TYPICAL PYROLYSIS COIL FAILURES
AND HOW TO COMBAT THEM

by:

Dr. D. Jakobi
Schmidt + Clemens Group
Kaiserau, Germany

R. Gommans
Gommans Metallurgical Services
Stevensweert, NL

Key words: ethylene pyrolysis furnace, carburization, oxidation, nitriding, creep, oxide scale, centrifugal cast tubes, heat resistant alloys,

Prepared for Presentation at the 2002 Spring National Meeting in New Orleans, LA on March 10-14, 2002

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ABSTRACT

This paper points out 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 ovalization of the tubes. Also, brittle fracture during furnace trips can result in large, longitudinal cracks on many tubes in the furnace.

The metallurgical background of the combined action of carburization and creep ductility exhaustion will be explained. Dense and stable oxide scales on the bore surface lower the amount of catalytic coke and also the carbon ingress into the alloy matrix (carburization). Carburization is also determined by the nickel content of the matrix. Creep ductility exhaustion is determined by the number of cycles (start/stop- and decoke cycles) and the nature (or severity) of these cycles.

Pyrolysis tube failures can be prevented by a combination of proper furnace operation, materials choice, regular inspections and good design.
1. Damage Mechanisms

1.1. Radiant Tubes

The two main failure mechanism for radiant tubes are ductile failures caused by carburisation, nitridation and creep ductility exhaustion and brittle failures caused by thermal shock.

The ductile failure can be recognized by a bulge on the tube and a short longitudinal crack on top of the bulge. In the micro-structure creep voids can be observed between matrix and carbides. Further explanation and the metallurgical background about carburization and ductility exhaustion is given in par. 2.1.

The brittle fracture can be recognized by a long longitudinal crack which “ends” in a fork-like appearance. Sometimes, the cracks result in circumferential rupture or “windows” that fall out of the tube. The cracks can be many meters long, and many times, a thick coke layer is present inside the tube.

In the micro-structure can be observed that the carbides have split. This is a marked difference to the ductile fracture and can be recognized easily.

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. It is generally known that not carburized HP-micro types creep less than 45/35 types. However, carbon uptake (carburization) leads to a higher specific volume of newly formed carbides and therefore to internal stresses which cause an increase in creep rate. The creep elongation of carburized ex-service centrifugal cast, high carbon
tube material has been examined in several studies. Investigations and calculations show, that carburization is a major contributor to longitudinal creep growth and thus shortening of tube life [Guttmann, Bürgel 1980, Guttmann, et al. 1988, Hendrix, Clark 1985, Hendrix, 1998].

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. The coils are warped and bowed, resulting in higher tube stresses and creep rates.

There is also a difference of the height of the firebox. In general, modern higher furnaces suffer more from creep elongation than older smaller furnaces.

Another failure mechanism is **overheating**, which results in local melting or overall melting of the tubes. Such an overheating can happen due to lack of flow, coke blockage or burner problems (flame impingement). Lack of flow can occur when inlet valves fail or in case of compressor problems.

Above 1100°C **nitriding** respectively internal nitride formation occurs from the OD of the radiant tube (flue gas side). Nitrogen penetrates through the oxide and reacts with chromium by precipitation of nitrides. The precipitation in most cases starts with the conversion of carbides into carbonitrides $M_2(C,N)$, $M(C,N)$ and $M_6(C,N)$ which grow by uptake of chromium and nitrogen [Aydin, Bühler 1980].

Also, the lack of oxygen in the flue gas plays a role. Under reducing conditions (many times caused due to flame impingement by badly adjusted burners) this can result in severe loss of wall thickness by alternating oxidation and nitriding. The nitrides then cause spallation of the oxides. As a result a thick layer of oxides (up to
10-20 cm (4-8”) thick!) can be found on the furnace floor. Sometimes, this is called oxide shedding.

Due to nitriding the rough as-cast surface disappears and the surface becomes a smooth and glazed appearance.

The changes in materials properties which are caused by nitriding and carburization are very similar (see par. 2.1.). In both cases internal precipitates are formed and the matrix is more or less depleted of chromium.

**Chromia evaporation** may become a problem for chromia forming at high surface temperatures >1050°C and high oxygen pressures, as in the flue gases of pyrolysis furnaces. Strong chromium depletion in the alloy subsurface region can be the consequence and also the formation of a thick carbide free zone which advances into the alloy. In this area there are no carbide precipitates for the alloy strengthening available, and the "sound wall thickness" of the alloy is reduced.

1.2. **Bends and Outlet Parts**

**Erosion** can be observed in 90° or 180° bends or in Y-pieces. This is caused by hard coke particles during the decoking procedure (most accepted theory). Some investigators believe that this erosion is caused by coke particles, which are present during normal operation. The remedy is to modify the decoking procedure, so that the coke is gasified instead of being spalled. Second remedy is to lower the gas velocity during decoke below 200 m/s. Third remedy is to apply “internally stepped fittings”, which have been applied successfully on many occasions.
Thermowells also suffer from erosion by coke particles. Successful solutions include e.g. thermowells fully made of Stellite and the rotation of the thermowell at regular intervals.

As in the radiant tubes, carburisation also occurs in fittings (bends, Y-pieces, tetra fittings etc.). In general, such carburization is not life limiting for the coils, because the radiant tubes will fail before the fittings do. This is because of the high wall-thickness of the fittings.

Thick-walled bends and outlet fittings (Y-piece, tetra-fittings, flanges) may suffer from carburization and thermal fatigue. The carburized zone is brittle and already cracks at low strains. The thermal stresses during start/stop-operation and decoke cycles cause thermal fatigue at the inside of such thick-walled components. A distinct feature is that the cracks are oriented in many directions and are opened widely. Some people call this “crazy cracking” or “mud cracking” because of this marked appearance. This type of cracking is not considered to be life limiting of the component.

2. Metallurgical Background of the Main Failure Mechanisms

2.1. Carburization and Creep Ductility Exhaustion

Carburization is an internal carbon enrichment and carbide formation which occurs mainly in industrial processes where Cr-Ni-Fe alloys are applied at high temperatures (T>800°C) in carbonaceous atmospheres. The carburisation rate is related to the carbon activity of the gas (occurs at carbon activities a_c≤1) and progresses exponentially in relation to temperature [Bagnoli, Krupowicz 1992; Grabke 1998; Grabke, 2000;].
Carbon pickup increases the metal volume resulting in internally induced stresses. It progresses from the tube inside surface causing compressive stresses in the inner wall (carburized tube material) and tensile stresses at the outside (non-carburized tube material). Intergranular cracking results, starting from the middle of the tube wall [Bagnoli, Krupowicz; 1992; Grabke 1998].

Carburization should be negligibly slow at temperatures below 1000°C for the usual materials with 25% Cr. They form protective scales composed of an outer spinel layer (Mn, Cr-oxide) and an inner chromia layer (Cr$_2$O$_3$) which are nearly impermeable for carbon diffusion from the atmosphere, since carbon solubility in these oxides is extremely low. However, there are several mechanisms leading to the failure of the oxide scale:

- Too large diffusion distance through the de-chromized zone: The periodic process of chromium oxide growth and spallation results in a gradual depletion of Cr in the alloy subsurface region. A critical thickness of the Cr-denuded zone is reached in operation at about 200µm [Petkovic-Luton, Ramanarayanan 1990; Ramanarayanan, Petrovic 1998]
- Conversion of Cr-oxides to non-protective carbide phases at high temperatures above 1050°C and high carbon activities $a_c \geq 1$. The surface carbides do not provide much protection against internal carburization [Grabke 1998; Grabke et al. 1976; Ramanarayanan, Petrovic 1998].
- Structural defects in the protective oxide layer (pores, cracks, etc.), e.g. cracks formed as a result of thermal cycling [Wolf, Grabke 1985; Wolf et al. 1988].

The resistance of materials against carburisation is given by the Ni-content and the presence of Si, which forms a silica sub-scale. Therefore, modern materials have a
high Ni content (well above 40%) and Cr contents of minimum 25-30% and contain 1.5-2.5% Si. The most modern Cr-oxide forming material in this respect is the 45Ni/35Cr-material (such as ET45 Micro) with certain alloying additions (rare earth elements) in order to improve the oxide scale adherence [Kirchheiner, Jimenez 2001].

**Creep ductility exhaustion** is a complex mechanism in which the creep ductility is exhausted by cyclic operation (such as decoke stops, plant shut-downs and trips). During normal operation a coke layer is deposited at the ID of the tube. At the end-of-run (EOR) such coke layers can be up to 20 mm thick. During the decoking the coke is gasified, with the purpose that the tube is clean after the decoke.

However, during the change between normal operation and decoking a temperature drop occurs. Because the thermal expansion coefficient of the metal is much higher than the coefficient of the coke, the metal-tube shrinks on the “coke-tube”. Because of the high compressive strength of coke, the metal does not crush the coke. This causes high tensile stresses in the tube metal, which relax during the (on-line) decoking procedure. The strain range that occurs is proportional to the difference in thermal expansion coefficient and the temperature range according to the equation given in *figure 1.*

\[
\alpha_{\text{metal}} \approx 19 \, \mu m/m/K \\
\alpha_{\text{coke}} \approx 4 \, \mu m/m/K \\
\Delta \varepsilon = \Delta \alpha \cdot \Delta T
\]

*Figure 1:* Tube metal and coke layer during a temperature drop
During a normal decoke such a temperature drop can be 100-200°C, this causes a strain range of 0.15-0.30 % which corresponds to high stress levels. During the subsequent de-coking procedure these high stresses relax because of creep. The damage mechanism is thus cyclic creep relaxation. During each cycle the tube creeps a small amount; and at end-of-life the material reaches it’s creep ductility. That is were the name “creep ductility exhaustion” comes from.

Tube life is thus dependent on:

- the number of de-coke cycles (n);
- the severity of the cycle (start/stop, on-line or off-line decoke, ΔT); and
- creep parameters (temperature, material, creep rate, creep ductility).

The combination of carburisation and creep ductility exhaustion is the “normal” failure mechanism for pyrolysis tubes in ethylene plants. It results in bulges, ovalisation and sometimes, tube bending as has been described in par.1.1. Each single occurrence is relatively simple to explain, but the complete process is complex and not yet fully understood.

2.2. Brittle Fracture Caused by Furnace Trips

As described in the previous paragraph the metal tube shrinks on the “coke tube” during a temperature drop. During a normal decoke the temperature drop is limited to about 100-200°C. During a furnace trip such a temperature drop can be 500-1000°C. The strain during such a furnace trip is then 0.75-1.5%. This equals the rupture ductility of aged, carburized and nitrided material between RT and ~600°C. Since materials tend to crack when their rupture ductility is reached … furnace tubes also crack. Because aged, nitrided and carburised furnace tube materials are brittle
at these temperatures, they crack brittle by splitting the carbides and subsequently the tubes. These brittle cracks can extend for many meters.

The risk for brittle cracks is dependent upon:

- the severity of the trip (temperature drop);
- the thickness of the coke layer inside the tube; thin coke layers at SOR will be crushed, but thick coke layers at EOR will not;
- the degree of brittleness of the material, which is determined by the amounts of ageing and carburization.

As a guideline brittle fracture occurs most frequently when the tubes are already a few years old and when the furnace is in the second half of its operation run. This “dangerous area” is given in the figure below.

**Figure 2:** “Dangerous area” for brittle cracks
3 Process Technological Background

The underlying problem for the main failure mechanisms of radiant tubes is deposition of coke at the ID of the tube. The coke deposition results in higher tube wall temperatures. For a tube life of about 6 years in high severity cracking furnaces EOR-temperatures can be up to 1100°C for HP-materials (such as G4852 and derivatives) and 1125°C for 45Ni/35Cr materials (such as ET 45 micro). At these high temperatures the materials carburize and creep harder.

Therefore, many problems are related to furnace operation. Overheating, flame impingement, nitriding, oxide shedding, reducing flue gases, erosion, and specially brittle fracture can all be prevented by proper furnace operation.

Creep elongation, carburization, and creep ductility exhaustion can be kept within limits by proper furnace operation, proper materials choice and good design.

Furnace inspections may give early detection of up-coming failures, and should therefore be performed at regular intervals (e.g. during decoke stops).

4 Relation to Inspection and Life Assessment

In the ideal case the inspection and life assessment tools take account of the failure mechanisms involved. However, there are no such tools available yet.

It can be helpful to measure carburization. Several companies offer traditional carburization meters based on magnetic principles (permeability, eddy current etc.). Recently, Shell Global Solutions International presented a new pulsed Eddy Current
technique, which showed promising results. However, a fully carburized tube can have a remnant life of 1-2 years (if no furnace trips occur).

Dimension measurements can be helpful as well. If creep elongation (stretching) is life limiting for the furnace, it can be monitored by the position of guide tubes. In most cases creep in circumferential direction (tube swelling, bulging and ovalization) is life limiting. Diameter measurements by simple strapping can be helpful. However, there will be tubes that fail at low ductility’s and tubes that will fail at higher ductilities (up to 15% has been observed !). This is dependent on the type of material (HK40, HP-Nb or 45/35), but also significant scatter between the individual tubes exists.

Accelerated creep testing of ex-service material is not suited to determine the remnant life of pyrolysis coils, because the relevant failure mechanisms (combined carburization and cyclic relaxation) can not be taken into account by a simple creep test.

For the time being, visual inspections and strapping (diameter measurements) are the best inspection tools. One should look for bulging, ovalization and appearance (smooth vs. rough). The results obtained can be used for trending. Many operators replace tubes about 9-12 months after the first bulges and ovalities are observed.

However, significant developments are being made in modeling the relevant failure mechanisms. Also, statistical approaches are under development. S+C is developing a statistical method to determine residual coil life based on operating conditions.
6. Conclusions

- The dominant failure mechanisms for radiant tubes are (a) the combined action of carburization and creep ductility exhaustion, and (b) brittle fracture during furnace trips. The first mechanism results in bulging, bending and ovalization of the tubes. The second mechanism results in large, longitudinal cracks.

- The metallurgical background of the combined action of carburization and creep ductility exhaustion are explained. Carburization is determined by the presence of protective oxide scales, and the nickel and silicon content of the matrix.

- Creep ductility exhaustion is determined by the number of cycles (start/stop- and deoke cycles) and the nature (or severity) of these cycles.

- Other mechanisms include creep elongation (stretching), overheating, nitriding, oxide shedding, thermal fatigue and erosion.

- Many failures are related to furnace operation. Overheating, flame impingement, nitriding, oxide shedding, reducing flue gases, erosion, and specially brittle fracture can all be prevented by proper furnace operation. Creep elongation, carburization, and creep ductility exhaustion can be kept within limits by proper furnace operation, materials choice and good design. Regular furnace inspections may give an early warning of up-coming failures.
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