

Mitigation of CRU Heater Tube Carburization by Modified High Heat Transfer Ceramic Cladding Materials

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ABSTRACT

Carburization is a failure mechanism common to the petrochemical industry in Catalytic Reforming Units (CRU's) where atmospheres containing hydrocarbons and/or carbon monoxide are prominent. Elevated fuel prices cause refineries to run with low excess oxygen to generate cost savings. The resulting atmosphere at elevated temperatures creates an environment where carbon is favorably transferred to iron and low alloy steels, forming a hardened layer of carbides that reduce the life of the steel tubing and vessels.

Ceramic coatings have previously been applied in CRUs to increase radiant efficiency. A dual functionality was hypothesized for select materials to aid in the prevention of carburization. To evaluate this potential, ceramic coatings were applied to a commonly used low-alloy steel tube material and exposed to a low-oxygen, high-temperature, carbon-rich environment. Chemical etching, optical microscopy, and microhardness evaluations were completed to determine the degree of carburization on the ceramic-coated and uncoated control tube surfaces. Results indicate that some ceramic coating materials are highly effective at the prevention of carburization of the treated tube surface when compared to the uncoated control. The implementation of cladding with this class of materials would be optimal for not just improving heat transfer but additionally extending the serviceable life of CRU units in low excess oxygen environments.

Key words: Protective coatings, Corrosion resistance materials, Carburization, Hydrocarbons

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INTRODUCTION

Common materials employed in catalytic reforming unit tubes are typically resistant to carburization due to protective chromium oxide films, but under low excess oxygen conditions can become compromised and allow carbon penetration and carbide formation at the exposed surface. Embrittlement and material wastage as a result of these mechanisms causes premature failures, with production loss, in addition to shutdown maintenance and replacement costs. Carburization in this environment is simulated in this paper through a pack carburizing method designed to create an environment optimal for diffusing carbon in an ASTM 335 9Cr-1Mo tube material.

Carburization in Catalytic Reforming Units

Catalytic reforming is the processing of primarily low-octane paraffins and into high-octane aromatics (92-103 RONC). Octane ranges (RONC) between 92-99 are typically used for gasoline manufacturing and blending, whereas octane between 100-103+ are further processed into chemical precursors for use in plastics production. A series of reactions at elevated temperatures, including paraffin cracking, isomerization, dehydrogenation, and dehydrocyclization,¹ occur within a chemical reactor over a platinum-based catalyst.²

Many of the reactions in the reactor are highly endothermic,¹ requiring great amounts of energy to be transferred into the process. This occurs by the combustion of fuel, either gaseous or liquid, within a fired heater to the process fluid which is flowing within tubular, metal coils. Further increasing RONC requires more energy to be introduced to the process, through the combustion of more fuel. Fired Heater combustion efficiency will increase with increased excess air, until the heat loss in the excess air is greater than the heat provided by more efficient combustion.³ Typical excess air values for optimal efficiency for natural gas is 5-20% and for fuel oil is 5-30%.

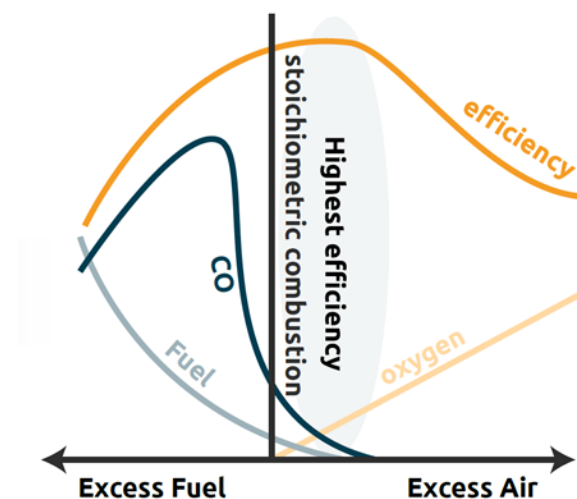


Figure 1: Effect of Excess fuel and Excess Air on Combustion Efficiency⁴

Excess oxygen in the post combustion flue gases ensures complete combustion of the fuel. Typical fired heater operation in some parts of the world utilize excess oxygen in the 10%+ range,⁵ typically in areas where fuel gas costs are relatively cheap and are not considered a major pain point. In this scenario, excess oxygen in the combustion air, at elevated temperatures, will oxidize iron within the process tubes. Over time, oxidation will continue to grow and create a porous, insulating surface. In typical furnace operation, fuel gas consumption is increased to maintain process conditions (RONC).

In other parts of the world, where fuel costs are relatively higher, the excess O₂ level is maintained at lower levels, around 2-3%, to save fuel. More efficient use of the fuel can be achieved closer to

stoichiometric levels. Besides a reduction in energy costs and lower CO₂ emissions through combustion, the benefit of lower excess O₂ levels is a reduction in oxidation.

There is a consequence of an increased tendency for carburization of the external surfaces of the process tubes. Process tube exposed to CO, CH₄ and other hydrocarbon gas such as C₂H₂, from fuel gas at elevated temperatures, such as in a Catalytic Reforming Unit, leads to grain boundary penetration of carbon, carbide formation, embrittlement of the surface, crack formation and loss of metal.



As a result, advanced in-field surveys are required to calculate the severity of carburizing and determine remaining service life. This diffusion mechanism is related to carbon activity of the surrounding environment and tube skin temperature.

Carburization of 9Cr-1Mo Steel

A primary reason for using 9Cr-1Mo tube material in catalytic reformers is the added oxidation protection provided by the alloy elements. These elements create a protective oxide film on the surface of exposed metal, most commonly in the form of Cr₂O₃,⁶ of which carbon is impermeable. However, an elevated temperature environment with low oxygen partial pressure favors reduction over oxidation, causing the protective oxide film to become unstable and less likely to reform when fresh surface metal is revealed. Differing thermal expansion coefficients between the tube material and protective oxide films also cause internal stresses that contribute to the oxide film rupture and reformation cycle.

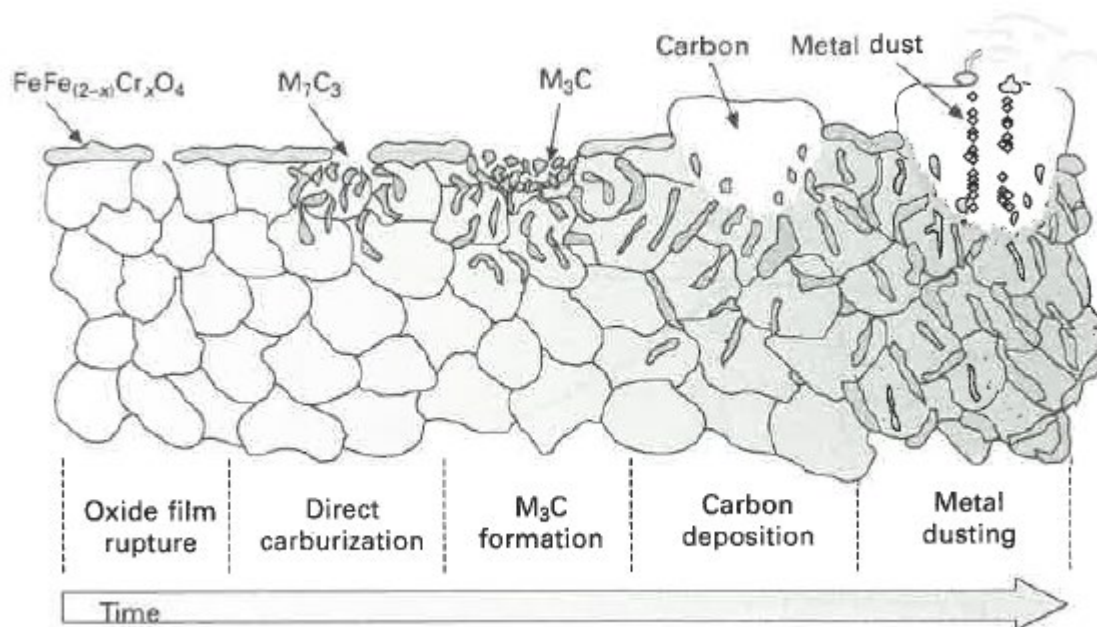


Figure 2: Schematic Representation of Low Chromium Steel Carburizing Progression ⁷

This recreation cycle slowly leeches chromium content from the 9Cr-1Mo material base until there is an insufficient amount of chromium readily available at the surface for the oxide to reform. When the protective oxide barrier is compromised, free carbon diffuses into the substrate precipitating M₇C₃ type carbides where M is typically chromium.⁸ This initial carburizing is to be replicated in this study, as it is the precursor to further carbide formation and material degradation.

Pack Carburization

Pack carburization is a carburizing methodology in which a solid carbon-based compound is packed around a steel sample in an enclosed container and heated to elevated temperatures. The degree of carburization achieved is dependent upon carbon potential of the environment, temperature, time, and composition of the steel.⁹

To achieve a high carbon potential, an enclosed container to limit oxygen supply along with high temperatures like those in CRUs are required. Under these conditions, carbon readily reacts with oxygen in the atmosphere to create carbon monoxide which favorably reacts with iron at the steel surface. This creates active carbon that is absorbed into the steel and carbon dioxide which reacts with the carbon media to produce more carbon monoxide,⁹ accelerating test conditions. These reactions are shown below:



This process is difficult to achieve in higher chromium grades of steel as opposed to carbon or low alloy steels due to the corrosion protection provided by the self-sustaining stable chromium oxide film.¹⁰ To achieve carbon penetration of a 9Cr-1Mo material, the protective chromium oxide barrier must be mitigated via surface activation.¹¹ This is achieved by adding an energizer or catalyst to the carbon source material, commonly barium-, calcium-, potassium-, and sodium-carbonates.⁹ A maximum of 15% activating agent is employed when conducting long term carburizing to simulate ethylene service conditions on low alloy steels,¹² while a 70% total activator content was employed for short term carburizing of stainless steels. Due to the medium alloy grade of 9Cr-1Mo, a 20% activator content is to be employed. A soak time of 24 hours at 760°C was chosen based on simulated potential for carburization of 9Cr-1Mo under low excess oxygen conditions.⁶

EXPERIMENTAL PROCEDURE

Various coating materials were assessed for their ability to inhibit substrate carburization in a low excess oxygen environment. Metallographic specimens were evaluated pre and post exposure utilizing optical microscopy of the resulting microstructures and confirmed with Vickers microhardness testing.

Sample Preparation

Ceramic coating and High-Velocity Thermal Spray (HVTs) cladding materials were selected based on previous use in CRUs and specifications that meet temperature and performance requirements for service. ASTM 335 9Cr-1Mo pipe was selected as the substrate as an alloy commonly used in the petrochemical industry.

Table 1: Sample Material Matrix

Sample Number	Coating Material Name	Notes
1	Control	Uncoated, as-received 9Cr-1Mo (P9)
2	M600 ⁺	Silica Metallic-based Ceramic, 2 mil DFT Heat Cure Max. Service Temperature: 2000F
3	Ceramic A	Silica Metallic-based Ceramic, 1 mil DFT Heat Cure Max. Service Temperature: 2000F
4	Ceramic B	Silica-based Ceramic, 2 mil DFT Air Cure Max. Service Temperature: 1800F
5	Ceramic C	Silica-based Ceramic, 4 mil DFT Heat Cure Max. Service Temperature: 1650F
6	5450 ⁺	NiCr-based HVTS, 12 mil Max. Service Temperature: 1800F

The selected coatings were evaluated chemically and microstructurally using a Hitachi S-3400N scanning electron microscope. Compositionally the ceramic coatings were all silica-based with varying concentrations of metallic modifiers. The HVTS cladding was a Ni-Cr base with trace modifying elements.

M600, Ceramic A, and Ceramic B were structured similarly with a sintered silica matrix with embedded metallic particles. M600 and Ceramic A exhibited dense structures at 1-2 mil thicknesses while Ceramic B has a slightly more porous structure and is applied at a higher thickness of 2-3 mil. Ceramic C had the highest porosity and highest application thickness of the ceramic materials at 4 mil. The 5450 cladding contained dense splats of metallic cladding with low oxide content and low porosity.

⁺trade name