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NEXT-GENERATION INERT AND CATALYTIC INTERNAL COIL COATINGS FOR HIGH SEVERITY CRACKING AND EXTERNAL COATINGS FOR HYDROGEN FIRING

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Abstract

The manufacture of olefins by steam hydrocarbon pyrolysis now exceeds 350 million tonnes annually in more than 3,000 furnaces globally. This requires ~5 billion GJ/year, mostly from natural gas firing of furnaces, with consequent Greenhouse Gas (GHG) emissions of ~400 MMT CO2e. Coke formation necessitates furnace shutdown for decoking every 20-60 days and impacts both energy efficiency and productivity. From a materials perspective, the process is extremely demanding due to its use of high temperatures and cyclic thermal, thermo-mechanical, oxidizing and carburizing corrosive loads on furnace coils. Quantiam has advanced a suite of next-generation coating technologies which enable: (i) increased gains in productivity through coking inertness; (ii) anti-coking gasification functionality; (iii) increased heat transfer; (iv) energy reduction from internal profiles of coatings; and (v) a further step-change in emissions reductions by enabling high levels of hydrogen firing of cracker furnaces.

Significant advancements in anti-coking technology have been made over the last 30 years with development of a wide range of products including chemical additives, coatings inert to filamentous (catalytic) coke-make, catalytic coatings which gasify coke to CO/CO_2, and new alumina-forming base steel alloys. Customer uptake of these technologies has been mixed, with greatest commercial success in lower-severity furnaces with end-of-life tube metal temperatures typically < 1090°C (1,994°F) and well controlled decoking. Best-in-class performance has been achieved with coatings such as the CAMOL^{TM} technology when properly utilized within their defined operating envelopes. These have reduced cracker energy consumption by up to 6% and increased run lengths, achieving over 500 days in ethane cracking and 150 days in naphtha cracking, over a full normal life cycle of the coated coils (4 to 7+ years). The coated products can also reduce the need for sulfur additions and are projected to increase coil life. Commercial success in higher severity furnaces has been more limited as these coating and surface technologies currently struggle to survive a full life cycle at EOR-TMTs that can exceed 1,130°C (2,066°F) and/or are exposed to aggressive oxygen-rich decoking cycles.

Quantiam has conducted five end-of-life coil autopsies, and the results strongly suggest that using EOR-TMTs as a metric for engineering coating properties and operating envelopes is of limited use in predicting coating benefits lifetime. Although only external TMTs are able to be measured, the concentration of key carbide species as a function of their position across the tube wall has allowed us to deduce the maximum temperature experienced by the tube innerwall surface region. The formation temperatures of these species, as assigned by an expert third party, allow their use as 'thermal signatures' within +/- 25°C (77°F) against calibrated standards. This has shown that the tube innerwall topmost 2.5 mm (0.10 in) can be exposed over its life to temperatures >70°C (158°F) above measured external wall TMTs. This is unlikely to result from the endothermic cracking process or steam-based decoking, but rather from exothermic

gasification of localized residual coke deposits within the coil if the air content is increased too rapidly during decoking of furnaces. This creates high temperature excursions on the innerwall's surface. If the coating is engineered only to the expected EOR-TMTs with a modest buffer, this excess internal surface temperature can be catastrophic because although the total time of decoking is typically <10% of coil lifetime, coating materials degradation rate is highly nonlinear with increasing temperature. This results in a drastically shortened coating benefits lifetime. Other degradation processes must also be considered, for example, carburization, oxidation, sulfidation and erosive wear, however the thermal and thermo-mechanical excursions on the inner wall appear to be the dominant factors which define the lifetime of key coating properties such as anti-coking benefits.

These autopsy findings have driven Quantiam's advancement of three new coating technologies targeting **higher severity furnaces,** with the first field trial delivered in 2024 and starting up in 2025. These new products are:

1. **Inert Coating for Higher Temperature Service:** A world-first ***intrinsically*** inert coating for mitigating filamentous coke make - inert-1300 High Temperature (i-1300HT). The i-1300HT matrix microstructure is inert to filamentous coke-make without the need for generating or repairing a protective (inert) surface oxide scale. It has high temperature stability and can withstand internal tube wall temperatures of ~1,150°C (2,102°F), and, in the event of coating disruption caused by thermal excursion beyond the coating's operating envelope, provides additional protection as it cannot form any species that catalyze filamentous coke-make. In addition to its intrinsic anti-coking properties, this coating is also available as an MnO-former and an alumina-former. Because of their high oxidation resistance, all three versions of this coating can also be used as external tubular coatings for hydrogen firing of furnaces at high levels.
2. **Inert Coating for Lower Temperature Service:** A next-generation alumina-forming inert coating - inert-1300 Low Temperature (i-1300LT). This coating has ~30 wt.% aluminum which ties up filamentous coke formers such as iron and nickel in the coating matrix as very stable aluminide phases, preventing their migration into the topmost innerwall surface region. This creates a world-first diffusion barrier with attractive chemical specificity that is stable to temperatures at least 50°C (122°F) higher than all prior coating technologies, that is, at least 1,100°C (2,012°F). Process requirements for formation of a contiguous and dense alumina surface layer are materially reduced compared to current coating state-of-the-art. The weldability of the coated steel remains high.
3. **Multi-Functional Catalytic Coke-gasifying Coating:** A next generation multi-function catalytic coke-gasifying coating (Super Gasifier SGX). As well as providing inertness to filamentous coke-make, this coating provides two pathways to gasify amorphous coke deposited from the gas phase. The dual function catalysts can utilize both: (i) process steam as a source of oxygen to gasify the coke to carbon monoxide and/or carbon dioxide; and/or (ii) the abundant hydrogen resulting from cracking to gasify the coke to methane.

A comparative assessment of both laboratory results and interim field trial results from the installation of the i-1300 coating will be provided against field learnings and successes to-date in **lower severity furnaces.** The new i-1300 and SGX anti-coking coatings target to achieve similar or better anti-coking and energy and emissions reduction benefits in **higher severity furnaces** which have higher operating severity and significantly higher coke-make.

1.0 Introduction

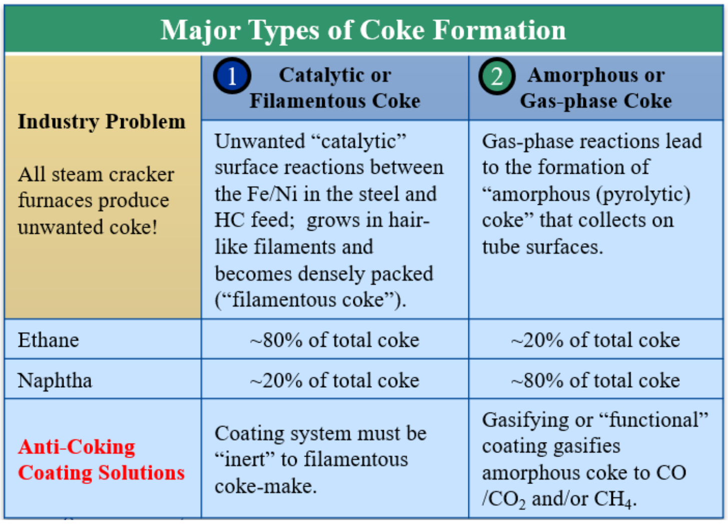
Significant advancements in anti-coking technology have been made over the last 30 years with development of a wide range of products including chemical additives, coatings inert to filamentous (catalytic) coke-make, catalytic coatings which gasify coke to CO/CO_2, and new alumina-forming base steel alloys. Customer uptake of these technologies has been mixed, with greatest commercial success in lower-severity furnaces with end-of-run tube metal temperatures typically <1090°C (1,994°F), and well controlled decoking. Best-in-class performance has been achieved with coatings such as Quantiam's CAMOL^{TM} technology when properly utilized within their defined operating envelopes. These have reduced cracker energy consumption by up to 6% and material increases run lengths, achieving over 500 days in ethane cracking and 150 days in naphtha cracking, over the full normal life cycle of the coated coils (typically 4 to 7 years) [1]. The coated products can also reduce the need for sulfur additions and are projected to increase coil life. Commercial success in higher severity furnaces has been more limited as these coating and surface technologies currently struggle to survive a full life cycle at EOR-TMTs that can exceed 1,130°C (2,066°F) and/or are exposed to aggressive oxygen-rich decoking cycles.

Since the 1960s furnace coil OEMs have attempted to enhance key steel alloy properties, primarily, creep, carburization resistance and oxidation resistance through refinements of steel metallurgy. As noted, ethylene furnace coils are subjected to severe operating and cyclic conditions at effectively the limits of ferrous metallurgy. The genesis of these alloys focused on HK40 (25Cr-20Ni) but has evolved into a range of high temperature alloys (HTAs) containing ever higher amounts of Cr and Ni with 35Cr-45Ni as the workhorse and as high as 45Cr-45Ni and the inclusion of micro-alloyed elements that include Nb, Ti, Ta, W and Zr to further enhance physical properties; very little has been accomplished metallurgically to enhance coil coking resistance other than the success with newer alumina-forming alloys [2]. The mode of manufacture has also shifted heavily from a wrought product to a centrifugally cast alloy that offers higher creep strength and other benefits [3].

The mechanisms of coke formation during elevated temperature processing of hydrocarbons have been well investigated and understood through both academic and industrial efforts in the last three decades. The two principal mechanisms are summarized below in Figure 1, along with the relative proportions of each found in cracking using light and heavy feedstocks and a description of the coating properties necessary for their mitigation.

In efforts to provide furnace tubes that exhibit reduced coking and enhanced carburization resistance, several steel OEMs now provide tubes containing low levels (typically <5 wt.%) aluminum to shift from a chromia-forming HTA to an alumina-forming one. These aluminum enriched steels, either after a pre-oxidative heat treatment or multi-years of service, form an alumina surface layer of various quality levels in thickness, adhesion and density that can reduce filamentous (catalytic) coke formation through surface inertness to this coking mechanism, but do nothing to reduce gas-phase or amorphous coke build-up.

NOVA Chemicals and Kubota advanced a tube product that formed an inert and thermo-mechanically stable Cr-Mn oxide spinel layer through an appropriate treatment. This anti-coking product, ANK400^{TM}, exhibited the ability to materially reduce coke-make [4] within its operating envelope and has gained a good foothold in a segment of the marketplace.



Major Types of Coke Formation		
Industry Problem All steam cracker furnaces produce unwanted coke!	① **Catalytic or Filamentous Coke**	② **Amorphous or Gas-phase Coke**
	Unwanted "catalytic" surface reactions between the Fe/Ni in the steel and HC feed; grows in hair-like filaments and becomes densely packed ("filamentous coke").	Gas-phase reactions lead to the formation of "amorphous (pyrolytic) coke" that collects on tube surfaces.
Ethane	~80% of total coke	~20% of total coke
Naphtha	~20% of total coke	~80% of total coke
Anti-Coking Coating Solutions	Coating system must be "inert" to filamentous coke-make.	Gasifying or "functional" coating gasifies amorphous coke to CO /CO_2 and/or CH_4.

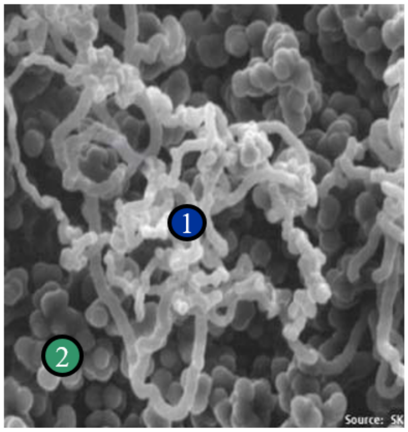


Figure 1. Left: table with descriptions of the two principal coke formation mechanisms, together with the relative amounts of each found in cracking with light and heavy feedstocks and the properties of anti-coking coating solutions necessary to mitigate their formation. Right: SEM micrograph showing the morphology of filamentous coke (1) and amorphous coke (2) as found on the furnace tube innerwall surface.

Several anti-coking coatings have been developed and have met varying degrees of commercialization and acceptance within the ethylene industry. The most relevant commercialized coatings are as described below:

Alon Surface Technologies developed a protective alumina scale called AlcroPlex^{TM} using a chemical vapor deposition (CVD) process [5]. The coating has received minimal industry acceptance due to its properties and performance across a range of operating service conditions.

The Coatalloy^{TM} series of coatings were developed by Westaim Surface Engineered Products and offered the following properties: low coking rate; enhanced carburization resistance; good thermo-mechanical robustness and high temperature stability [6,7], targeting medium severity service. These coatings generated a stable alumina continuous, well-adhered and dense oxide surface scale that helped mitigate filamentous coke formation.

Quantiam Technologies presented to the marketplace in 2012 the first anti-coking product aimed at mitigating both filamentous coke-make and reducing amorphous coke build-up by gasification to CO/CO_2: *Catalyst-Assisted Manufacture of Olefins (CAMOL^{TM})* anti-coking coatings [8]. These coatings targeted medium severity furnaces with a TMT <1,090°C, shutting down filamentous coke-make and gasifying amorphous coke to the limits of available oxygen from steam and surface catalyst loading. Key results from completion of 12 field trials in both Medium and High severity furnaces and 5 full end-of-life autopsies are discussed below in Section 2 as the driving force for the advancements of this paper.

The YieldUp^{TM} coating technology product currently marketed by Veolia uses a perovskite-based ceramic coating to reduce coke build-up [9]. This catalytic gasifying coating is in plant trials.

The collective knowledge of the last 30 years and most critically, the five CAMOL^{TM} autopsy findings have driven Quantiam's advancement of three new coating technologies targeting higher severity furnaces, with the first field trial scheduled to start-up in 2025. These new products are:

1. **Inert Coating for Higher Temperature Service:** A world-first intrinsically inert coating for mitigating filamentous coke make - inert-1300 High Temperature (i-1300HT). The i-1300HT matrix microstructure is inert to filamentous coke-make without the need for generating or repairing a protective (inert) surface oxide scale. It has high temperature stability and can withstand internal tube wall temperatures of ~1,150°C (2,102°F), and, in the event of coating disruption caused by thermal excursion beyond the coating's operating envelope, provides additional protection as it cannot form any species that catalyzes filamentous coke-make. In addition to its intrinsic anti-coking properties, this coating is also available as an MnO-former and an alumina-former. Because of their high oxidation resistance, all three versions of this coating can also be used as external tubular coatings for hydrogen firing of furnaces at high levels.
2. **Inert Coating for Lower Temperature Service:** A next-generation alumina-forming inert coating - inert-1300 Low Temperature (i-1300LT). This coating has ~30 wt.% aluminum which ties up filamentous coke formers such as iron and nickel in the coating matrix as very stable aluminide phases, preventing their migration into the topmost inner wall surface region. This creates a world-first diffusion barrier with attractive chemical specificity that is stable to temperatures at least 50°C (122°F) higher than all prior coating technologies, that is, at least 1,100°C (2,012°F). Process requirements for formation of a contiguous and dense alumina surface layer are materially reduced compared to current coating state-of-the-art. The weldability of the coated steel remains high.
3. **Multi-Functional Catalytic Coke-gasifying Coating**: A next generation multi-function catalytic coke-gasifying coating (Super Gasifier SGX). As well as providing inertness to filamentous coke-make, this coating provides two pathways to gasify amorphous coke deposited from the gas phase. The dual function catalysts can utilize both: (i) process steam as a source of oxygen to gasify the coke to carbon monoxide and/or carbon dioxide; and/or (ii) the abundant hydrogen resulting from cracking to gasify the coke to methane.

2.0 Learnings from CAMOL™ Field Trials and Autopsies

Although CAMOL™ was engineered for medium severity furnaces, certain clients wished to test it in high severity operations. It is critical in crystallizing the engineered and targeted performance benefits of a coating to operate materials within their operating envelope. Operating outside this envelope at the very least consumes installed benefits at an accelerated rate, similarly to base steel tubes that can last from 24 months to 11 years depending on the operator's willingness to stay within their accepted operating envelope.

Quantiam, with assistance from a major steel producer, has conducted five end-of-life coil autopsies of field trialed furnace coils coated with CAMOL™. The results strongly suggest that **using end-of-run tube metal temperatures (EOR-TMT) as a metric for engineering internal tube coating properties and its operating envelopes is of limited use in predicting coating benefits performance and lifetime**. Although only external TMTs are able to be measured, the "signatures" of key carbide species across the tube wall has allowed us to deduce the maximum temperature experienced by the tube inner wall surface region as the isothermal temperature equivalent used in developing a calibration database (it is recognized that an ethylene furnace is anything but isothermal given its cyclic nature but the carbide signatures provide a non-reversible estimate of the maximum temperatures observed in service). The assignment of this maximum temperature by a third-party expert is believed accurate to +/- 25°C (77°F) against their calibration standards database. The autopsies and comparison of these temperature assignments against TMT records by the furnace operator has shown surprisingly that the tube innerwall topmost 2-3 mm (~0.10 in) can be exposed over its full life to temperatures >70°C (158°F) above the measured external tubewall TMTs measured at near-identical locations. This is unlikely to result from the endothermic cracking process or a steam-based decoking but rather by the exothermic coke gasification by oxygen. Air-based decoking is a near-universal necessity in industry, however, the use of such can be detrimental when operating with an anti-coking coating or surface product.

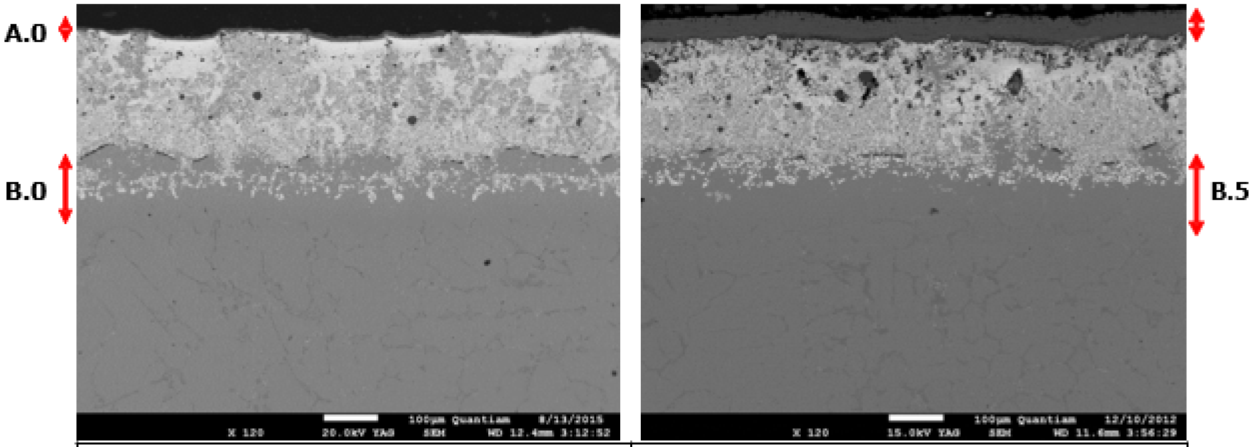
When residual coke is still present, whether due to non-uniform coke buildup due to coil geometry or coke delamination from the decoking process, its presence may not be picked up by the CO/CO_2 concentration monitoring which is used to drive the air ramp-rate. This may result in premature ramping of the air component. On analyzing the decoking process where autopsies were undertaken and good TMT data was available, results indicated a poor correlation between internal tubewall temperatures, and the maximum TMTs measured. If this model is correct, the premature ramping to reduce decoking time creates high temperature excursions on the tube innerwall surface where residual coke remains, caused by the exothermic gasification reaction. This can be catastrophic to the anti-coking technology installed and to the integrity of the topmost few internal millimetres of the base steel.

To date, coating providers have generally engineered their anti-coking products to the expected EOR-TMTs defined/stated by the olefins-manufacturing industry, including a modest buffer enabled by technological and materials limitations (usually the thermal stability of their diffusion barriers). The excess internal tubewall temperature noted above can be catastrophic because although the total time of decoking is typically <10% of coil lifetime, coating materials degradation rate is highly nonlinear (near-exponential) with increasing temperatures and is irreversible. This would result in a drastically shortened coating benefits lifetime and likely why **nearly all anti-coking coating/surface technologies trialed over the last 30 years globally have struggled to provide anti-coking benefits for their targeted benefits lifetimes due either to: (a) operation outside of engineered operating envelopes; or (b) premature (accelerated) ramping of the O_2 component during decoking; or both.** In full furnace field trials undertaken with CAMOL^{TM} products with select operators who solidly operate within Medium Severity conditions (targeting <1,090°C TMTs) and with well-controlled ramping of air-based decoking, the CAMOL^{TM} product has consistently succeeded in delivering fully targeted benefits over the entire normal-course lifetime ranging from 4-7 years depending on feedstock and operator with the final end-of-life runs similar in length to those at start-of-life.

Of the 12 field demonstration trials undertaken to-date, five autopsies have been completed, three at the end-of-life with two for Medium Severity ethane cracking at 4.5 years and 6.6 years, and one in medium severity naphtha cracking at 4.5 years. The key results of one such autopsy in ethane cracking at a normal course 4.5 years operation prior to retubing are summarized in Figures 2-5 below. The trial operated reasonably within the operating envelope of both the coating and the base steel and utilized reasonable decoking cycles that ramped the O_2 content of air-steam decoking respectful of residual coke deposits/pockets to minimize damage to the internal tube (coating) surfaces from exothermic reactions.

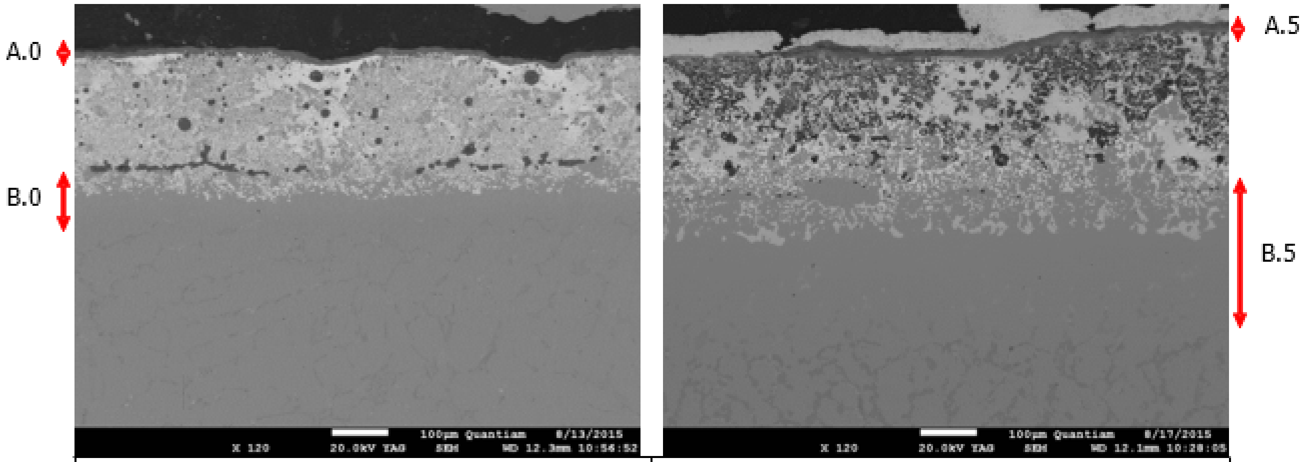
Figure 2, below, shows cross-sectional SEM micrographs of a CAMOL™ coated inlet tube the at installation (left) and at end-of-life after 4.5 years of operation (right) with a maximum EOR-TMT of ~1,020°C. Minimal degradation of the coating is seen, with a significant increase in the catalytic MnO surface layer thickness, and a negligible change in the denuded zone caused by Cr loss below the coating.

Figure 3, below, shows cross-sectional SEM micrographs of a CAMOL™ coated outlet tube at installation (left) and at end-of-life after 4.5 years operation (right) with an EOR-TMT maximum of ~1,080°C. Greater internal evolution/degradation of the coating matrix compared to the inlet tube is seen, but the coating remains essentially intact and with an adequate supply of the original Mn-enrichment in the coating matrix sufficient to continue operation and generate/regenerate the gasifying MnO-based surface.



T = 0 Years, as installed	T = 4.5 years at ~1020°C EOR
A.0 Oxide thickness = ~ 5- 10 µm	A.5 Oxide thickness = ~ 40 µm
B.0 Denudedzone thickness = ~100 µm	B.5 Denuded zone thickness = ~110 µm

Figure 2. Cross-section SEM micrographs of a CAMOL™ coated inlet tube at installation (left) and after 4.5 years operation with a maximum EOR-TMT of ~1020°C (right). Also indicated are the MnO surface oxide layer and the Cr-denuded zone.



Outlet, T = 0 Years as installed	Outlet, T = 4.5 years at ~1080°C EOR
A.0 Oxide thickness = ~10 µm	**A.5 Oxide thickness = ~15 µm**
B.0 Denuded zone thickness = ~100 µm	**B.5 Denuded zone thickness = ~250 µm**

Figure 3. Cross-section SEM micrographs of a CAMOL^{TM} coated outlet tube at installation (left) and after 4.5 years operation with a maximum EOR-TMT of ~1080°C (right). Also indicated are the MnO surface oxide layer and the Cr-denuded zone.

Figure 5, below, shows cross-sectional SEM-EDS elemental maps of the same CAMOL^{TM} coated inlet tubes at installation (top left), 4.5 years (top right), and the outlet tubes at installation (bottom left) and after 4.5 years (bottom right). Figure 6, below shows cross-sectional SEM-EDS elemental maps at higher magnification showing the topmost surface oxide layers of the CAMOL^{TM} coated inlet tubes at installation (top left), after 4.5 years (top right). The outlet tubes at installation and after 4.5 years are shown at bottom left and bottom right, respectively.

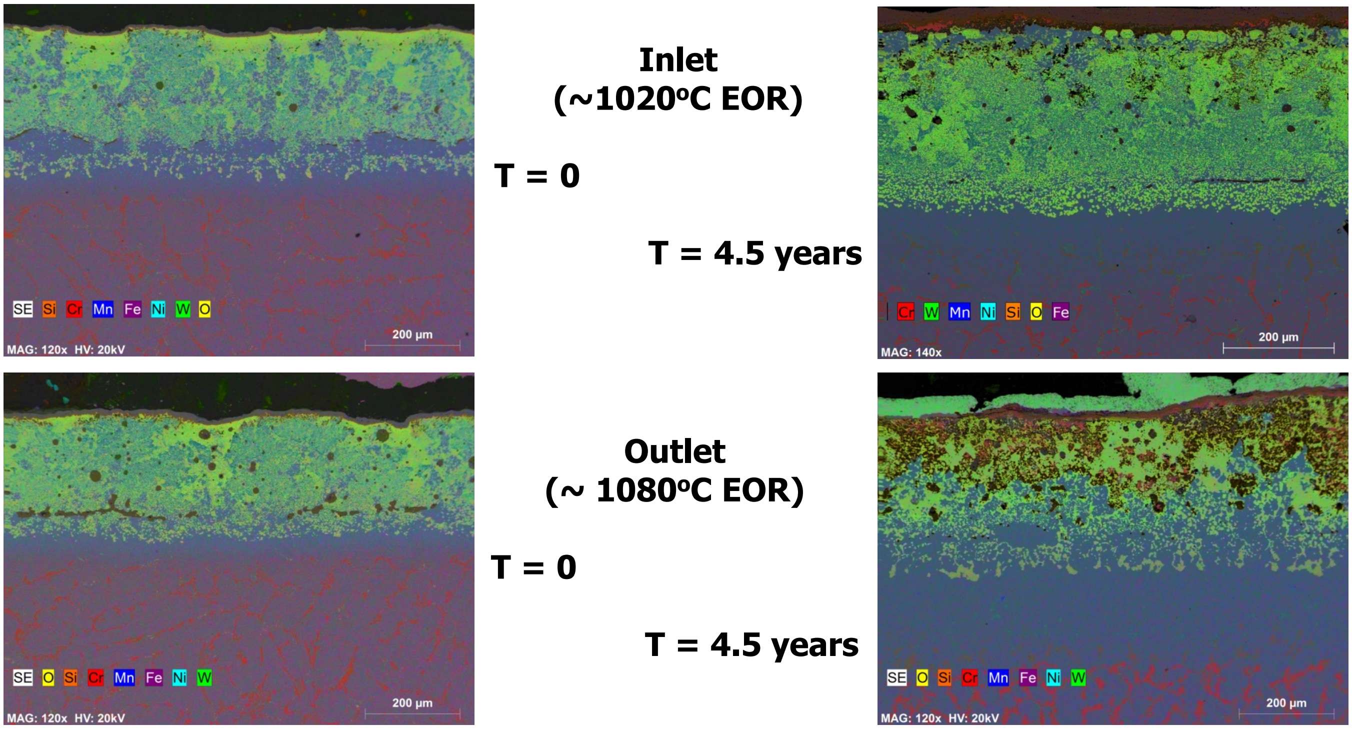


Figure 4. Cross-sectional SEM-EDS elemental maps of a CAMOL™ coated inlet tube at installation (top left) and after 4.5 years operation with a maximum EOR-TMT of ~1020°C (bottom left). At bottom left is the CAMOL™ coated outlet tube at installation, and bottom right shows the outlet tube after 4.5 years operation with a maximum EOR-TMT of ~1080°C.

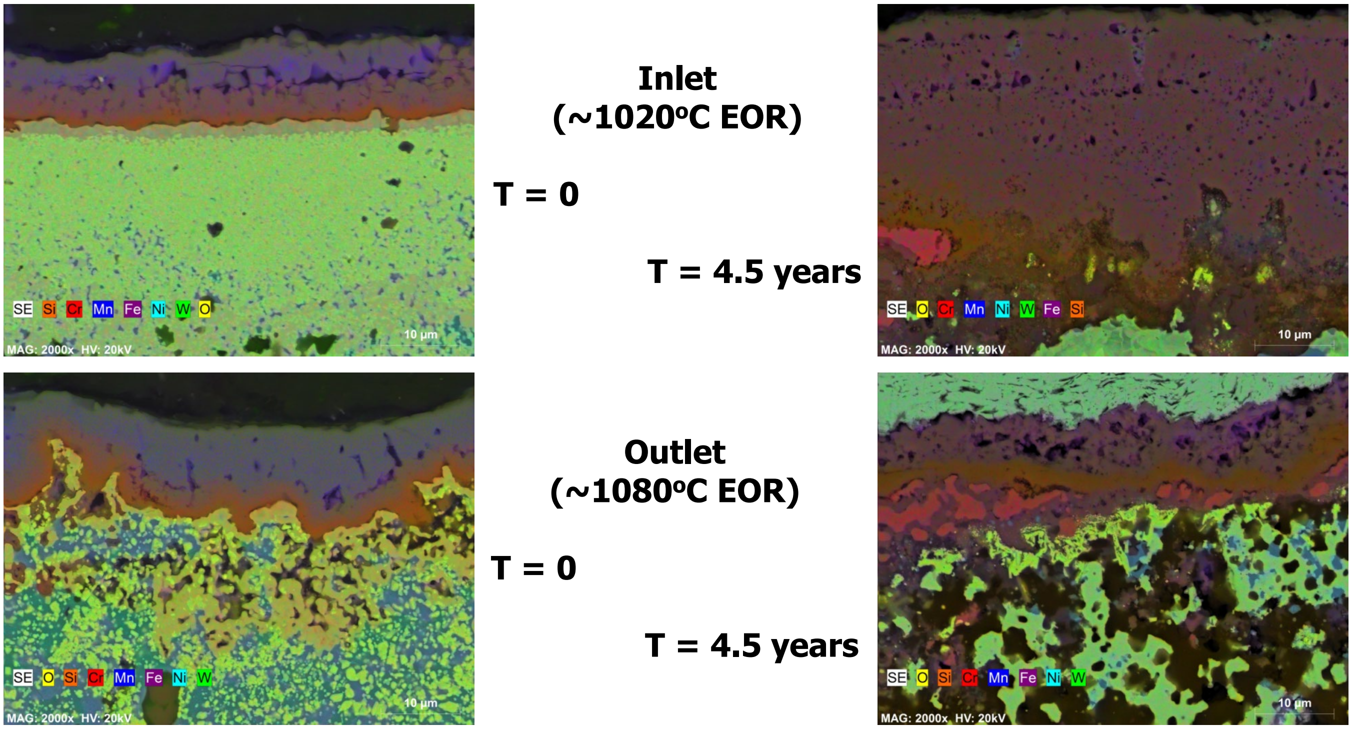


Figure 5. Cross-sectional SEM-EDS elemental maps of the topmost surface oxide layer of a CAMOL^{TM} coated inlet tube at installation (top left) and after 4.5 years operation with a maximum EOR-TMT of ~1020°C (bottom left). At bottom left is the topmost surface oxide layer of a CAMOL^{TM} coated outlet tube at installation, and at bottom right is the outlet tube after 4.5 years operation with a maximum EOR-TMT of ~1080°C.

3.0 Anti-coking Technology Targets and Status

The collective learnings from the development and deployment of the CAMOL^{TM} technology, as summarized in Section 2 above, and the drive to higher cracking severities from olefins producers, have led Quantiam to develop its next-generation coatings with the following characteristics as technology targets:

- Inertness to filamentous coke;
- Ability to gasify amorphous coke;
- Enhanced heat transfer properties to lower operating costs and reduce GHG emissions; and
- Reduced filamentous and amorphous coke deposition via the intrinsic properties of the coating matrix without relying on a surface-grown oxide scale.

Quantiam has developed three inert coating products for application in ethylene furnaces: inert-1300 High Temperature (i-1300HT), inert-1300 Low Temperature (i-1300LT), and Super-gasification (SGX), and all are briefly introduced below. A summary of the three product lines and their intended applications and locations within the cracking furnace coil are shown below in Table 1.

Table 1. Intended applications and positions within the furnace coil of i-1300HT, i-1300LT and SGX coating systems.

Coating	Type	Functionality	Furnace Location	Surface Inertness to Filamentous Coke-make	Inertness Mechanism	Carbon Gasification Activity	Carburization Resistance
inert-1300 High Temperature ("i-1300 HT")	Tube Internal	Inert	Radiant Section Higher Temperature Regions	High	**Intrinsic** Properties of Coating Matrix	N/A	High
	Tube External	Oxidation Resistance For High H_2 Firing	Radiant and Convection Section External	N/A	N/A	N/A	N/A
inert-1300 Low Temperature ("i-1300 LT")	Tube Internal	Inert	Convection Section and Lower Temperature Regions of Radiant Section	High	Alumina-forming Surface	N/A	High
Super Gasification ("SGX")	Tube Internal	Catalytic Coke Gasification	Radiant Section; Higher Temperature Regions	High	Intrinsic Properties with Catalytic Loading	High (>>3 monolayers of C/s to surface)	High

The i-1300HT coating system was developed with the aim of providing protection to both the ethylene coil during normal operation conditions and in situations where severe tube metal temperature (TMT) values are encountered. It is intended that the coating system be applied to coil sections located in the radiant part of the furnace, both internally for anti-coking performances, and externally for compatibility with hydrogen firing. The coating chemistry exhibits thermal stability if TMT values >1,150ºC are achieved. The i-1300HT coating satisfies the following three sets of targeted properties criteria (shown in the Venn Diagram in Figure 6, below):

Criterion 1 – Surface Properties:
- inertness to extreme filamentous coke-make.

Criterion 2 – Bulk Matrix Properties:
- carburization resistance;
- oxidation resistance;
- sulfidation resistance; and
- thermal stability.

Criterion 3 – Microstructural Integrity:
- high coating density with low porosity;
- extreme metallurgical bond strength (steel substrate);
- ductility and weldability;
- thermo-mechanical robustness (matching CTE – coating/substrate); and
- hot erosion wear

To date, sulfidation resistance is the only performance metric yet to be evaluated.

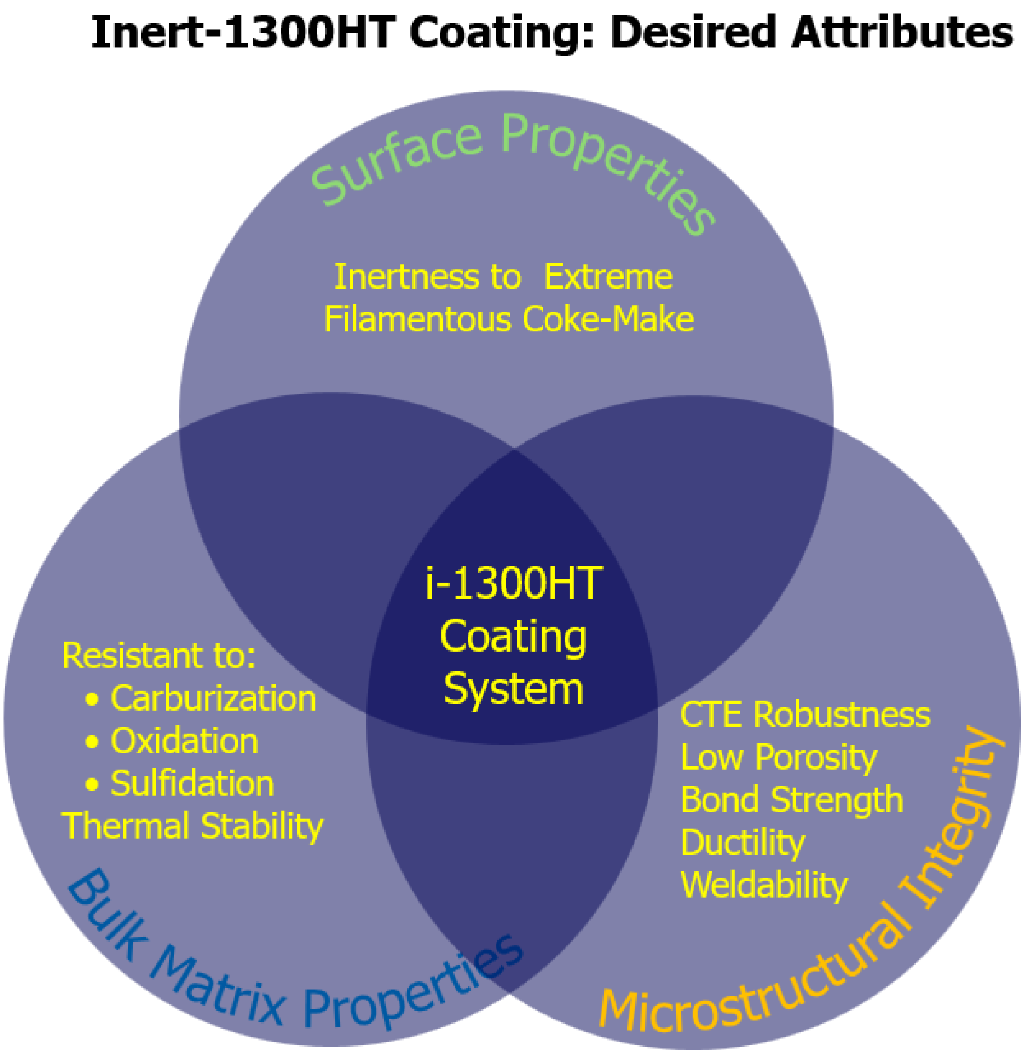
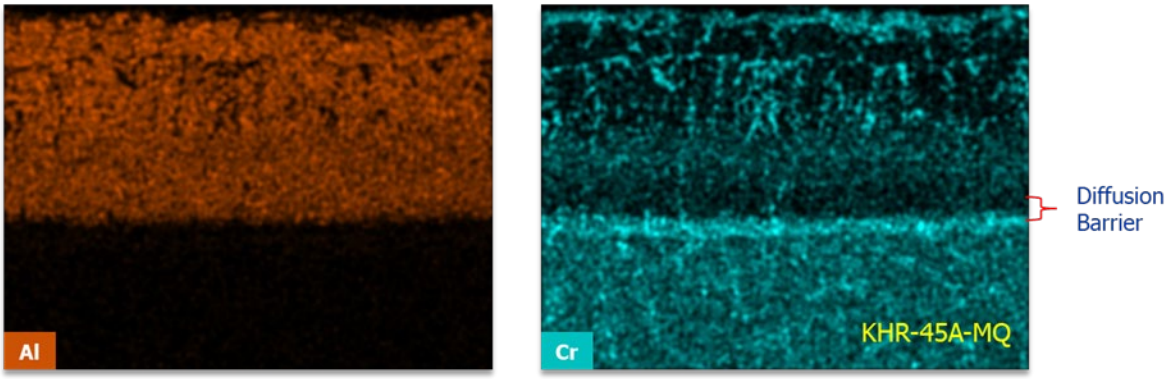


Figure 6. Targeted properties for the i-1300HT coating system deposited onto KHR-45A and KHR-45A-MQ, where KHR-45A denotes a commercial HTA chemistry (35Cr-45Ni-Fe) and KHR-45A-MQ a similar composition containing a narrower compositional range of elemental carbide formers.

The i-1300LT coating system was developed with the aim of providing protection to the ethylene coil in the lower temperature portions of the furnace, both within the radiant section and, if warranted, in parts of the convection section. The coating offers surface inertness to filamentous coke-make via the generation prior to shipment of a highly adherent, dense and contiguous alumina surface. It is an Al-Si based coating with Al levels never previously achieved, with a composition >30wt.% Al. This allows the formation of highly stable aluminides within the coating matrix of transition metals (Fe, Ni and Cr) that mostly diffuse from the base steel. The conversion of the highly filamentous-coking species of Fe and Ni to their stable and inert aluminides is a major material accomplishment in negating the participation of these two species and their reacted forms at the process surface. The coating microstructure also exhibits a unique diffusion barrier as shown in Figure 7, with: (a) exceptional thermal stability for an Al-based coating that has not previously been achieved in the marketplace; and (b) unique chemical specificity for keeping aluminum and silicon within the coating matrix and preventing chromium from the base steel below the coating from diffusing to the surface and ultimately being lost.



Distribution of Aluminum

Distribution of Chromium

Figure 7. Cross sectional SEM-EDS elemental maps showing Al and Cr distribution in a cross-section of an i-1300LT coating showing the unique diffusion barrier that forms its stated properties.

Quantiam's SGX coating is intended to mitigate both filamentous and amorphous coke build-up at high cracking severities, allowing longer production run lengths, and reducing overall energy requirements and GHG emissions. The extreme operating environments needed for high ethane cracking severities (20-50°C higher than current tube metal temperatures of ca. 1090°C at end-of-run for medium-severity furnaces) require the development of novel coating systems with unique physical, chemical and thermo-mechanical properties that can withstand these temperatures whilst handling very aggressive coke formation. The SGX platform technology's gasifying catalysts are non-oxide based and target non-steam-based ("steam limited") gasification pathways. As shown in Figure 8, below, there are three principal pathways by which carbonaceous material can be gasified in a cracking furnace. The most thermodynamically favorable mechanism is for gasification to CO_2 using oxygen, which is utilized during the decoking process to remove deposited coke. However, this reaction is of limited use during cracking operation to prevent coke buildup as there is a very limited supply of oxygen through the steam dilution. Gasification promoted by a coil catalytic inner surface during cracking is therefore limited to using either hydrogen (R1), water (as steam, R2), or CO_2 (R3) to gasify coke being deposited from the process stream. Most catalytic coating technologies, such as YieldUp^{TM} (perovskite based) and Quantiam's CAMOL^{TM} (MnO-based) utilize the steam pathway (R2) to convert coke deposited from the gas phase into CO/CO_2. This takes advantage of the steam in the process stream but there is a tradeoff in that the catalytic species advanced to commercial availability thus far globally must be oxide-based. An inherent weakness in attempting to generate an oxide based active surface on a metallic substrate is the often-low thermo-mechanical stability caused by the poor coefficient of thermal expansion (CTE) matching of the oxide catalyst and its adherence with the HTA coil base material. Additionally, such gasification produces CO/CO_2 into the process stream which can add expense and increase direct GHG emissions. However, the large amount of hydrogen by-product in the product stream (as much as 4% by mass, >20% by volume) affords the opportunity to gasify depositing amorphous carbon into methane (R1), using **non-oxide based catalytic species**. Moving to a platform technology not based on oxides provides for greater CTE matching, high temperature thermo-mechanical stability, and incorporation within the metallic coating matrix at high levels of loading. This enables a highly robust coating system with excellent anti-coking and other critical benefits.

$$\text{R1: } C + 2H_2 \rightarrow CH_4$$

$$\text{R2: } C + H_2O \rightarrow CO + H_2$$

$$\text{R3: } C + CO_2 \rightarrow 2CO$$

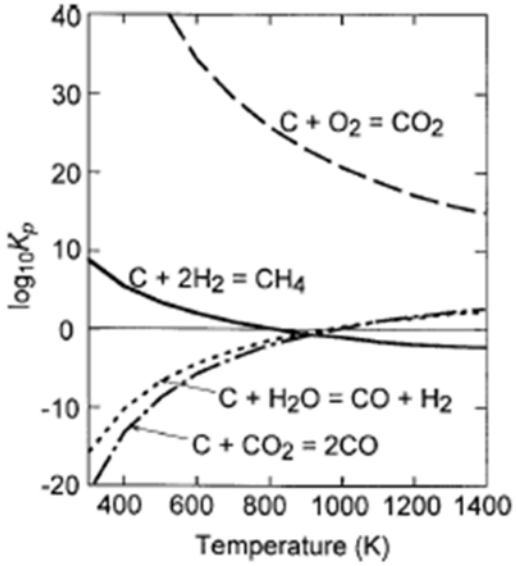


Figure 8. Reaction pathways for carbon gasification using non-oxide-based catalysts in ethane steam cracking (left). The right-hand figure shows equilibrium constants for R1-R3, and for the oxidation pathway against temperature.

The principal technology properties targeted for the SGX coating were therefore:

- a material increase in solid carbon gasification given available catalysts and catalyst loading;
- resistance to filamentous coke formation;
- chemical and thermo-mechanical viability under extreme process conditions.

4.0 Laboratory-Scale Testing of New Coatings

4.1 Experimental

4.1.1 Inert Coating Development of i-1300HT and i-1300LT

4.1.1.1 Surface Performance under Pyrolysis Conditions

The ability of the coating to inhibit the growth of filamentous coke-make during service performance is a defining attribute of any successful i-1300HT and i-1300LT coating. The coking test used dry ethane as a feedstock to probe the coating's surface reactivity towards filamentous coke growth and was termed a **"dry ethane pyrolysis coking test"**. The coking test consisted of heating a coated coupon in a laboratory quartz tube to at least 780°C and then delivering a defined flowrate (200 sccm) of ethane to its surface for an exposure time of 2 hours. It should be noted that screening coking propensity by dry ethane cracking at 780°C has extreme coking rates versus steam-based cracking at ~830°C. The tested coupon's surface was then examined using SEM for the presence of carbon filaments. Coatings that exhibited inertness to catalytic coke-make under these severe dry ethane pyrolysis conditions showed little evidence of any significant filamentous coke build up. Prior to the coking test, coupon samples were honed using a 120 grit silicon carbide stone to reduce surface topography followed by a recrystallization heat treatment (780°C, 2h, 1.5 Torr vac, Ar) to restore the original surface microstructure.

Accompanying the coated coupon were two reference samples, namely, an iron-rich sample (high propensity for catalytic coke formation) and an (inert) alumina sample. These reference samples helped to determine the repeatability of each conducted dry coking test.

Coking deposition results were plotted on a horizontal bar graph as a visual area percentage value and included both amorphous and filamentous coke-make type. Further analysis using SEM was required to differentiate between filamentous and amorphous coke types.

4.1.1.2 Carburization resistance

Coating carburization resistance was determined by how effective the coating was at mitigating the influence of carbon ingress in a carburizing environment on the morphology and dimensions of the base steel's carbide structure. Coated coupons were embedded within graphite powder (carbon activity ~1) and heated to 1125°C (to simulate an internal surface temperature with a corresponding TMT in the field of 1,150 to 1,175°C range). The test used an inert atmosphere of 1.5 Torr (vac, Ar) for a 500 hour exposure time. On completion, the carburized sample was brushed to dislodge any loose scale and the coating's surface was subjected to XRD analysis. The carburized coupon was then cross sectioned and metallographically prepared for examination using OM and SEM techniques. The carbides within the steel were then assessed for changes in morphology, size and distribution with respect to virgin steel. Due to the potential placement of the i-1300HT coil within the radiant section of the furnace, only this higher temperature coating system was subjected to the carburization testing, in efforts to probe severe service conditions.

4.1.1.3 Oxidation resistance

Static, cyclic and oxidation resistance under decoking conditions and hydrogen firing conditions were limited to the i-1300HT coating system. Regarding the i-1300LT coating, oxidation parameters were optimized to enhance the growth of an initial alumina oxide scale with contiguous coverage, good adhesion with an acceptable thickness (4-5 microns) for service life within the ethylene furnace.

Static oxidation resistance testing was conducted by heating coated coupons to 1125°C in air for an exposure time of 24 hours. The oxidized surface was probed using XRD analysis for surface species and, if required, the surface scale imaged using SEM. The oxidized coupon was then cross sectioned and metallographically prepared for examination using OM and SEM techniques. An oxidized coating's cross structure that revealed a contiguous dense oxide surface scale in cross-section generally indicated high oxidation resistance. Minimal coating wastage and no noticeable coating volume expansion were signatures of good oxidation resistance. In addition, the lack of any oxide products associated with any internal porosity sites also inferred the ability of the coating structure to inhibit any ingress of oxygen and/or species into the substrate region.

A cyclic oxidation test, used by some steel producers and operators, was undertaken to simulate the coating system's ability of cyclic repair/regeneration and overall thermo-mechanical robustness. Test coupons were firstly coated on all 6 sides prior to testing and the initial weight recorded. One cyclic oxidation run consisted of the following parameters: 8 hours, 1050°C, air flowrate 200 sccm. After the cycle was completed, the coupons were removed from the furnace, visually examined for signs of any spallation and weighed. If any coupon exhibited significant oxide spallation (there is no coating spallation), the coupon was removed from the test. If no signs of surface oxide spallation were evident, the mass change (mg/cm^2) was plotted against a cycle number, up to 19 oxidation cycles. The mass change was plotted against reference data provided by a supplier of a major alumina-forming steel as a benchmark.

A cycle number of 19 was considered by the steel supplier and several olefins producers to reasonably represent and project a full service life of a radiant tube.

4.1.1.4 Oxidation Resistance of Furnace Tube Alloys for High Hydrogen Firing

In private consultation with a world class expert in olefins manufacturing and current needs driving increasing levels of hydrogen-based firing, Quantiam has projected the flue gas composition inside a hypothetical 100% hydrogen firing, ethane-feed steam cracker furnace to be up to 29 vol.% steam, and 3 vol.% oxygen [10]. The high firing temperature and the steam-rich environment leads to severe steam-led corrosion of the exteriors of the furnace coils.

It is generally accepted that the oxidizing potential of H_2O is greater than that of CO_2, raising concerns of an accelerated oxidation of coil outer surfaces as operators ramp to higher levels of hydrogen firing in an effort to reduce CO_2 emissions. It is unclear if tube suppliers are enhancing the oxidation resistance of key alloys for the industry given this accelerated degradation of the tube outerwalls at high firing temperatures. Quantiam is providing its i-1300HT coating for both internal and external tube surfaces optimally selected for anti-coking properties on the internal tube surfaces and for extreme temperature oxidation on exterior surfaces through the use of MnO-forming or alumina-forming versions of that coating family. If both coatings are applied at the same time, cost is greatly reduced.

Cyclic steam oxidation resistance testing was conducted to understand the corrosion degradation. HTA coupons were coated on all sides prior to testing and the initial weight recorded. One cyclic oxidation run consisted of the following parameters: 8 hours, 1150°C, process feed flowrate 200 sccm (30 vol.% steam, 3 vol.% oxygen, balance nitrogen). After the cycle was completed, the coupons were removed from the furnace, visually examined for signs of any spallation and weighed. If any coupon exhibited significant coating spallation, the coupon was removed from the test. The recorded mass change per unit coated area was plotted against cycle number. The samples were subjected to three or more oxidation cycles. The mass change was plotted against that of Kubota's KHR45A-MQ high temperature alloy as a benchmark.

4.1.1.5 Thermal Stability

Thermal stability studies were conducted by heating coated coupons to an elevated temperature, typically within the range of 950 – 1150ºC in an inert atmosphere (vac/Ar, 1.5

Torr) for test times varying from 100 - 500 hours, depending on the inert coating system. After completion of each test, the coating (i-1300HT) cross sections were examined and compared to initial microstructures by comparing SEM-EDS elemental line scans. High thermal stability was attributed to coatings where there was little change in phase distribution/chemistry (elemental line scan) across the coating thickness, under the influence of temperature and time. Thermal stability results for the i-1300LT coating system were evaluated by assessing the microstructure (cross section) for signs of degradation, namely Kirkendall voids and crack formation.

4.1.1.6 Thermo-Mechanical Robustness by Matching Coefficient of Thermal Expansion

Thermal shock testing, using both air and water as quenching mediums helped determine the thermo-mechanical robustness and coefficient of thermal expansion (CTE) compliance between the coating matrix and the steel. The coated sample was heated at temperatures of 900 to 1,100°C and quenched; water quenching from say 1,000°C to 25°C in milliseconds represents an extreme quench rate that is never achieved in the field. A quenched coating exhibiting no coating cracks or spallation damage inferred good CTE compliance and exhibited good CTE matching. Thermally shocked coatings that exhibited a few radial cracks within the coating were acceptable and passed testing. A quenched coating associated with either coating spallation or a networked crack formation (radial and longitudinal) implies poor thermo-mechanical robustness and were considered to have failed the test, indicating poor CTE matching.

4.1.2 Multi-Functional Catalytic Coke-Gasifying Coating (SGX) Coating Development

4.1.2.1 Catalyst Gasification Screening using H2-based Thermogravimetric Analysis (TGA)

SGX catalyst candidates were non-oxidic as reacted forms of key transition metals, and highly thermally stable. This shift from an oxidic gasification catalyst (CAMOL^{TM}) to non-oxidic (reacted transition metals) catalysts greatly facilitates the incorporation of such catalysts into a metallic coating matrix enabling very high surface loadings. The SGX candidate catalysts were initially evaluated and screened for their catalytic activity toward carbon gasification under hydrogen, steam, and hydrogen/steam atmospheres. The intent was to identify catalysts that showed functionality with H_2 to form methane but equally important, we sought dual-function gasification capacity via both oxygen-to-CO/CO_2 and H_2-to-CH_4 pathways. These two searches proved very successful.

Three different carbon materials were identified as analogues of the amorphous and filamentous cokes formed during steam hydrocarbon cracking, namely activated charcoal, carbon black, and graphite. Activated charcoal was selected for catalyst candidate screening experiments, as it is amorphous, has a high hydrogen content and surface area. As such, it more closely resembles amorphous coke, and the literature indicates that it is the most reactive of the three carbon types allowing for more facile discrimination of catalyst candidate performance.

Catalyst candidate materials were prepared for testing in two ways: (a) impregnated onto an amorphous carbon support as aqueous solutions of catalyst precursor before heat treatment to generate the active catalyst species; or (b) the catalyst species was physically mixed with amorphous carbon. Catalyst candidates were impregnated onto the amorphous carbon as the intimate contact between catalyst species and carbon allowed for more sensitivity to catalytic activity vs the physical mixture. Catalytic performance was quantified using thermogravimetric analysis (TGA) via analysis of carbon weight loss under reactive atmosphere conditions.

Hydrogen gasification pathway testing at low hydrogen concentrations was conducted in a Discovery TGA (TA Instruments). 30 – 50 mg samples were loaded into the instrument and heated to 1000°C at a ramp rate of 20°C/min under a flow of 5% H_2/Ar, followed by a 30-minute hold at 1000°C under the same atmosphere. Samples were cooled to room temperature under inert gas flow (Ar) to prevent post-analysis oxidation of the sample, to enable post-reaction characterization of the species involved in the gasification process.

For testing in high (25 mol.%) concentrations of hydrogen, a SETSYS Evolution TGA-DSC instrument (Setaram) was used. Samples (ca. 20 mg) were loaded into the instrument and heated to 1000°C at a ramp rate of 5°C/min. under a flow of 25% H_2/Ar followed by a 10 hour hold at 1000°C under the same atmosphere. Samples were cooled to room temperature under inert gas (Ar) flow to prevent post-analysis oxidation of the sample to enable post-reaction characterization.

Testing for the steam gasification pathway was conducted in a Mettler-Toledo Star TGA-DSC system. Steam delivery was achieved via mass flow controllers (MFCs) used to evaporate water under a controlled flow of argon, to produce a TGA feed stream of humid gas. Samples (~25 mg) were loaded into the instrument and heated to 1000°C at 20°C/min under a <2% v/v H_2O/Ar atmosphere, followed by a 30 minute hold at 1000°C under the same atmosphere. Samples were again cooled to room temperature under inert gas flow (Ar) to enable post-reaction analysis of the species involved in gasification.

Testing for mixed H_2/H_2O gasification was also conducted in the Mettler-Toledo Star TGA-DSC system; testing conditions were identical except for being conducted under a 1% H_2O/4% H_2/balance Ar atmosphere.

4.1.2.2 Surface Performance under Steam-Ethane Pyrolysis Conditions

A shortlist of catalyst candidates identified in the screening was brought forward for assessment of carbon gasification capacity under steam-ethane cracking conditions. For testing, catalysts were incorporated at a 60 mol.% concentration into an inert alumina-based matrix and coated onto 19x7x1 mm high purity alumina coupons.

Testing was undertaken in a modified Setaram SETSYS Thermal Gravimetric Analysis TGA-DSC unit. This was used to probe catalyst performance under simulated industrial conditions, i.e., in a steam-ethane cracking reaction. To achieve this, a Setaram WETSYS humidity generator was added to the system, together with a custom upgrade which mixes steam from the humidity generator with ethane feedstock such that a dilute steam/ethane mixture can be used to probe the catalyst-coated coupons under steam-ethane cracking conditions. The system monitors in real time coupon mass and qualitative tail gas composition via a residual gas analyzer, and off-line quantitative tail gas composition via a Gas Chromatograph (GC). This enables real-time monitoring of coking of coatings during ethylene production, and carbon gasification as a function as varying amounts of coke is deposited to gather effective snapshots of catalyst performance at various points in projected steam-hydrocarbon cracking furnace runtimes.

Typical testing conditions for the cracking reaction were temperatures of 700 – 875°C, ethane flow 60 ml/min, with an ethane:steam ratio of 3:1 by weight, and total gas flow (ethane, steam, argon, helium) of 300 ml/min. The sample was held under these cracking conditions for a period of 2 hours, after which time the ethane and steam flows were discontinued, and the instrument cooled to room temperature at a rate of 5°C/min. under a high flow of inert gas (argon, 600 ml/min) to purge the system. Tail gas samples were collected in 1L Tedlar^{TM} sampling bags at three points during each experiment: the first after 20 minutes of reaction time, the second after 60 minutes, and the third at 100 minutes. The GC instrument used was a Varian CP-3800 equipped with three channels. The front TCD channel was equipped with Hayesep Q and Molsieve 13x columns used to measure hydrogen; the middle TCD channel was used to quantify Ar, CO_2, and CO with Hayesep Q and Molsieve 5A columns. The rear FID channel used an alumina plot column to quantify hydrocarbon species.

4.2 Results and Discussion

4.2.1 Inert Coating for Higher Temperature Service (i-1300HT)

Coating Microstructure

The coating composition has been engineered using a minimalist element approach and would support the selected SGX catalyst(s). The coating would offer protection to the coil from environmental degradation associated with the furnace operation by one or a combination of the following mechanisms:

- **Intrinsic** coating properties and protection (requiring no surface oxide generation or repair); and/or
- **Surface** barrier protection.

Coating formulations based on selected transitions metals, metals and metalloids were evaluated as potential i-1300HT coating systems. In total combinations of approximately 2,000 coating chemistries were reduced to practice and investigated. The final i-1300HT coating chemistry was multi-elemental consisting primarily of key non-coke forming and high temperature resistant transition metals and silicon. The cross-sectional microstructure of the **world-first intrinsic anti-coking coating,** able to provide high inertness to filamentous coke-make WITHOUT the need for or repair of a surface oxide, is shown below in Figure 9.

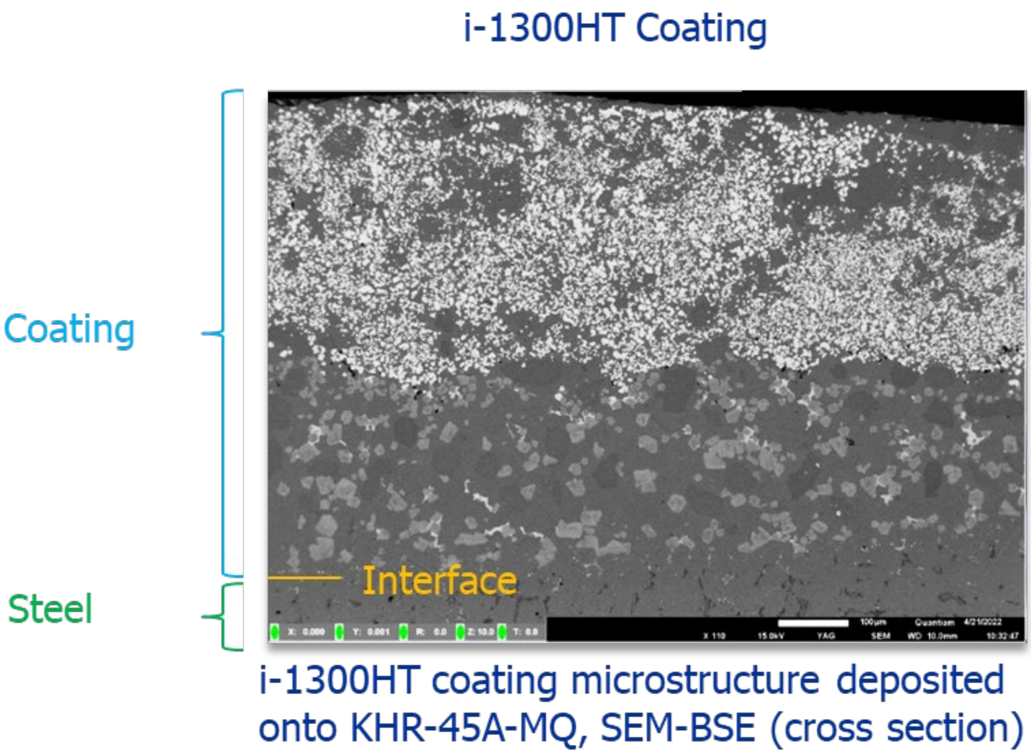


Figure 9. Cross-sectional SEM micrograph of the i-1300HT coating microstructure metallurgically bonded to KHR-45-MQ steel.

Performance Metrics

Filamentous coke-make inertness

The most significant property of the i-1300HT coating is its ability to provide a surface that is inert to the formation and growth of filamentous coke-make without the need to generate a surface oxide scale (surface barrier protection). This surface inertness attribute is an intrinsic property of the coating matrix within any arbitrary plane through the coating. The bar graph shown in Figure 10 below shows a summary of the resistance to coking provided by the standard i-1300HT coating and i-1300HT containing 5wt.%Mn. Coking propensity is shown as a percentage scale relative to the two benchmarks used in the coking test: a catalytically inert surface (alumina, 0%), and a highly active surface for filamentous coke-make (iron, 100%). The purple bars show intrinsic surface coking resistance (without any surface pre-treatment), that is, the equivalent of a bored tube surface finish with an arbitrary ground plane through the coating. Orange bars indicate surface barrier protection coking resistance, i.e. after an oxidation pre-treatment to generate a reasonable-quality surface oxide. The standard i-1300 HT (top) coating exhibits excellent world-first intrinsic coke resistance, with coking resistance reduced after formation of a surface oxide barrier layer. In contrast, the i-1300HT+5Mn coating (bottom) coating shows superior coking resistance after the formation of a MnO surface barrier layer. In all cases, results showed a low coking performance, comparable to an alumina-like inert surface. The most inert surface to filamentous coke-make was the standard i-1300HT without a surface oxide scale.

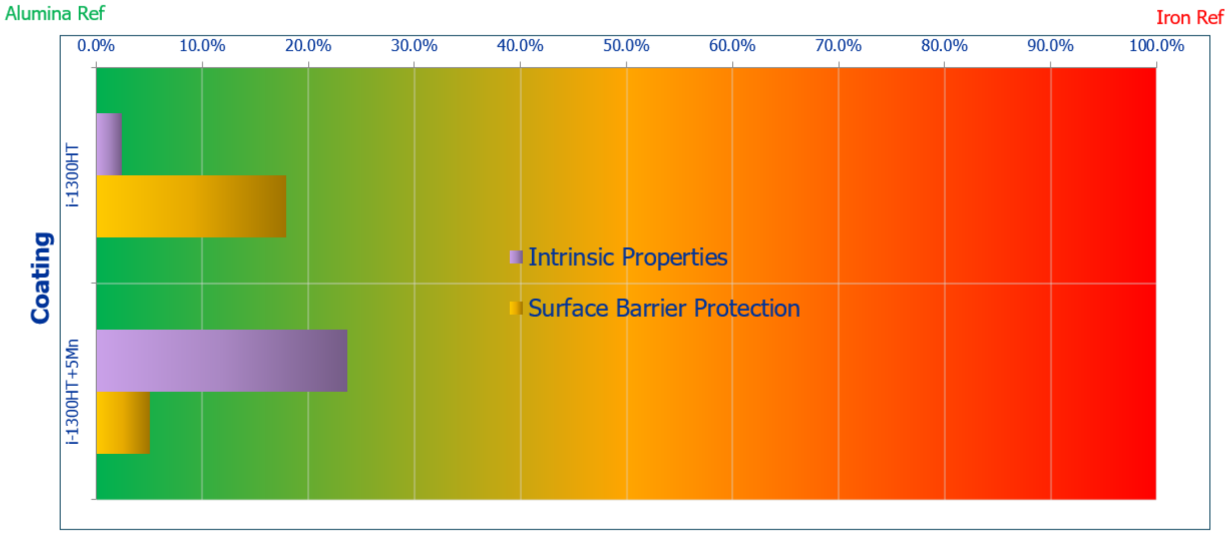


Figure 10. Resistance to coking for standard i-1300HT and [i-1300HT+5%Mn] coatings for both intrinsic and surface barrier protection. Bar plots represent percentage area coke depositions which include both filamentous and amorphous coke types. Measurements were taken using image analysis from SEM images at two different magnifications (150X and 500X). Coking propensity is shown as a percentage scale relative to inert alumina (0%), and an iron surface highly active to filamentous coke-make (100%) benchmarks.

Analysis of SEM images of the i-1300HT coating post-coke resistance testing was used to characterize the intrinsic surface protection property of the i-1300HT coating towards coke formation in terms of both distribution and coke morphology. Small discrete clusters of coke deposits were found containing both filamentous and inert coke. However, the majority of the coating surface area was devoid of any coke deposition. A typical SEM micrograph of the i-1300HT coating surface after testing is shown in Figure 11, below.

A cyclic coking study was conducted to probe if the i-1300HT coating would retain this inertness property after repeated coking/de-coking cycles. A coated coupon was honed and recrystallized ready for coking. The coupon was coked, SEM imaged for coke deposition and then de-coked. This procedure was repeated a further four times (4 cycles). The de-coke heat treatment was atmosphere: 25% steam, 25% air, 50% Ar, 800°C, 2 hours. As the coking cycles increased, coke deposition percentage did not exceed 6%, as shown in Figure 12, below. More importantly, the fraction of filamentous coke-make detected after each coking cycle was very low.

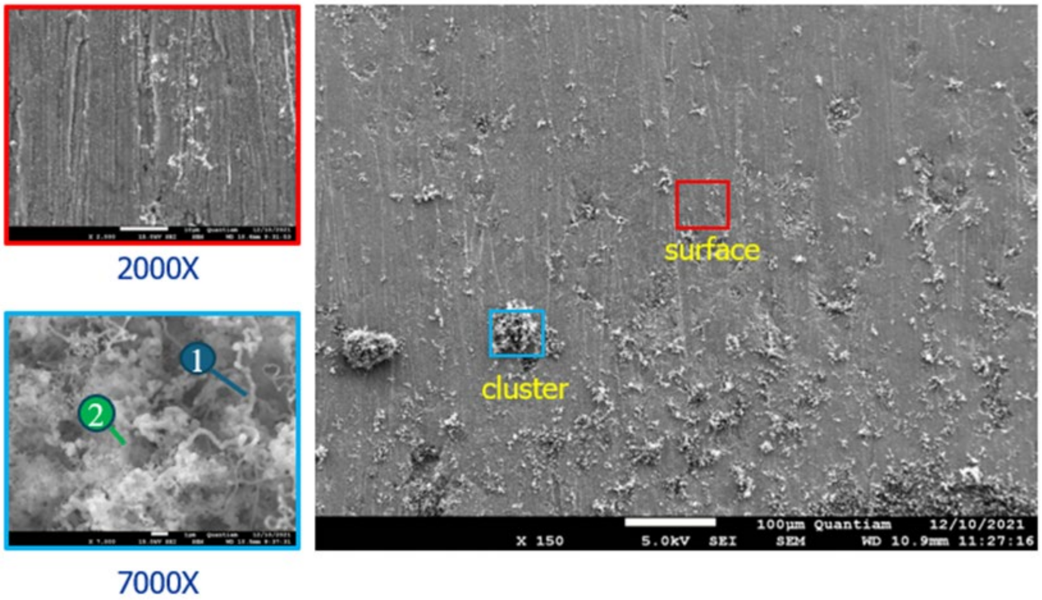


Figure 11. Distribution and morphology of deposited coke onto i-1300HT coating surface, after a coking test, showing low coke coverage sites. Both (1) filamentous, and (2) amorphous coke types are present at very low levels, collectively <5% surface coverage, coke cluster comprises both coke types (blue box).

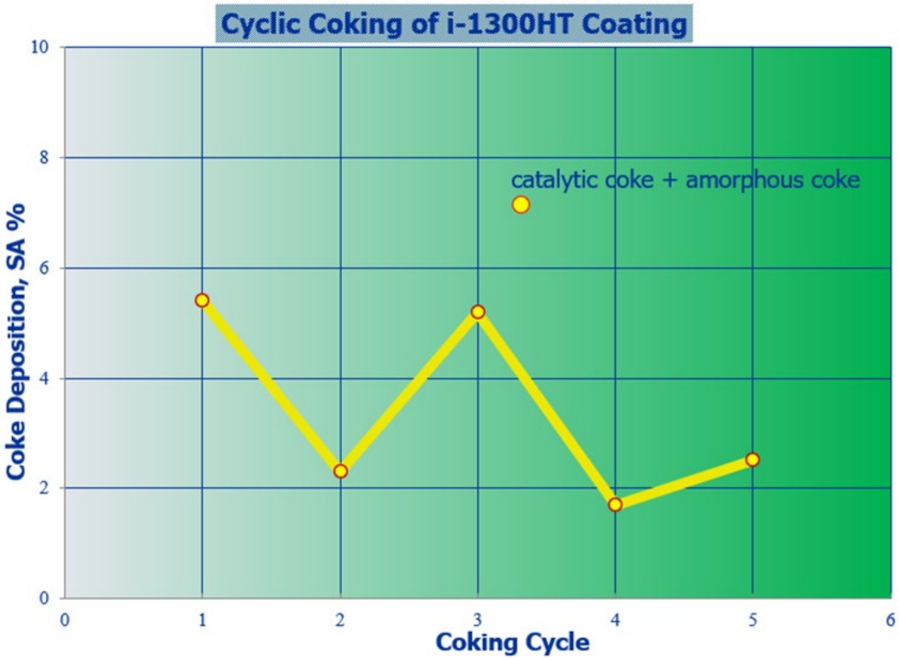


Figure 12. Response of the i-1300HT inert surface to repeated coking cycles.

Carburization resistance

Carburized KHR-45A-MQ steel exhibited a significant surface depth devoid of the characteristic Cr/Nb carbide structure (carbide denuded zone), as shown in Figure 13, below. With respect to a furnace coil, poor carburization (loss of carbide structure) would result in a reduction in creep resistance and mechanical strength. As can be seen in Figure 14, below, the carbide morphology adjacent to the denuded zone and to a depth within the middle of the steel (regions a to d) generally showed little change in shape and size.

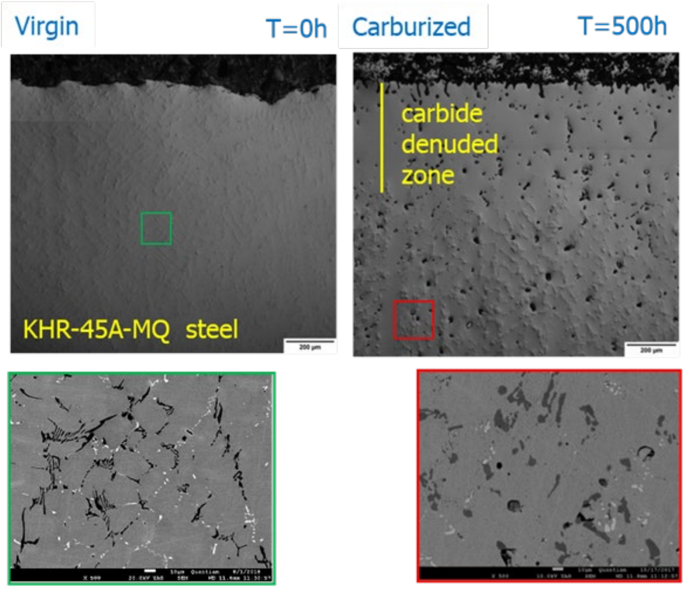


Figure 13. OM and SEM cross sectional micrograph comparisons of (left) virgin and carburized (right) KHR-45A-MQ steel microstructures.

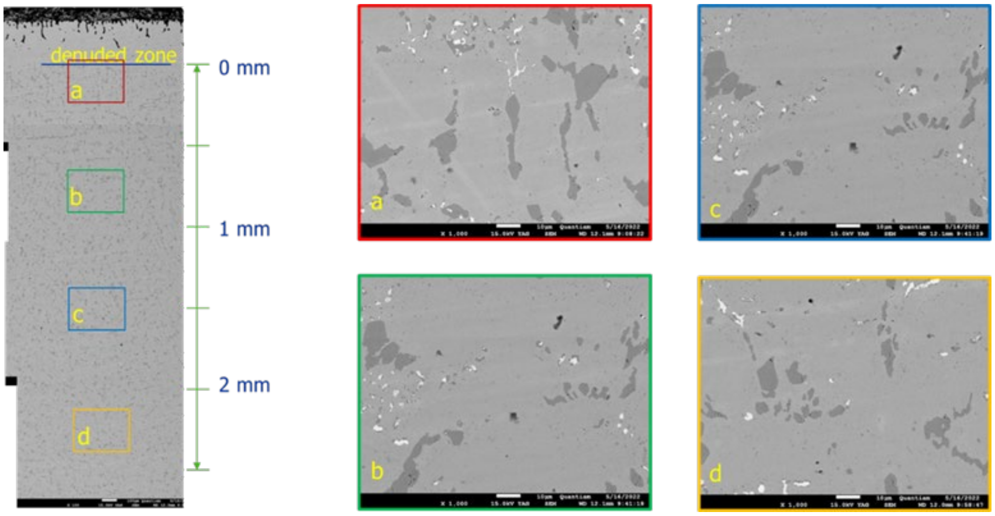


Figure 14. Cross sectional SEM micrographs showing the influence of carburization on carbide chemistry within uncoated KHR-45A-MQ steel microstructure. At left is shown a cross-section of the entire tube-wall thickness. At right, a-d, are higher magnification images showing the carbides present in the steel microstructure at the indicated positions.

The carburized i-1300HT coating protected the KHR-45A-MQ steel from the effect of this degradation. No carbide denuded zone formation was evident in the coated steel, as shown in Figure 15, below. A minor change in carbide chemistry near the coating interface was found, as shown in in region “a” indicated on Figure 16, below, with an enriched Nb-carbide structure evident. This was due to the short-range diffusion of Nb within the coating into the steel. At lower depth, (Figure 16, regions “b” and “c”) a normal Cr-Nb carbide morphology was retained. In summary, a coated coil would offer excellent carburization resistance during furnace operation resulting in minimal loss in creep resistance and strength.

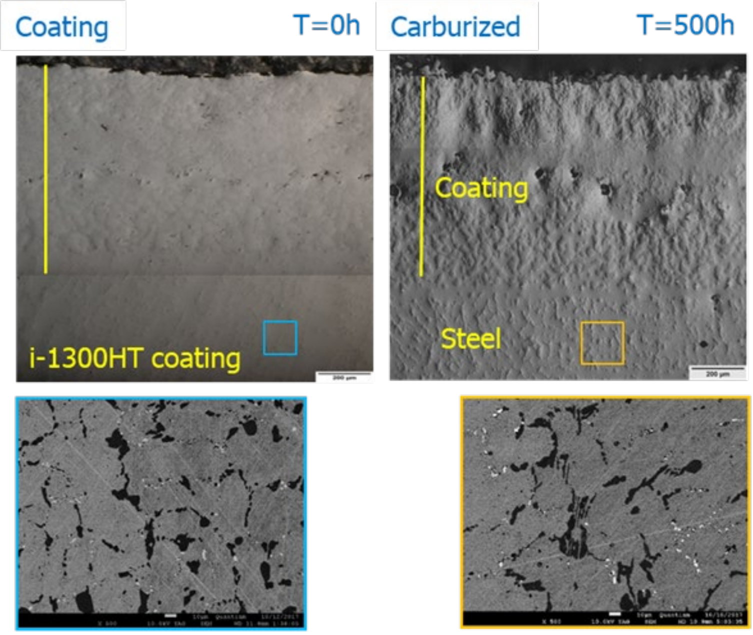


Figure 15. OM and SEM cross sectional micrograph comparisons of (left) as-produced and (right) carburized i-1300HT coating microstructures.

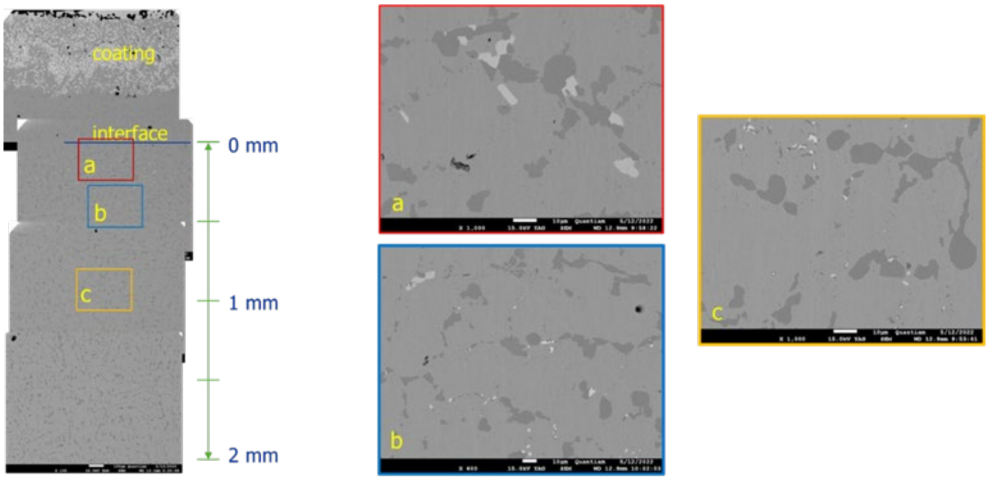


Figure 16. Cross sectional SEM micrographs showing the influence of carburization on carbide chemistry within an -1300HT-coated KHR-45A-MQ steel coupon. At left is shown a cross-section of the entire tube-wall thickness. At right, a-c, are higher magnification images showing the carbides present within the steel microstructure at the indicated positions.

Oxidation Resistance

Static oxidation behavior

The KHR-45A-MQ steel and i-1300HT coating were subjected to the same oxidizing conditions (1125°C, 24 hours, air) and then probed for differences in oxidation behavior.

The oxidized HTA steel generated an unstable oxide scale (low protection), comprising of predominantly loosely adhered chromia. The surface scale was prone to removal by spallation. The scale was thin, approximately 20 μm in thickness.

The oxidized i-1300HT coating formed a highly protective surface scale, thin (~30 μm), dense and contiguous in nature, indicative of a more protective oxide scale. The oxide scale formed was non-invasive with no internal oxide sites present.

Generation of Surface Barrier Oxide Scale

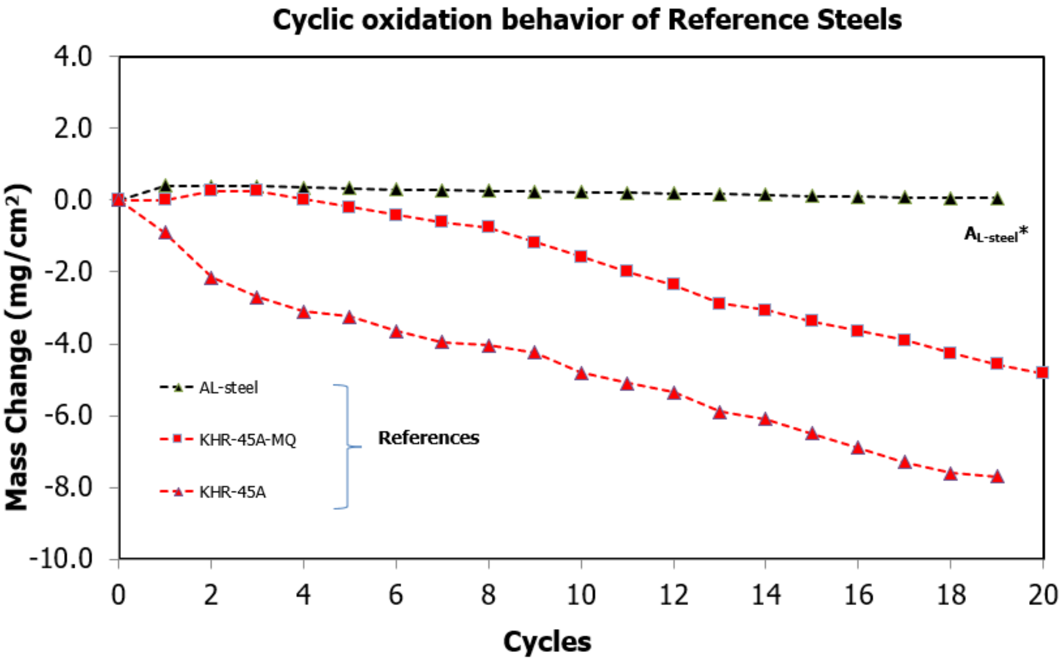
The ability of the i-1300HT coating to provide an inert surface to filamentous coke-make via the generation of a surface oxide scale was probed. The following oxidation heat treatment: 970ºC, 8 hours and atmosphere composition of 33% air, 66% Ar formed a contiguous, uniform oxide surface coverage with minimal spallation. This oxidation heat treatment was selected for the surface barrier protection study. Using these optimum conditions, the surface oxide growth that formed was approximately 5 μm in thickness.

With the desire to expand the operational range of the i-1300HT coating system, the coating chemistry was modified with the addition of either manganese (≤20 wt.%) or aluminum (≤6 wt.%). Coatings containing Mn have previously been reported to exhibit anti-coking properties in ethylene furnace applications [1,8]. HTAs modified with small additions of aluminum (≤4 wt.%) are commercially available from various OEM tube suppliers, namely, Kubota (AFT) [11], Manoir [12] and Scmidt & Clemens [13]. Only i-1300HT coatings modified with Mn are reported here, focusing on i-1300HT containing 5wt.% Mn additions.

In comparing the surface barrier scales grown under these oxidizing conditions, the addition of Mn promoted a denser, more contiguous surface scale. The oxide scales containing 5 to 6 wt.% Mn produced a denser coating with less coating spallation.

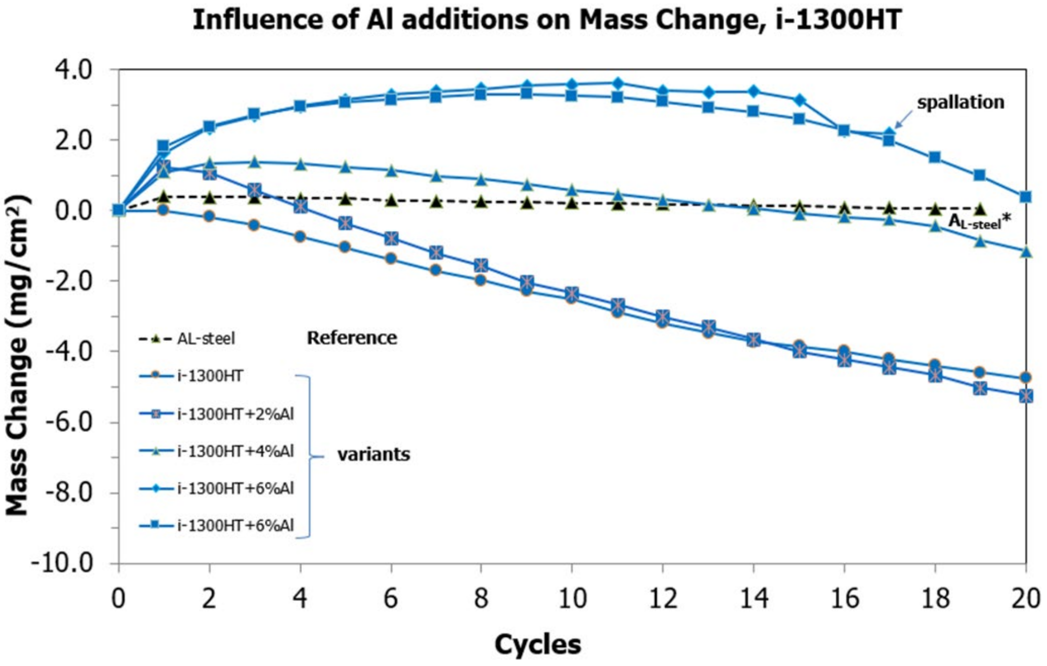
Cyclic Oxidation Behavior

To probe the potential development of an alumina forming coating, several aluminum containing i-1300HT coatings were made and subjected to cyclic oxidation conditions. Aluminum additions were limited to a range of 2 to 6 wt.%. The cyclic oxidation results are shown in Figures 17 and 18, below.



* For $A_{L\text{-steel}}$ test results, air flowrate and geometry are unknown

Figure 17. A comparison of cyclic oxidation behavior for two commercial KHR-45A steels and a alumina forming steel ($A_{L\text{-steel}}$).



* For $A_{L\text{-steel}}$ test results, air flowrate and geometry are unknown

Figure 18. A comparison of cyclic oxidation behavior for i-1300HT variant 1 compositions with aluminum addition.

With reference to Figure 17, the alumina forming steel ($A_{L\text{-steel}}$) demonstrates an insensitivity towards mass change with increasing cycle number, whereas, the KHR-45A steels exhibit a continual decrease in mass with increasing cycle. In summary, $A_{L\text{-steel}}$ steel indicates a high cyclic oxidation resistance as observed with minimal degradation under a cyclic oxidation environment. Both KHR steels continually suffered physical degradation with cycle number in the form of increasing mass loss due to surface spallation.

In comparing the i-1300HT variants (Figure 18), all revealed a similar trend. An increase in aluminum content resulted in an increasing positive mass change with cycle number. Therefore, increasing the aluminum addition within the coating composition promoted a higher resistance to the degradational effects of cyclic oxidation. It should be noted that most commercially available alumina former steels typically contain a maximum aluminum content of 5 wt.%. In this study, an upper limit of 6 wt.% aluminum was investigated. The i-1300HT coating modified with 4 wt.% aluminum mimicked the cyclic oxidation behavior of the $A_{L\text{-steel}}$ steel. None of the 2 and 4 wt.% aluminum modified i-1300HT variants showed any signs of surface spallation.

Oxidation Resistance of i-1300HT Coatings for High Hydrogen Firing Conditions

There is a material shift in parts of the world to fire cracking furnaces with increasing amounts of hydrogen, offsetting methane, with interest through to 100% hydrogen firing. It is generally recognized that steam can be a greater oxidizing agent than carbon dioxide and it is unclear if the tube metallurgy and external tube surfaces as installed have the necessary resistance to the increase oxidation potential of the hydrogen firing flue gas. An accelerated study was undertaken to assess both the virgin workhorse 35Cr-45Ni base steel and i-1300HT external tube surface performance using a test gas mixture appropriate to 100% hydrogen firing at 1,150°C with all six surfaces of test coupons fully coated or fully in a virgin state.

Figure 19, below, shows a comparison of the cyclic oxidation behaviour of three i-1300HT coating variants against the base KHR-45A HTA under conditions simulating 100% hydrogen firing of the furnace coil exterior, with one oxidation cycle being exposure to 30% volume steam, 3 vol.% oxygen, balance nitrogen at 1,150°C for 8 hours. The KHR-45A shows an initial mass gain in the first oxidation cycle, followed by loss of mass on subsequent oxidation cycles. This indicates that under these test conditions, the oxide scale of the virgin steel may not be adequately thermo-mechanically stable and protective, but rather increases in thickness initially and then delaminates. This growth and spallation with increasing thermal cycling could result in mounting loss of tube sound wall in the field with each cracking and de-coke cycle, consistent with field observations by some operators that are ramping to higher levels of hydrogen firing.

The i-1300 coating family tested thus far, both as intrinsic and as an MnO-former shows superior scale protection with greater thermo-mechanical robustness. This observation of cyclic oxidation using a projected 100% H_2 firing flue gas is consistent with earlier results on the cyclic oxidation of the same base steel and i-1300 coatings in air at 1,050°C through to 19 cycles. The alumina former version of i-1300HT (i-1300HT+Al(Ox)), however, while initially showing good scale growth in the first five oxidation cycles demonstrates a combination of scale spallation and coating delamination thereafter, indicating poorer thermo-mechanical robustness for the alumina scale as compared to the manganese oxide scale of the i1300-HT+Mn(Ox) or the intrinsic protection of i-1300HT.

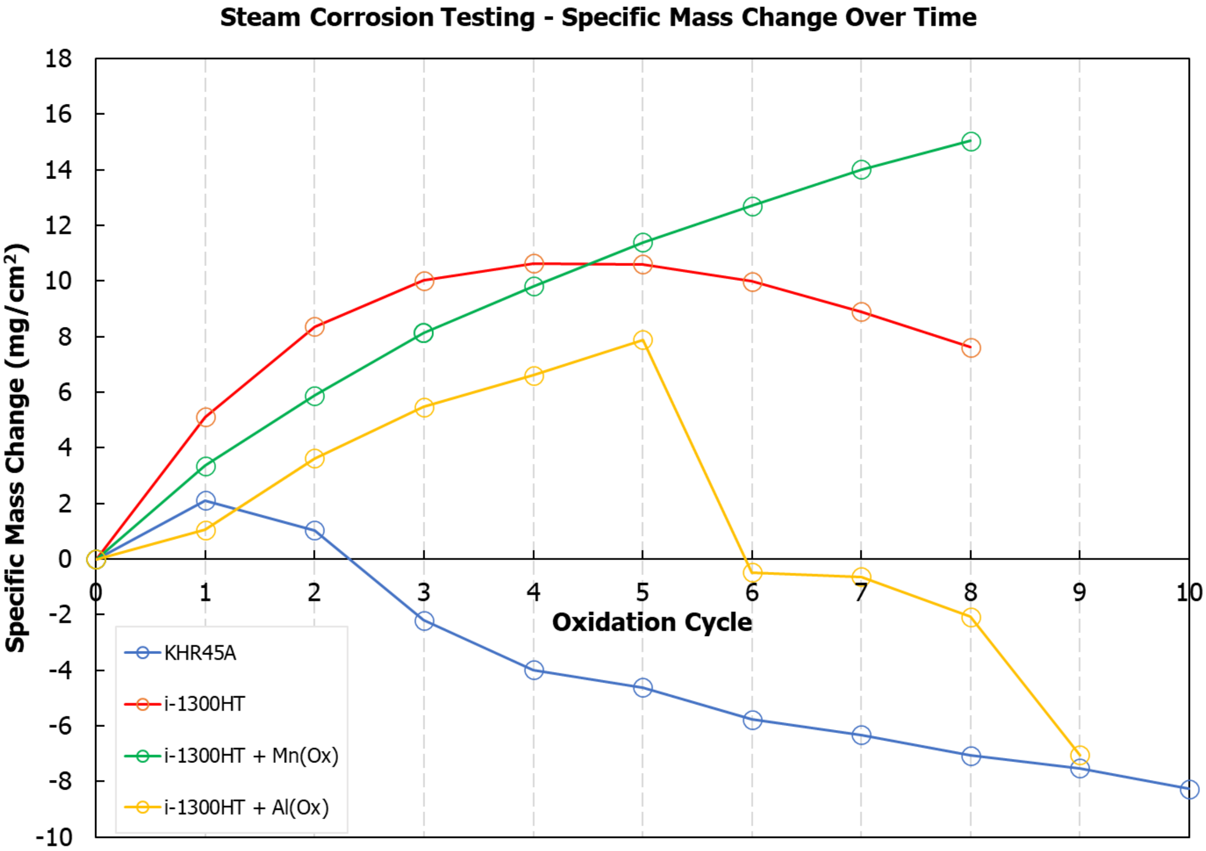


Figure 19. Comparison of cyclic oxidation behaviour of i-1300HT intrinsic and i-1300HT surface barrier coatings against reference KHR-45A HTA in 30 vol.% steam, 3 vol% oxygen, balance nitrogen at 1,150°C to simulate the effect of 100% hydrogen firing on the external surface of furnace coil tubulars.

Thermal Stability

Any variations within the microstructural chemistry of the i-1300HT coating with respect to consolidation (coating heat treatment), thermal stability and carburization were probed using SEM-EDS line scans. These results are displayed in Figure 20 below. A comparison of each line scan profile set revealed that there was little variation in coating composition from the consolidation heat treatment to thermal stability or carburization. None of the cross sectioned images exhibited any signs of Kirkendall void formations, indicating that the diffusion coefficients for the coating microconstituents and that of the steel were "well matched".

In summary, the initial i-1300HT coating chemistry and the important inherent surface inertness towards filamentous coke-make would not change with service life if this coating was chosen to protect radiant tubes in a furnace.

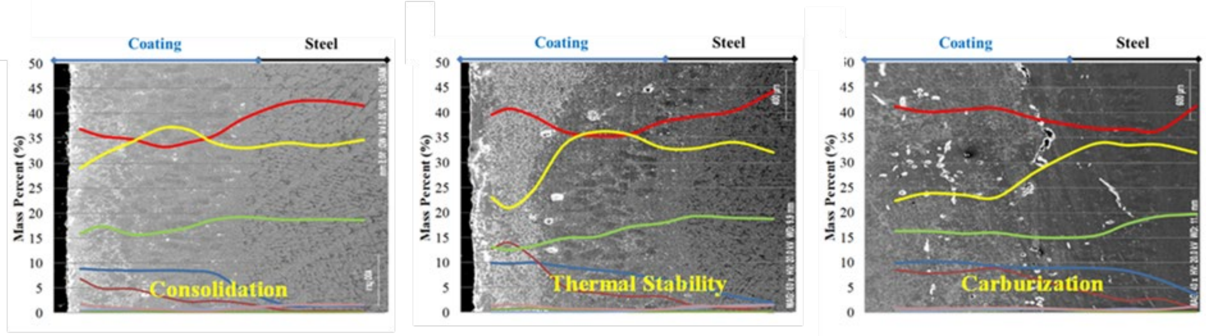


Figure 20. Cross-sectional SEM images with superimposed elemental concentrations as determined by EDS analysis used to generate elemental concentration depth profiles for comparing i-1300HT coating chemistry after (left) consolidation, (middle) thermal stability and (right) carburization testing. The coating surface is at extreme left in each image.

Thermo-mechanical Robustness

The thermal shock heat treatments (air and water quench) used to quantify the level of thermo-mechanical robustness for the i-1300HT coating indicated superior CTE matching between the coating and steel. Only minor radial cracks were observed in the water quenched coupons; these cracks initiated at the surface but were arrested within the coating. No signs of longitudinal or networked crack formations were evident. No evidence of coating spallation was found.

A summary of the performance metrics results with respect to the i-1300HT coating is shown in Table 2 below.

Table 2. Summary of i-1300HT coating performance metrics.

Result	Metric	Strategy	Parameters	Observations
✓	**Surface Inertness Intrinsic Property**	Inhibit deposition of catalytic coke-make.	• Dry ethane pyrolysis • 780°C, 2 hours • feedstock, ethane	• Inhibit/significantly reduce deposition of filamentous coke-make. • Target <5% total surface area coverage of carbon and repeatable through coking/decoking cycles.
✓	**Carburization**	Coating's ability to inhibit carbon ingress.	• 1125°C, 500 hours • 1.5 Torr (vac/Ar) • coupons embedded in graphite powder (carbon activity ~ 1)	• No detrimental coating wastage. • No change in carbide morphology. • No change in carbide dimensions.
✓	**Oxidation of surface and coating matrix**	Protective oxide scale, surface limiting.	• Static oxidation, 20 cycles to simulate one lifetime • 1125°C, 24 hours, air • Cyclic oxidation, 1 cycle - 1050°C, 8 hours, air 200 sccm	Static oxidation • Discontinuous surface scale: thin & dense. • Non-invasive (no internal oxidation). Cyclic oxidation • Probed weight change as a function of coating chemistry.
✓	**Thermal Stability**	Coating consistency.	• 1,100°C, 25 to 500 hours • 1.5 Torr (vac/Ar)	Temperature limit selection requiring: • No change in microstructural chemistry. • No Kirkendall void formation. • No change in coating thickness.
✓	**Thermo-Mechanical Robustness**	CTE compliance of coating and steel.	• Coupon heated to 1,000°C, air • Method 1 - air quench • Method 2 - water quench	Positive result requires: • No spallation of coating. • No longitudinal cracks or networked cracks.
✓	**Wear Resistance**	Coating's high wear resistance.	ASTM G65 Procedure A	• i-1300HT coating has twice the wear resistance of KHR-45A steels. • Coating wear loss, 52 mm^3 • Steel wear loss 93 mm^3
	Sulfidation	*to be completed*		

4.2.2 Inert Coating for Lower Temperature Service (i-1300LT)

Coating Microstructure

The i-1300LT coating chemistry is rich in aluminum and silicon and was engineered to generate a surface oxide scale that rendered the surface inert to filamentous coke-make. The coating chemistry formed highly stable aluminides of Fe, Ni and Cr within the coating matrix that helped to mechanically stabilize the thermally grown surface oxide scale. This can be seen in Figure 21, below, which shows both a cross-sectional SEM micrograph of the i-1300LT coating with elemental composition as a function of distance from the surface superimposed (left), and cross-sectional elemental maps of Si, Al, and Cr distribution (right).

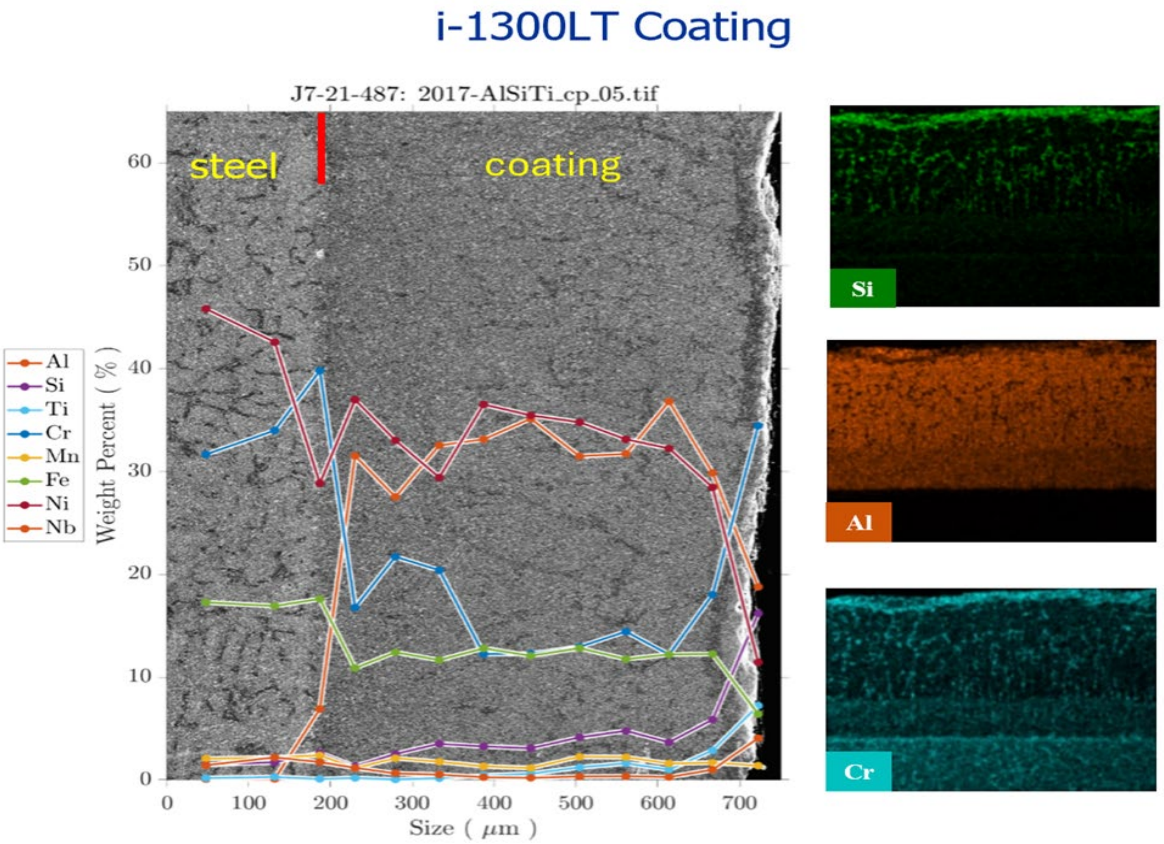


Figure 21. Left: Cross-sectional SEM micrograph (surface at extreme left) of the i-1300LT coating microstructure metallurgically bonded to KHR-45-MQ steel, showing diffusion barrier (red line) and elemental composition as a function of distance from the surface. Right: cross-sectional SEM-EDS maps (surface at image top) of the same coating showing distribution of Si (top), Al (middle) and Cr (bottom).

Performance Metrics

Surface barrier protection – generation of a protective inert oxide scale

Generating an optimal surface scale required fulfilling the following metrics:

- oxide phase – presence of correct oxide phase;

- oxide morphology –dense packed layers vs non-packed needles;
- oxide surface coverage – complete contiguous coverage (minimize localized spallation);
- oxide thickness – even vs uneven thickness; and
- suppression of other oxide species – minimize presence and growth of Cr, Fe, and Ni oxides.

Oxidation parameters were developed that generated a contiguous surface alumina oxide scale on the i-1300LT coating. These oxidation parameters were then utilized in the trial manufacturing of a coated tubulars and fittings for a field trial by a major European ethylene producer. A comparison of the X-ray diffraction patterns for as-produced and oxidized i-1300LT coatings is shown below in Figure 22. Post-oxidation, the XRD results show diffraction peaks consistent with the formation of alumina at the coating surface.

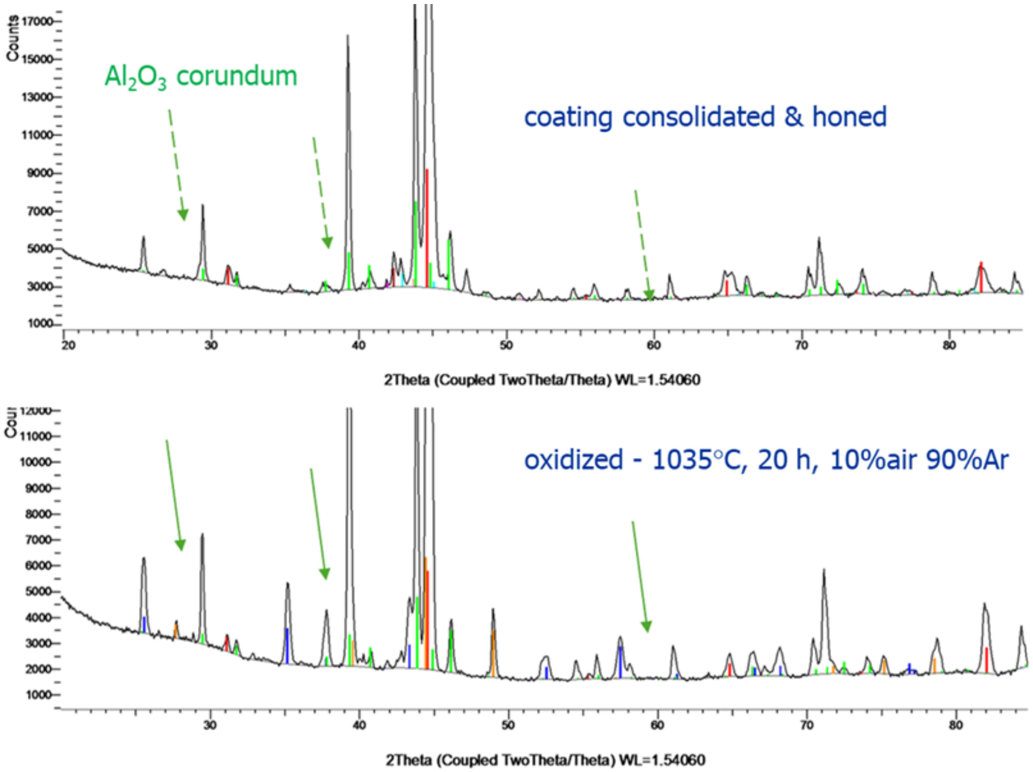


Figure 22. X-ray diffraction patterns of (top) as-produced and oxidized (bottom) i-1300LT coating, showing evidence of generated alumina species during the optimized oxidation heat treatment.

Using these optimal oxidation parameters, a dense, contiguous and thermally stable aluminum oxide scale can be generated at the i-1300LT surface, as illustrated below in Figure 23 which shows cross-sectional SEM micrographs and EDS elemental maps for the surface oxide scale.

Optimal oxidation conditions resulted in the generation of a predominantly thin (1 – 5 μm) alpha phase alumina surface scale with 98% surface coverage, covering surface species of AlNi and silicides. The oxidation parameters successfully suppressed the growth of other transition metal oxides.

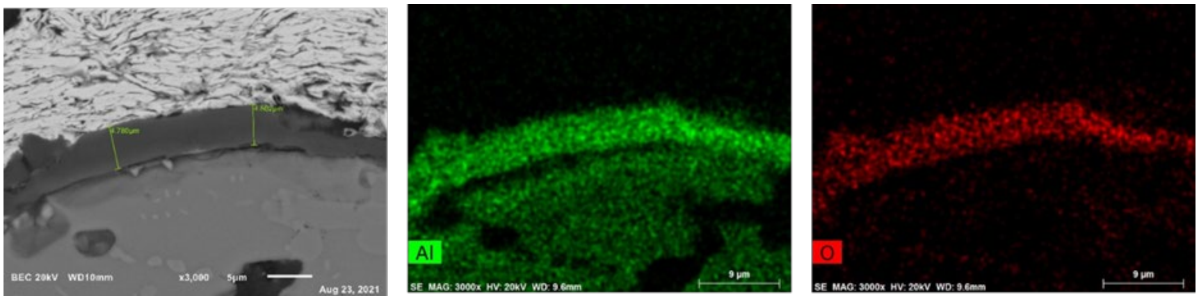


Figure 23. Cross-sectional SEM micrograph (left) and elemental maps of Al (middle) and O (right) of the alumina surface scale generated on i-1300LT coating.

Inertness to Filamentous Coke-Make

Duplicate coupons of the i-1300LT coating system were subjected to the optimal oxidation treatment to generate the protective inert oxide scale and then individually coked according to the "*dry ethane pyrolysis coking test*" described in Section 4.1.1.1 above. Each coked coupon was then surface imaged (SEM-EDS) for evidence of coke-make deposition (both filamentous and amorphous types). As indicated in Figure 24 below, areas of alumina-covered surface are void of any filamentous coke, but the portion of the surface not yet protected by alumina shows formation of discrete coke deposits demonstrating the criticality of growing a **contiguous, dense and well adhere surface oxide** when intrinsic protection is unavailable.

In general, the surface topography of the oxidized i-1300LT coating was very undulating with the "valley regions" containing deposits of amorphous coke.

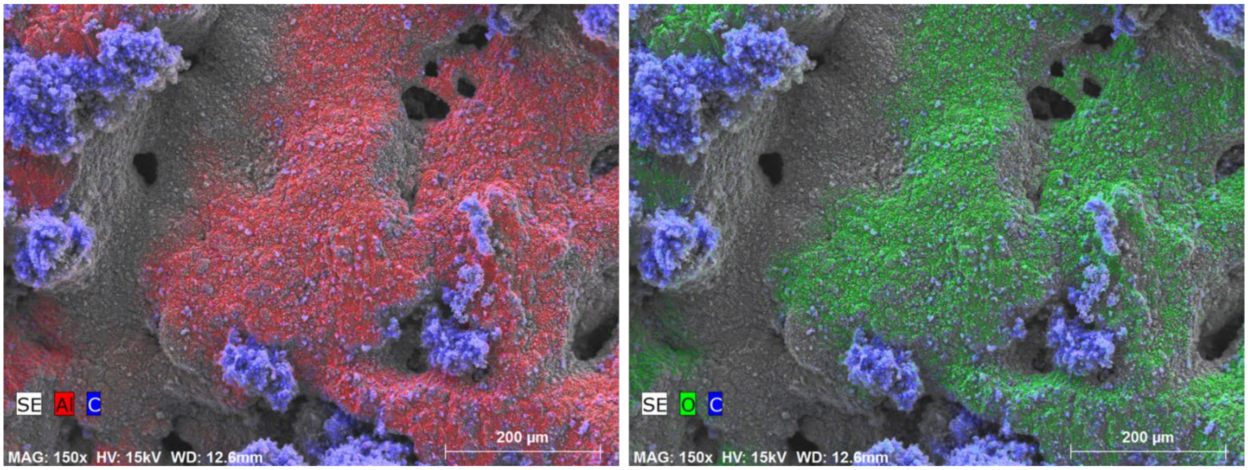


Figure 24. Surface SEM micrographs of an i-1300LT coating with a partially oxidized surface after coking testing with: (left) Al and C; and (right) O and C EDS elemental distributions superimposed. Alumina coverage at this early stage of alumina oxide growth is not yet fully contiguous. Growth of filamentous coke is evident on the non-oxide covered areas.

Thermal Stability

The optimization of coating heat treatment parameters resulted in the elimination of Kirkendall voids at the coating-steel interface, resulting in a coating that exhibited high thermal stability, with minimal interfacial and intra-coating porosity, as indicated in Figure 25 below.

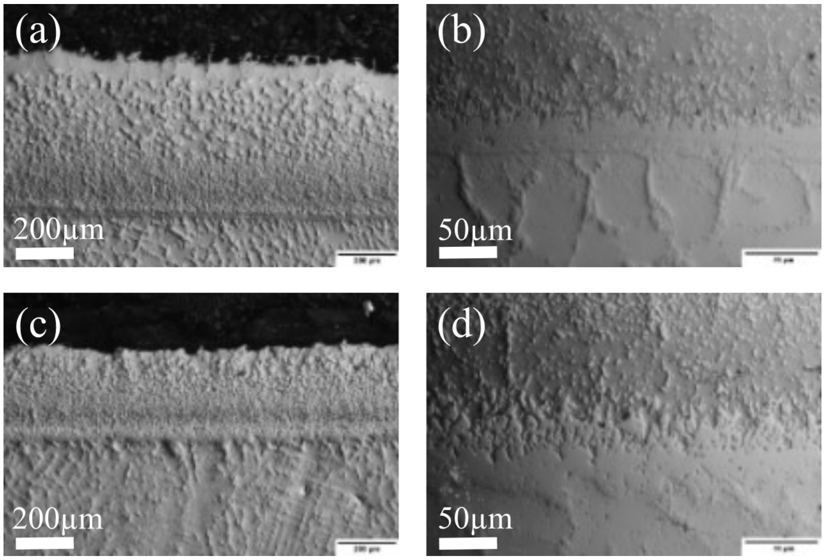


Figure 25. Cross-sectional optical micrographs of i-1300LT coating microstructures as-consolidated (a, b), and after thermal stability testing under Ar at 1050°C for 100 hours (c, d). Note the almost complete elimination of both interfacial and intra-coating porosity and absence of any cracks.

Thermo-mechanical Robustness

The i-1300LT coating exhibited no evidence of crack propagation or spallation as result of the thermal shock testing, indicating that the coating possessed a high level of thermo-mechanical robustness.

4.2.3 Multi-Functional Catalytic Coke-Gasifying Coating (SGX) Coating Development

A number of catalyst species were identified during initial TGA carbon gasification screening which were catalytically active in H_2 to form CH_4. From this, a shortlist of catalyst candidates for further assessment was compiled. Of these, several non-oxide transition metal compounds were found to be both stable under the mildly oxidizing conditions of steam (H_2O) or H_2/H_2O TGA testing, and to show catalytic activity toward carbon gasification and were selected as the final SGX catalyst candidate species. An example of H_2 gasification activity in a physical mixture of a selected SGX catalyst in 25% H_2/Ar shown in Figure 26 below. At temperatures above 600°C, the rate of mass loss for an SGX catalyst/activated charcoal physical mixture was greater than that for activated charcoal alone. This indicates catalytic gasification is taking place; the SGX catalyst alone (not shown) did not exhibit any mass loss under the same testing conditions. Pre- and post-testing characterization by XRD of the most promising catalyst candidates indicated that the catalyst carbide species was reduced by the hydrogen to a metallic species by the formation of methane. The available carbon then reacts with the metallic species, reforming the carbide. This cycle then repeats, resulting in overall gasification of the carbon species. This (tentative) proposed mechanism is illustrated schematically below in Figure 27.

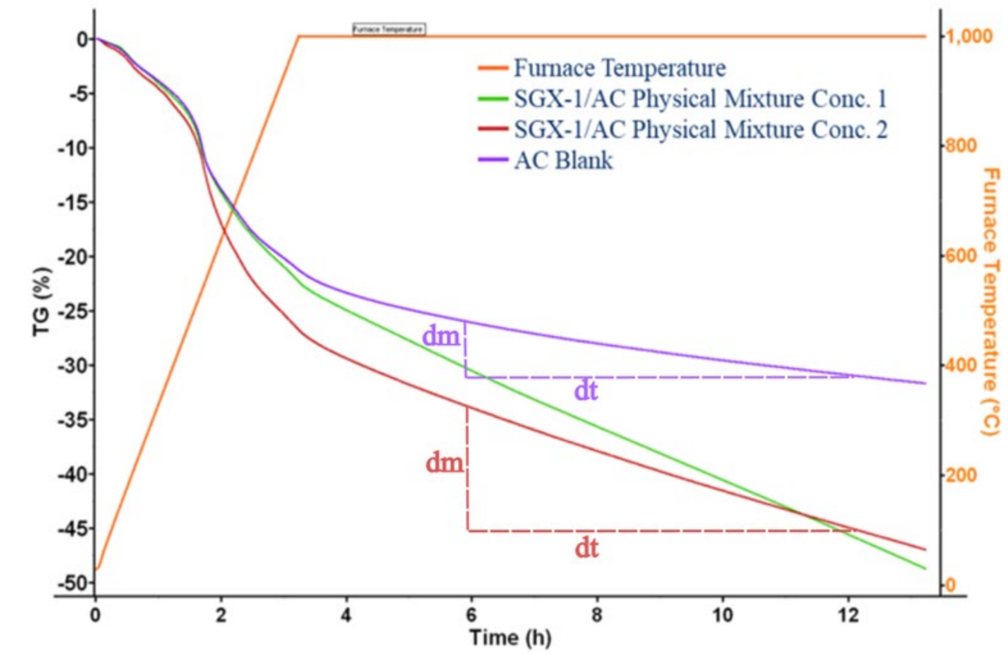


Figure 26. Thermogravimetric results from TGA testing of physical mixtures of powders under 25% H_2. Furnace temperature profile is indicated in orange; mass loss vs time profiles for the activated charcoal (AC) control is shown in purple; the SGX catalyst/AC physical mixture is shown in green and red.

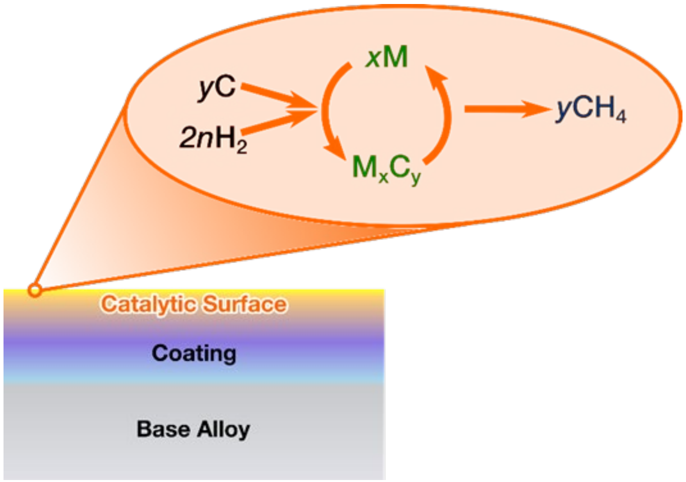


Figure 27. Proposed 'metastable' carbide carbon gasification mechanism for amorphous coke conversion to methane by hydrogen.

The coking rate of the selected SGX catalyst under cracking conditions at 850°C in a 5 vol.% ethane-steam (3:1 by mass), balance Ar process stream is shown below in Figure 28, along with the coking rates of reference surfaces of inert (alumina), catalytic coke promoter (Ni) and an oxide-based coke gasifier (CAMOL^{TM}) species. Coking rates have been normalized to that of the alumina surface. The coking rate is defined as the mass change per weight of catalyst, per unit surface area, per unit time caused by accumulation of gas phase coke on the coupon surface. The cracking severity represented in these experiments is much higher than that under industrial conditions because, although the gas temperature was reflective of that of the cracker process gas, the residence time in the TGA is much higher (~2s). This results in much higher ethane conversion rates (>95% above 800°C) than in the industrial case even at these low overall steam-ethane concentrations. As the coupon and process gas are perforce isothermal in the TGA there is therefore a tradeoff between achieving a catalyst temperature sufficient for activation of the catalytic reaction and overwhelming the catalyst with over cracking. Even at these very severe conditions, the SGX catalyst easily outperformed the current generation oxide-based catalysts, indicating considerable promise for performance under industrial conditions.

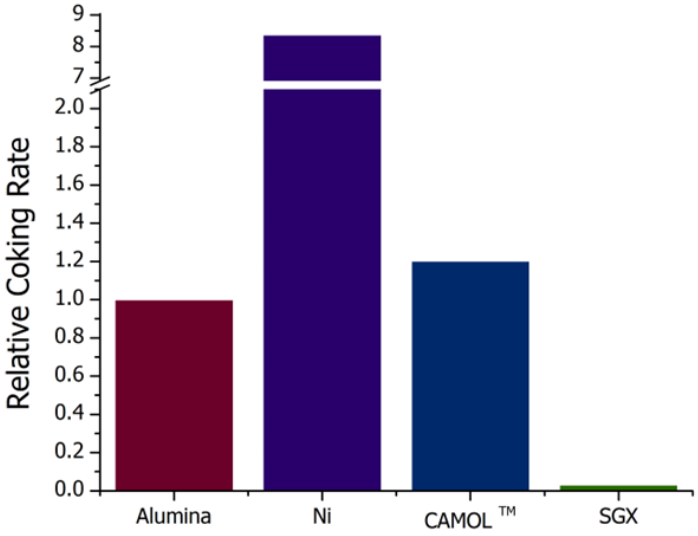


Figure 28. Relative coking rate in TGA steam-ethane testing of SGX coated alumina coupons.

Figure 29, below, shows a SEM micrograph and SEM-EDS elemental map of the catalyst embedded in the inert matrix post-cracking testing. Very little carbon deposition was seen, with no filamentous coke formation, indicating excellent resistance to filamentous coke-make. The catalyst species itself showed no significant change in morphology or composition caused by exposure to steam-ethane cracking conditions.

Now that assessment and selection of the SGX catalytic gasifying species has been completed, the next stage will be the development of the SGX coating system. It is envisaged that the coating matrix supporting the catalyst will be the i-1300HT coating chemistry or a modified/refined composition of such, thereby having both high temperature capability and high carbon gasification capacity. The SGX coating system must exhibit similar performance metric results as found with the i-1300HT coating in its core properties. For superior matrix support and to maintain catalyst functionality, there should be limited catalyst-coating chemical interaction (wetting and reaction) during formation of the coating across a broad range of catalyst loading. This work is in its initial stages.

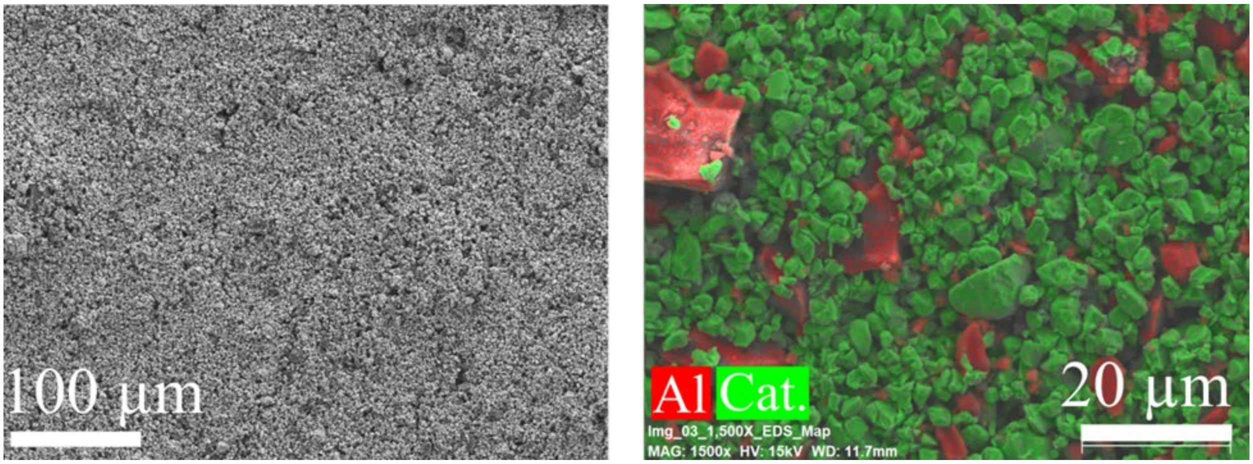


Figure 29. SEM micrograph (left) and SEM-EDS elemental map (right) of the surface of an SGX catalyst coated alumina coupon after testing in steam-ethane pyrolysis conditions in the modified TGA.

5.0 Conclusions and Future Work

The following conclusions can be derived from the present work:

1. **Inert Coating for Higher Temperature Service (i-1300HT)**

- The i-1300HT coating developed by Quantiam demonstrates a surface inertness quality with respect to filamentous coke deposition in the following ways:
  - Intrinsic properties of the coating composition in single and repeated (cyclic) coking tests; and
  - Ability to generate a surface barrier oxide scale by additions of Mn or Al.
- The i-1300HT coating displays a superior resistance to carburization overtime (> 500 hours) to a commercially accepted HTA coil steel (Kubota KHR-45A).
- Under static oxidation conditions, the following observations were evident:
  - The i-1300HT coating generates a thin (~ 30 µm), dense, contiguous, protective oxide surface scale; and
  - KHR-45A steel generates a thin (~ 20 µm) unstable oxide scale consisting of predominantly loosely adhered chromia.
  - Utilizing optimal oxidizing parameters, the standard i-1300HT could generate a thin surface barrier coating with an outer oxide layer of Mn-Cr spinel. This surface barrier layer formed was denser and thicker if manganese was added to the coating composition (≤ 6 wt.% Mn).
- Under a cyclic oxidizing environment, the following were apparent:
  - Two KHR steels (typically 35Cr-45Ni-Fe) continually suffered physical degradation with oxidizing cycle number in the form of increasing mass loss due to surface spallation;
  - The alumina forming steel demonstrated high cyclic oxidation resistance as observed with minimal degradation under a cyclic oxidation environment;
  - The standard i-1300HT coating exhibited a similar resistance to cyclic oxidation as displayed by the KHR steels; and

  - Cyclic oxidation resistance of the i-1300HT coating improved with increasing additions of aluminum to an optimal 4 wt.%.

2. Inert Coating for Lower Temperature Service (i-1300LT)

- The formation of a diffusion barrier at the coating/steel interface retained the high aluminum content (>30 wt%) within the coating and mitigated chromium diffusion into the coating from the steel, thus promoting optimal conditions for the generation of a thermally grown oxide scale for surface barrier protection.
- Oxide scale exhibited high coverage (~98%) was thin (1 – 5 µm), predominantly an alpha rich phase, covering surface species of Al-Ni intermetallics and silicides.
- Surface barrier protection provided by the inert alpha-rich oxide scale significantly hindered the formation of filamentous coke.
- i-1300LT coating exhibits both high thermal stability and thermo-mechanical robustness.
- A commercial field trial of the i-1300 coating family has been manufactured and delivered to a Tier-1 customer. Startup is scheduled for 2025.

3. Multi-Functional Catalytic Coke-gasifying Coating: SGX

- Quantiam has developed a multifunctional catalyst for gasifying amorphous coke in high severity cracking which can use either steam or hydrogen to convert carbon into carbon monoxide or methane.
- The catalyst is non-oxide based, without the disadvantages of relying on a fragile active oxide surface layer with poor CTE matching to the substrate.
- Gasification performance easily outperforms oxide-based catalysts in lab-scale testing at very high ethane conversion levels.

4. i-1300 Coatings (MnO-forming and Al_2O_3-forming) for External Tube Coating for High Hydrogen Coil Firing

- The i-1300HT family can provide good resistance to the tube external wall in field service using increased hydrogen firing to 100% and higher flue gas oxidation potential in all three forms of the coating: intrinsic, as an MnO-former and as an Al-former.

Acknowledgments

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References

1. Petrone, S.S.A et al. Catalyzed-Assisted Manufacture of Olefins (CAMOL): Year-(4) Update on Commercial Furnace Installations, Proc. 2010 Spring national Meeting, March 21-25, 2010, AIChE (2010).
2. Verdier, G., et el., Consider new materials for ethylene furnace applications, Hydrocarbon Processing, (2011) May.

3. Symoens, S.H., et al., State-of-the-art of coke formations during steam cracking: anti-coking surface technologies, Ind. Eng. Chem. Res., (2018) 57 16117-16136.
4. Györffy, M., et al., Proc. 18th Ethylene Producers' Confer., Apr 24-26 2006, AIChE (2006). Ganer, B., et al., Operational experience with diffusion coatings on steam cracker tubes, Mater. & Corr., (1999) 50, 700-705.
5. Petrone, S., et al., Proc. 10th Ethylene Producers' Confer., Mar 9-12 1998, AIChE (1998).
6. Petrone, S., et al., Proc. 11th Ethylene Producers' Confer., Mar 14-18 1999, AIChE (1999).
7. Petrone, S., et al., Catalytic surfaces and coatings for the manufacture of petrochemicals, US Patent 9421526 (2016).
8. Dees, J., et al., Proc. 33rd Ethylene Producers' Confer., Apr 18-23 2021, AIChE (2021).
9. Benum, L., Private communications (2025).
10. Hashimoto, K., et el., Cast product having alumina barrier layer, US Patent 2011/0318593 A1.
11. Pons, F., et a., Nickel- and chromium-base alloys possessing very-high resistance to carburization at very-high temperature, US Patent 4248629 (1981).
12. Schmidt+Clemens Group, Centralloy^{TM} HT E, Material data sheet, (2014).