decoke cycles, oxidizing and nitriding flue gases at the outside and carburizing atmospheres at the tube inside surface. Therefore, high-alloyed centrifugal cast Ni-Cr-Fe alloys with adequate high temperature corrosion resistance, good high temperature strength, good machinability and weldability (even after years of service) are required.

Radiant coils have a limited life and failure is caused by a variety of factors, many being related to furnace operation. However, each pyrolysis plant experiences specific operational conditions and operational philosophies. Therefore, each plant has typical causes for radiant coil failure and it is of importance for operators to analyze and to understand the typical failure mechanisms. This will enable them to consider the material grades, which would be best suited for those particular conditions and also to keep failures within limits by proper furnace operation.

Damages of the furnace coils may be produced by creep, carburization, thermal shocks and accidental overheating [9]. Any failure in these tubes results in shut-down of the cracking furnaces and wasting both cost and time. Replacement of these coils is expensive and difficult. Carburization and creep are the main causes of failure in the heat resistant tubes of ethylene cracking furnaces, leading to a decrease in ductility and embrittlement of the cracking tubes.

The radiant coil assembly (figure 1) of the ethylene furnace was investigated at Stock Company for Production of Petrochemicals, Raw Materials and Chemicals „HIP-Petrohemija" Pančevo – Republic of Serbia. The furnace tubes were fabricated from HK40 steel casting with an internal diameter of 63.5 mm and wall thickness of 16 mm. A section of failed tube was analyzed to determine the cause of failure.

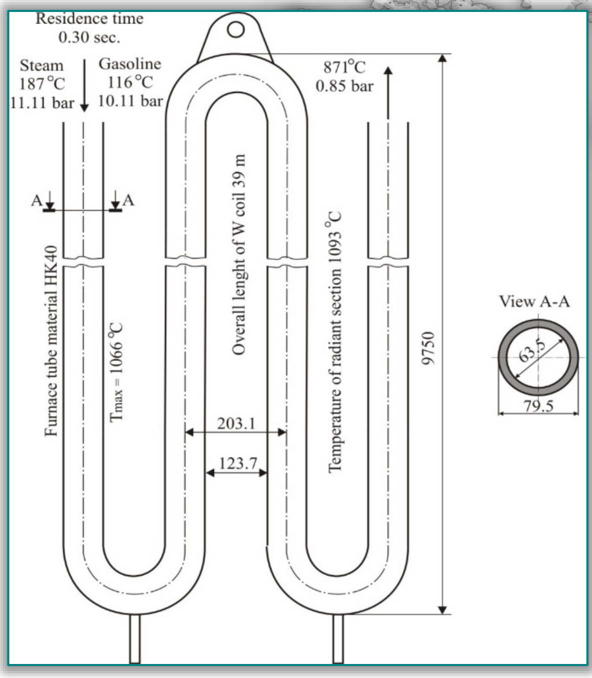


Figure 1. The radiant coil assembly

It is the purpose of this paper to investigate the main failure mechanisms for tubes and outlet parts of pyrolysis furnace coils. In most cases there is a combination of factors which ultimately lead to the failure, e.g. carburization and creep ductility exhaustion. This results in bulging, bending and vocalization of the tubes. Also, brittle fracture during furnace trips can result in large, longitudinal cracks on many tubes in the furnace.

MATERIAL OF FURNACE TUBE

The radiant coils used in our cracking furnace are made by centrifugal casting process. They have appropriate ductility and weldability in as-cast conditions, and lose their ductility and weldability after being used in service. As normally produced, the HK alloy type is stable austenitic over its entire temperature range of application. The austenitic matrix in this kind of high-temperature alloy provides a great mechanical resistance at high temperatures.

Extended exposure at the normal operating temperature of 1093°C have three detrimental effects in these microstructures: grain boundary voids and cracking of the protective oxide scale due to creep, carburization attack and the evolution of intermetallic compounds [1]. All these reduce both mechanical strength and ductility during service life.

Chemical composition and mechanical properties of the steel are presented in tables 1 and 2, respectively [Kubota Metal Corporation].

Table.1. Chemical composition of HK40 (wt%)

Comp.	C	Mn	Si	Cr	Ni	P	S
Min. %	0.35	0.4	0.5	23	19	-	-
Max. %	0.45	1.5	1.5	27	22	0.03	0.03

Table. 2. Mechanical properties of HK40

Mechanical properties		Centrifugal castings at Temperature [^{0}C]					Static castings
		21	760	870	980	1090	21[°C]
U.T.S. Rm	[MPa]	579	262	165	103	38	324
Y.S. Rm	[MPa]	303	165	110	62	34	310
El.	%	20	13	16	42	55	17

CARBURIZATION

During service, hard deposits of carbon (coke) build up on the inner wall of the tube, reducing heat transfer and restricting the flow of the hydrocarbon feedstock which requires that the furnace must be periodically taken off-line and "decoked" by burning out the accumulated carbon. Carburization is the carbon enrichment and carbide formation in the tube material under influence of the presence of carbonaceous gases and high temperatures. This accelerates carbon diffusion in tube material, especially during the decoking period. Carburized material in the inner wall of the radiant tube has a higher thermal expansion coefficient and tends to increase in volume and place stresses on the tube. These thermal stresses make the tube more susceptible to creep failure [9].

The deposition of the coke at high temperature is generally inhibited by the presence of a chromium oxide (Cr_2O_3) layer on the inner surface of the tube. When this film in present carbon diffusion into the tube is retarded. However, during decoking, the tube may be subjected to severe thermal shock that results in removal of the chromium oxide layer, so the carburization attack is increased [10]. Because of exposure of tube at elevated temperature, carbon diffusion could promote formation of continuous and/or separated carbides in grain boundary and matrix [1, 10,]. These carbides decrease the creep resistance and ductility at high temperature. Figure 2. Pyrolysis furnace radiant zone - consequence of a high creep rate Metal dusting is a catastrophic form of carburization that can result in rapid metal wastage in both ferritic and austenitic alloys. This damage mechanism typically has the appearance of localized pitting, or grooving, along the inner walls of pipe and tubes [10].

The ethylene cracking reaction releases free carbon that can deposit on tube surfaces accelerating carbon diffusion and hence carburization in tube material [8].One of the main problems with pyrolysis furnaces is carbon deposition on inner wall of the tubes and creation of a porous layer of coke. Coke formed in the pyrolysis furnace tubes is classified as catalytic and pyrolytic. Adherent coke can have two detrimental effects. First, it acts as a thermal insulator which requires a higher tube wall temperature in order to maintain the same gas temperature. Secondly, it accelerates carburization attack of the tube material.

Carburization leads to the formation of metal carbides in the grains and grain boundaries that consequently reduce the mechanical properties, creep resistance, service life time and weldability of the tubes. The non-magnetic (austenitic) microstructure of these tubes becomes ferromagnetic due to carburization reaction.

Coke is normally removed using decoking technique which consists of shutting off the hydrocarbon feed and passing a mixture of air and steam through the coil. During decoking cycles because of sapling the oxide scale, carburization was accelerated to inner surface that results in an increase of inner surface hardness with respect to outer. Tubes can be subjected to a severe thermal shock where the temperature is increased above normal leading to creep which results in sagging of the tubes. In practice, the need for decoking is dictated by the process parameters particularly gas temperature, flow rates and conversion ratio [4].

CREEP

Creep is the primary cause of the furnace tube damage. It usually initiates within the tube wall some two-thirds of the way through from the outer surface, making it impossible to detect by in situ metallography [7]. This is opposite to boiler super heaters and headers where creep damage initiates at the outside surfaces, making it much easier to detect.

Creep elongation (also called stretching) occurs because of creep by the self-weight of the tube and the coke layer present in the tube and is influenced by temperature, the load carrying cross section of the tube, and the material used. A consequence of a high creep rate is the need to shut down the furnace and to shorten the coils (some end-users have lowered to bottom floor). Failures can occur if tubes are not shortened before they reached the heater floor (figure 2). The coils are warped and bowed, resulting in higher tube stresses and creep rates.

Figure 2. Pyrolysis furnace radiant zone – consequence of a high creep rate

LIFE ASSETMENT

Predicting the life of furnace tubes has long been a problem for petrochemical and refinery industry. Even though failure of heater tubes is not a major safety issue, the prediction of remaining life is important because of cost savings resulting from the optimization of process parameters or reduction of inspection frequency and avoidance of unscheduled outages.

INSPECTION

The tube coils should be inspected closely for bulging, cracking, bowing, sagging, splitting, scaling, corrosion, and deposits from fuel gas. Fittings may show signs of damage, distortion or corrosion.

In order to investigate the mechanical properties, tensile, hardness and micro hardness tests were performed. Microstructures were characterized by using optical microscopy and scanning electron microscopy (SEM). Examinations are focused on three regions, namely inner surface marked I, middle section (region II) and outer surface (region III).

SAMPLES PREPARING

Samples (figure 3) were machined from the as-received tube section for evaluation, one unused piece, one used but not cracked piece (one year in use), one piece showing sagging and different degrees of cracking (five year in use) and one piece which was not sagged but contained cracks (five year in use) at the inner surface that did not penetrate the entire thickness. Cutting was performed by using a precision sectioning machine with direct water-cooling of the specimen.

Figure 3. As received samples

The specimens were ground with SiC papers of the grades 180, 220, 320, 500, 1000 down to grit 2400 (Struers Standard 43-GB-1984, DIN69176, Part 1,2,4) with a pressure of 70-80 N and water as a lubricant. Polishing was done on nylon cloth with 0.3-lm alumina paste. Then, the specimens were etched in Kalling's etching reagent (1.5g $CuCl_2$ in 33ml H_2O, 34ml ethanol and 33ml HCl) to determine the size and location of precipitates in the matrix. For more investigation, the specimens were electrolytically etched with KOH solution.

HARDNESS AND MICRO HARDNESS TESTS

Brinell hardness measurements (HB 5/750/20) were performed on the tube wall cross section to evaluate mechanical strength and to determine a possible carburization /decarburization. The hardness of unused, unfailed and damaged tubes is presented in table 3. It is found that the longer service time results in the higher hardness value which can be attributed to the formation of metallic carbides due to carbon diffusion into the matrix of material at elevated temperature.

Table 3. Brinell hardness of analyzed samples

Sample	Time in use	$[HB_{5/750/20}]$ Inner surface	Middle section	Outer surface	Average
1	new	186	185	186	186
2	1 year	191	187	188	188
3	5 year	258	237	223	239
4	5 year	284	261	248	264

Micro hardness measurements were performed by Vickers method applying a load of 25g ($HV_{0,\ 025}$) for hardness determination of the particular micro constituents. Measurements were carried out at inner, middle and outer sides of the samples. In the as-cast condition (tube never used in service), the micro hardness of the austenite at the inner tube surface was measured to be HV 246 (average of three readings).

Microhardness measurements showed a significant increase in the hardness at the tube's internal surfaces (table 4). The hardness decreases as the distance from the tube's internal surface is increased, suggesting a decrease in the carburization density.

Table 4.Micro hardness of analyzed samples

Sample	Location	$[HV_{0.025}]$ Inner surface	Middle section	Outer surface	Average
1	grain boundary	250	242	247	246
	grain	102	96	98	98
2	grain boundary	267	246	250	254
	grain	149	97	101	115
3	grain boundary	362	308	269	313
	grain	202	176	106	161
4	grain boundary	401	340	297	346
	grain	224	192	147	187

MICROSTRUCTURE

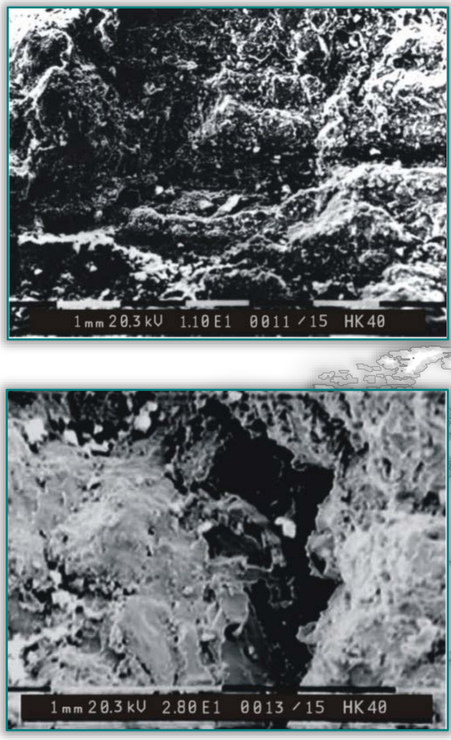
Microstructure of the samples from the tubes analyzed by optical microscope and scanning electron microscope. The microstructure of as-cast HK40 alloy consists of an FCC gamma matrix and a cellular structure, which involves $M_{23}C_6$ carbides on the dendrite boundaries (Figure 4).

a)

b)

Figure 4. As-cast structure of the alloy HK40,
a.) optical - x 150, b.) sem - x 600

The sample 2 material that presumably had been exposed to less severe service conditions displayed only coarse $M_{23}C_6$ type carbides. In sample 3 and 4, $M_{23}C_6$ eutectoid carbides of the as-cast condition were observed to have coarsened and transformed into M_7C_3 carbides with a heavily faulted structure. This carbide transition was observed to have occurred via an in-situ mechanism and also resulted in γ precipitation in M_7C_3. The crack in sample 3 and 4 was visible to the unaided eye, and its propagation appeared to be associated with the carburization and oxidation phenomena. It is evident that the cracks are propagated along the grain boundaries of the austenite grains (Figure 5). This structure was altered in all of three samples due to prolonged exposure to high temperatures, and it was observed that a continuous network of coarse carbides decorated the dendrite boundaries. Across the used tube wall, the materials were observed to have formed three distinct zones with different microstructures: the zones beneath the inner and outer surfaces and the region in between. The microstructure of this centrifugally cast tubular material consist of dendrite grains aligned in the direction of tube diameter and a protective oxide scale is usually present on the inner and outer surfaces.



a)

b)

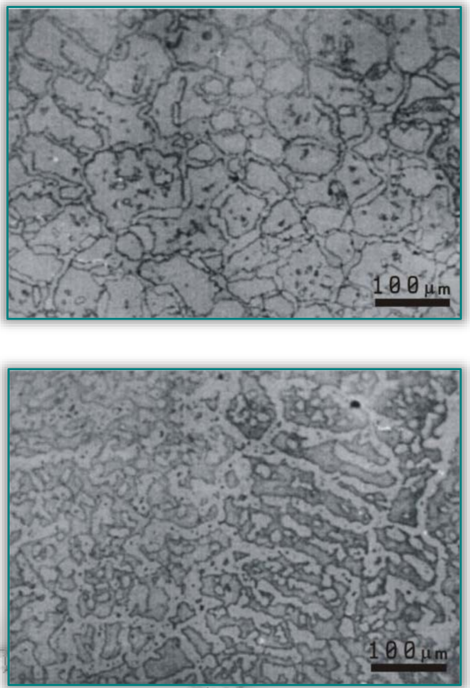
Figure 5. SEM images of sample 3 - a.) Surfaces with crack extended along dendrite grain boundaries – intergranularly, b.) Area with the presence of secondary cracks

The results of the fractured surface analysis presented in figure 5 could be used for explanation of the fracture initiation and propagation mechanisms. The fracture was initiated on oxidation/corrosion products from the inner side of the tube wall. The crack propagates intercrystally, i.e. along the grain boundaries of fine dendrites. Secondary cracks were also identified.

In sample 3, the volume percent of carbides varied across the tube cross-section (fig. 6), gradually increasing from the outer to the inner surface, being 36.2% and 44.7%, respectively. Sample 3 also contained, unlike sample 2, circular intra granular carbides in addition to a macrocrack.

Sample 3, which had been removed from the same furnace as sample 4, showed more severe microstructural degradation to approximately Stage IV in the model of Petkovic-Luton and Ramanarayanan [5].

In both samples, the carbides appeared to have coarsened and become continuous along the grain boundaries during service. This was more pronounced in Sample 3, suggesting that it had experienced more carburization than Sample 4.



a)

b)

Figure 6. Light micrographs from areas beneath: (a) the inner and (b) the outer surfaces of sample B.

CONCLUSION

In this study, ethylene pyrolysis furnace tube damage inspection was performed. The experimental results showed that the mode of tube failure was a combination of high temperature carburization attack and creep damage leading to intergranular cracking. Analyzed cracks in the failed tubes have their origin in the inner side of the tube walls, and propagating across their thickness.

Brinell hardness measurements were performed on the tube wall cross section to evaluate mechanical strength and to determine a possible carburization/ decarburization. This maximum hardness is associated with internally carburized zone where the amount of carbides is maximum in this region. The hardness of the radiant tubes decreases as the distance moves from the inner surface to the middle section.

To avoid such degradation it is necessary to check the operation and decoking temperature and to ensure that the temperature is less than the design temperature. All heater tubes should be inspected, preferably early in life, to establish base-line conditions for tube diameter, wall-thickness, microstructure, and metal hardness.

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