New Alloy Materials for Reformer Outlet Systems

This paper describes the work performed on the development and characterization of new alloy materials used in steam methane reformer furnaces (SMR) outlet systems. New material developments allow outlet components to operate at more severe conditions without the need of increasing the wall thickness of these parts. In existing designs, reduction of wall thickness is possible while decreasing thermal stresses in such components. Selected results from improved materials, including results of creep and accelerated ageing tests carried out, are presented. Additionally, finite element case studies on existing outlet designs showing the benefits of new materials are also described in this paper.

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Introduction

Outlet systems are a main part in steam methane reformer furnaces (SMR). Although these elements are typically located outside the reformer firebox, they operate at severe conditions up to the metallurgical limits. Traditionally, centrifugally cast low carbon materials are used instead of wrought components [1]. The most commonly used material is alloy GX10NiCrNb32-20 or ASTM CT 15C (20Cr-32Ni-Nb), commercially named as Centralloy® G 4859 for the Schmidt + Clemens Group.

This paper will discuss new material developments done by the Schmidt+Clemens Group in outlet manifold components. New materials with superior ductility after ageing and better creep strength have been developed and placed into service under the most stringent conditions of steam methane reformer furnaces.

Results of different comparison tests performed between newly developed materials and previous ones, including case studies and finite element analysis (FEA) simulation on real outlet components, will show the benefit of these improved materials.
Objective

The main objective of this paper is to show new material improvements in outlet components for steam methane reformer furnaces. These components are operated with a process gas temperature in the range of 800ºC [1472ºF] to 950ºC [1742ºF] at a pressure of approximately 40 bar [580 psi]. Consequently, component lifetime is consumed by the combined effects of creep and alternating thermal and mechanical stresses (creep ductility exhaustion) [1]. Oxidation/corrosion processes typically have a lower impact on material damage mechanisms.

While significant research efforts have been made in improving alloys used for steam reformer catalyst tubes, no significant efforts were devoted in improving outlet system materials over the last 30 years.

The main requirements for these alloys are an excellent material ductility after ageing and an adequate creep resistance. Several studies have related ductility reduction with the transformation in service of niobium carbides (NbC) into intermetallic phases like G-phase (Ni16Nb6Si7) and η’-phase (Nb3Ni2Si) [2, 3, 4]. Additionally, it has been suggested that such intermetallic phases offer less inhibiting dislocation movement as compared with niobium carbides, leading to a lower material creep resistance [2].

Chemical composition optimization has a strong potential in inhibiting/reducing the presence of such phases. Schmidt+Clemens has been working in areas like optimum Si content, controlled Nb/C ratios and micro additions, developing superior materials for outlet header components.

Material Description

Outlet manifold materials differ depending on reformer designer preferences. Typically, low temperature systems having design temperatures below 829ºC [1525ºF] can either use 800 HT or cast equivalent 20Cr-32Ni, while those designs targeted for higher temperatures would use cast materials 20Cr-32Ni almost exclusively [5].

20Cr-32Ni alloy material supplied by the Schmidt+Clemens Group is named Centralloy® G4859. This alloy is a low carbon alloy designed to maintain good ductility after ageing and a good creep resistance in the range of 800ºC [1472ºF] to 1000ºC [1832ºF]. Niobium is used as carbide forming element (20Cr-32Ni-Nb). A substantial benefit of the cast alloy with Nb is that the creep strength is about 50% higher than the wrought alloy (800 HT) with Al and Ti [6].

Two materials have been considered as a potential replacement of alloy 20Cr-32Ni-Nb. Alloy material Centralloy® G4859 Micro (micro alloyed version of standard 20Cr-32Ni-Nb) and Centralloy® H 101 Micro (low carbon version of standard reformer tube material 25Cr-35Ni-NbTi). Nominal composition of these materials is represented in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>Ti/Zr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Centralloy® G4859</td>
<td>0.1</td>
<td>1</td>
<td>1.5</td>
<td>20</td>
<td>32</td>
<td>1</td>
<td>-</td>
<td>Balance</td>
</tr>
<tr>
<td>Centralloy® G4859 Micro</td>
<td>0.1</td>
<td>1</td>
<td>1.5</td>
<td>20</td>
<td>32</td>
<td>1</td>
<td>-</td>
<td>Additions</td>
</tr>
<tr>
<td>Centralloy® H101 Micro</td>
<td>0.13</td>
<td>0.5</td>
<td>0.5</td>
<td>25</td>
<td>37</td>
<td>0.5</td>
<td>-</td>
<td>Balance</td>
</tr>
</tbody>
</table>

*Table 1. Typical composition of Schmidt+Clemens low carbon alloy materials for outlet components.*
Centralloy® G4859 Micro

A logical improvement of 20Cr-32Ni-Nb is the development of a micro alloy version. This material is commercially known as Centralloy® G4859 Micro. Addition of small quantities of elements like titanium and composition optimization has enhanced significantly material performance. Like standard material G4859, this alloy has a maximum operating temperature of 1000ºC [1832ºF].

Centralloy® G4859 Micro was available in the market since 2011. Currently more than 102 outlet manifold arms and 2950 outlet reducers have been installed in service, together with more than 40 T-pieces and transition cones. Performance of these components in operation has been regarded as excellent.

Centralloy® H 101 Micro

Low carbon versions of HP-Nb (25Cr-35Ni-Nb) were originally designed for operation under severe corrosion conditions only requiring a moderate ductility. These conditions are typical in steam cracker applications.

Nevertheless, these materials were described in the literature as a potential replacement of 20Cr-32Ni-Nb materials [6, 7], especially in designs requiring higher operational temperatures.

Unfortunately, lower ductility after ageing performance compared with 20Cr-32Ni-Nb has been regarded as the main drawback. Therefore, material replacement in outlet manifold components was not advisable [6, 7].

Schmidt+Clemens has designed a micro alloyed version of this low carbon material, with an optimized chemical composition, capable of enhancing creep resistance and ductility after ageing over existing 20Cr-32Ni-Nb materials. Furthermore, higher chromium and nickel contents would allow outlet components to be designed for higher temperatures up to 1050ºC [1922ºF].

First reference in reformer outlet components was supplied in 2016.

Characterization and Results

Schmidt + Clemens did an extensive characterization of tensile properties and creep performance. Additionally, significant efforts were made on material microstructural characterization and accelerated ageing tests in order to study the driving forces regarding material ductility exhaustion.

Tensile Tests

Room temperature (RT) and high temperature tensile tests were performed on these three materials. 0.2% Yield Strength, Ultimate Tensile Strength and elongation to rupture (l=5d) properties were measured.

Results for 0.2% Yield Strength are shown in Figure 1. Addition of micro alloying elements has improved material yield strength in comparison with alloy G4859. Figure 2 shows the comparison of Ultimate Tensile Strength (UTS) for these materials. No relevant differences can be seen between G4859 and G4859 Micro, while H101 Micro UTS values seem to be slightly inferior.

Figure 1. 0.2% Yield Strength comparison.
Elongation to rupture values are shown in Figure 3. Results indicate a superior ductility of G4859 at low temperatures, while H101 Micro has a better ductility at higher temperatures. G4859 Micro alloy has a slightly lower ductility.

It is important to remark the relevant reduction on ductility seen for alloy G4859 in the range of 700-900°C [1292°F-1652°F]. Such behavior might be related to the stability of brittle intermetallic phases like G-phase [8], leading to a localized embrittlement of the alloy material.

**Creep Tests**

Creep resistance is one of the major requirements for these type of materials. Creep strengthening is accomplished by the formation of carbides in the microstructure [2,8]. Material creep resistance is typically shown in Larson Miller curves (parametric stress rupture strength). Minimum parametric stress to rupture values for a life time of 100,000 hr is represented in Figure 4.

Both micro-alloyed materials have a superior creep resistance compared with G4859. Small additions of strongly carbide forming elements lead to the formation of stronger and more evenly distributed secondary carbides in the austenitic matrix [8].

**Ductility after ageing**

Ductility after ageing is a major requirement for these type of materials. Material samples are aged in a furnace (controlled temperature and time of ageing), and later aged samples are tensile tested at room temperature to measure elongation to rupture. Ageing conditions and test results are shown in Figure 5.

![Figure 2. Ultimate Tensile Strength comparison.](image)

![Figure 3. Elongation to rupture comparison.](image)

![Figure 4. Minimum creep resistance comparison.](image)

![Figure 5. Ductility after ageing comparison.](image)
Considering all three materials, superior ductility after ageing performance is achieved with alloys H101 Micro and G4859 Micro in comparison with alloy G4859. Such superior behavior might be explained by the formation of more thermodynamically stable primary carbides and due to delay/suppression of intermetallic phase formation [9].

**Microscopy Inspection**

Microstructure typically consists of austenitic dendrites surrounded by carbides in the interdendritic region. In addition to this network of primary carbides formed during material solidification, fine secondary carbides precipitates form in the austenitic matrix at service temperature [8].

Results for “as cast” and aged G4859 are presented in Figure 6. Carbide precipitation is almost continuous in interdendritic areas, while the aged sample has a secondary carbide precipitation around interdendritic zones.

![Figure 6. Microstructure of G4859 -a) As cast b) Aged at 850°C-1000hr.](image6)

Figure 7 shows similar results for material G4859 Micro. Titanium carbides provide some disruption on the continuous interdendritic carbide precipitation which enhances creep material resistance.

![Figure 7. Microstructure of G4859 Micro -a) As cast b) Aged at 850°C-1000hr.](image7)

Microstructure of H101 Micro samples is shown in Figure 8. Carbide structures are similar to those seen in previous samples. Nevertheless, austenitic matrix is more stable due to the higher content in Ni and Cr.
Figure 8. Microstructure of H101 Micro -a) As cast b) Aged at 850°C -1000hr.

No G-phase was detected in aged G4859 Micro and H101 Micro. Addition of elements like Ti are inhibiting and controlling the transformation of niobium carbides (TiNb)C into G-phase [3,4].

Effect of Material Selection on Expected Life

Lifetime calculations of these components are determined by the creep rupture strength of alloy material. In outlet components, the normal design method is the standard ASME B31.3, for a typical design time of 100,000 hr [10]. Based on design data (temperature, pressure, tube OD/ID), ASME B31.3 provides the stress thickness (ts), which is the minimum required wall thickness for a 100,000 hr design time:

\[
t_s = \frac{P(d + 2 \cdot c)}{2[S \cdot E - P(1 - Y)]}
\]

where:
- \( P \) = design pressure (MPa).
- \( d \) = inside diameter (mm).
- \( c \) = additional thickness for corrosion/erosion (mm).
- \( E \) = quality factor.
- \( Y \) = coefficient.
- \( S \) = 67% of average/80% of minimum stress to rupture at design temperature.

ASME B31.3 includes several quality factors, coefficients which are tabulated [10]. Examples of wall thickness calculations are presented in Table 2. Selection of an alloy material with a higher creep resistance would reduce minimum wall thickness of the component.

Unfortunately, this model does not consider the effect of cycling and extra wall thickness allowance is required to consider such cyclic operation [5].

The main benefits of wall thickness reduction would be: weight reduction (cost reduction) and increased resistance to thermal shock.

Alternatively, maintaining original wall thickness with the same design and operating conditions, more creep resistant materials can substantially increase the lifetime of such components as indicated in Table 2.
FE Modelling of Outlet Manifolds

Finite Element Analysis (FEA), provides the opportunity of testing real components simulating the continuous operation in the furnace. Accuracy of these FEA models depend mainly on the quality of the creep model, boundary conditions, geometrical models and correct meshing.

Creep modeling is clearly the most complicated issue. Manufacturers like Schmidt+Clemens provide stress to rupture values parametrized in models like Larson-Miller. Such stress to rupture data is not adequate for dynamic modeling where creep elongation and stress relaxation behavior information is required.

Therefore, having a good creep behavior modeling is imperative in providing good FEA results.

FEA Model Description

ANSYS v. R.19.0 FEA software was used for these outlet header simulations. One standard outlet system was selected, with three supports for the outlet manifold tube arms. Location of these supports was based on existing designs (Figure 9).

<table>
<thead>
<tr>
<th>Centralloy®</th>
<th>P (MPa/psi)</th>
<th>T (°C/°F)</th>
<th>ID (mm)</th>
<th>OD (mm)</th>
<th>ts (mm)</th>
<th>Design time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G4859</td>
<td>2.94/426.4</td>
<td>940/1724</td>
<td>160</td>
<td>213.8</td>
<td>26.9</td>
<td>100000</td>
</tr>
<tr>
<td>G4859 Micro</td>
<td>2.94/426.4</td>
<td>940/1724</td>
<td>160</td>
<td>207.1</td>
<td>23.6</td>
<td>100000</td>
</tr>
<tr>
<td>H101 Micro</td>
<td>2.94/426.4</td>
<td>940/1724</td>
<td>160</td>
<td>211.8</td>
<td>25.9</td>
<td>100000</td>
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<tr>
<td>G4859 Micro</td>
<td>2.94/426.4</td>
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<td>160</td>
<td>213.8</td>
<td>26.9</td>
<td>128000</td>
</tr>
</tbody>
</table>

Table 2. ASME B31.3 Calculations. Effect of alloy material over wall thickness of component.
As a first approach for material creep modelling, ANSYS creep model 10 (Norton equation) was selected. Norton is a power law model, only valid for the secondary creep stage. Nevertheless, stress relaxation behavior is considered in this model.

\[
\dot{\varepsilon}_{cr} = C_1 \sigma C_2 e^{-C_3/T}
\]

where:
\( \dot{\varepsilon}_{cr} \) = material creep rate (mm/(mm s)).
\( \sigma \) = material stress (MPa).
\( T \) = temperature (°C).
\( C_1, C_2, C_3 \) = material parameters to be evaluated.

Regarding outlet header design conditions, homogeneous internal pressure of 2.5 MPa [391.5 psi] and temperature of 930°C [1706°F] were selected.

**Case Studies and Results**

Two simulation steps were considered for all three materials selected (Centralloy® G4859, G4859 Micro and H101 Micro).

First step considers a static structural simulation of just 1 second, to evaluate stress/strain distribution on the outlet header. Second step is a 1-year simulation of the part under creep regime.

Wall thickness of the component was estimated using ASME B31.3 calculations for alloy material G4859 considering a design time of 100,000 hr.

**Loading Effect**

Some surprising results were obtained from the static structural simulation. Even considering that reformer tube counterweight system was compensating all weight stresses over the material, significant part deflection was observed on header tube arms due to the thermal expansion of the transfer line as illustrated in Figure 10.

![Figure 10. Outlet header deformation – a) Deformation Y-axis b) Total deformation.](image)

**Effect of Material Selection**

Average Norton stress distribution (Von Mises) plots for material G 4859 are presented in Figure 11 as examples of creep stress distribution in these materials. All material results are showing that the outlet header tube support location has a strong impact on the stress distribution in the component. Supported areas and T-piece/arm tube zones have the highest stresses in these models. Therefore, these parts are the most susceptible to failure due to creep damage.

![Figure 11. Average Norton (Von Mises) stress distribution in outlet header, alloy G 4859.](image)
Life time predictions can be applied into the model considering the Larson Miller curves for each material. Most stressed portions of the outlet header are determining the lifetime of the component in operation.

Time to rupture on the T-piece/arm tube zone for each material is represented in Figure 12. Minimum stress to rupture values are considered. According to this simulation, material G4859 will have a time to rupture of 133,000 hr in such area. On the other hand, more creep resistant material like G4859 Micro (255,000 hr) and H101 Micro (220,000 hr) will have a significantly higher time to rupture in operation.

Lack of maintenance or inadequate alignment of header components (like arm supports) might add additional stresses on the part and, consequently, reduce dramatically the lifetime of the outer header. Figure 13 shows the effect of over-stressing of the cast parts in material H101 Micro produced by the support. In this case time to rupture decreases to a value of just 81,403 hr.

Results of these simulation efforts show that material selection is the most critical part in ensuring that the outlet system is able to achieve the required design time.

Also, components of the entire header system like tube supports, can also have a significant impact in the outlet header performance/ life if they are not working adequately.

**Conclusion**

New Schmidt+Clemens materials are available for outlet header components as alternatives to standard material GX10NiCrNb32-20 or ASTM CT15C (20Cr-32Ni-Nb).

These materials named as Centralloy® G4859 Micro and Centralloy® H101 Micro can significantly improve creep resistance and ductility after ageing over the standard alloy 20Cr-32Ni-Nb.

The main advantage for plant operators are wall thickness reduction of outlet header components, with benefits in weight reduction and increased resistance to thermal shock.

Alternatively, maintaining original wall thickness, lifetime of such components can be substantially increased keeping the same design and operating conditions.
Finite element analysis (FEA) can be carried out on outlet header systems, but the model accuracy strongly depends on the quality of the creep model, model design and part meshing. Creep modeling with existing data (Larson Miller plots) is especially complicated and requires additional efforts in developing a model with enough accuracy.

Analysis results indicate that new materials are improving time to rupture compared with standard 20Cr-32Ni-Nb materials. Nevertheless, inadequate operation or maintenance of outlet header components can lead to overstressed zones that can lead to early component ruptures in operation, even if the entire header is securely designed according corresponding standards.

References