Centricast Materials for High-Temperature Service

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The latest reformer tube materials offer improved creep rupture strength, longer tube life, improved heat transfer, reduced tube skin temperature and lower fuel consumption. This paper discusses the development of centricast materials for high-temperature service in steam reformer furnaces.

Steam reforming furnaces are an integral part of syngas process plants. They are also one of the costliest pieces of equipment in the plant, in terms of both capital and maintenance cost. Reformers generally contain several hundred vertically oriented straight centrifugally cast tubes, commonly known as reformer tubes. These tubes have a significant impact on replacement cost and can be a major cause of plant unavailability, especially in the case of unexpected failures. Reformer tubes operate at severe conditions and the development in steam reformers has resulted in increasingly high operating temperatures and pressures.

While reformer tubes operate at high temperatures and internal pressures, the primary cause of tube failure is creep damage (Fig. 1). However, reformer tubes are subjected to other life-limiting mechanisms, such as overheating and thermal shock. Consequently this is one of the major concerns of a plant operator.

During the life of a reformer tube, it will also experience a significant number of full thermal and pressure cycles caused by plant start-ups and shut-downs. The cumulative effect of these cycles can be very damaging and lead to accelerating creep cracking.

The phenomenon of creep is caused by progressive alteration of the material matrix. Dislocation flow through the alloy gathers at the grain boundaries and causes voids. These voids align and subsequently form micro cracks.

Fig. 1: Alloy requirements
Therefore, not only for a sensible economic balance but also to maintain high levels of reliability, structural integrity and safety, operators would like to use the most advanced materials for their reformer tubes and associated outlet components.

Experience shows that reformer tube assemblies, produced by centrifugal casting in heat-resistant materials, are in the very best position to withstand the ever more rigorous operational conditions. Schmidt + Clemens (S+C) has been incorporating the latest improvements and innovations in the design of new tube materials. The very high degree of continuous improvements of S+C researchers in applying new features for the optimum and correctly balanced properties is the basis for S+C’s global leading position in this field.

Extensive feedback of operating data, combined with a close relationship to a large number of operators, has provided and continues to provide S+C with substantial background for yet more efficient tube materials.

Centrifugally- or spun-cast materials are the preferred choice for reformer tubes which are working under severe operational conditions. The spun-cast materials contain around 0.4 wt-% carbon and therefore provide very good creep strength. Over the years, special cast alloys with increased creep strength have been developed to allow tube wall thickness to be reduced and to increase resistance to overheat and give longer tube service life.

Modern alloys such as the HP types that have been available since the early 80s all contain a large amount of chromium and nickel (Table 1). This contributes to strength and corrosion resistance at high temperature.

### Table 1
Nominal Composition of Principal Alloys Used for Tubular Reformers

<table>
<thead>
<tr>
<th>Common name (ACI)</th>
<th>C %</th>
<th>Cr %</th>
<th>Ni %</th>
<th>Nb %</th>
<th>Other</th>
<th>S+C Centralloy® grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-Nb</td>
<td>0.40</td>
<td>25.0</td>
<td>35.0</td>
<td>1.0</td>
<td>–</td>
<td>G 4852</td>
</tr>
<tr>
<td>HP-Micro-alloy</td>
<td>0.45</td>
<td>25.0</td>
<td>35.0</td>
<td>1.0</td>
<td>Micro-alloy additions</td>
<td>G 4852 Micro</td>
</tr>
<tr>
<td>HP-Micro-alloy</td>
<td>0.45</td>
<td>25.0</td>
<td>35.0</td>
<td>1.0</td>
<td>Micro-alloy additions</td>
<td>G 4852 Micro R</td>
</tr>
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</table>

Alloys rely upon creep strengthening by the formation of carbides in the microstructure. The microstructure typically consists of austenitic dendrites surrounded by eutectic carbides in the interdendritic region. In addition to a network of primary carbides forming on the grain boundaries during solidification, fine secondary carbide precipitates form in the austenite at service temperature.

In addition to chromium carbides, the HP-Nb type alloys usually also precipitate primary and secondary niobium carbides. The HP-Microalloy type material has small additions of strongly carbide-forming elements, particularly titanium and zirconium and also rare earth elements, which are added to the base HP-Nb Modified Alloy. The strengthening effect in the HP-Microalloy materials is achieved by the phenomenon known as “synergism”. This means that if two additions are both known to have a strengthening effect, when added together in only small amounts, the combined effects is greater than the summation of their effects.

In the latest generation of the HP-Microalloy material, S+C’s Centralloy® G 4852 Micro R, small controlled additions of strongly carbide-forming elements cause precipitation of very fine, nano-sized (Nb,Ti)(C,N) particles during exposure to operating conditions. These are uniformly dispersed in the matrix (Fig. 2).

However, to obtain long-lasting high-temperature strength it is important to balance the chemical composition of the alloy, since the key requirement is to achieve an optimal precipitation pattern as well as to tailor the micro-alloying additions.

**MATERIAL DEVELOPMENT**

The task to develop such an alloy was a clear request from the syngas industry to provide a material with significantly improved...
Fig. 3: Parametric stress rupture strength of Centralloy® G 4852 Micro and G 4852 Micro R

creep rupture properties compared with those of the typically used materials. With the support of its alliance partners, S+C started a vigorous R&D program and the result can be summarised, as follows:

- S+C generated a unique specification for the Centralloy® G 4852 Micro R material with substantially improved creep rupture strength compared to the conventional reformer tube materials (Fig. 3).
- The material has small controlled additions of strongly carbide-forming elements, which are added to the base HP-Nb modified alloy. The balance of elements leads to intragranular precipitation of secondary nano-size particles. In general, the nucleation of secondary carbides is promoted in the “as cast” structure and growth is inhibited when the material is aged. The even dispersion and the size of such particles (in particular the nano particles) significantly prolong the secondary stage and therefore the onset of creep.
- Alloy characterisation and micro-structural analysis were performed with sophisticated equipment such as, FGM-SEM-EDX, TEM-EDX, etc.
- New melting and casting techniques were established to guarantee the improved creep properties.
- S+C developed a special weld material based on matching chemistry. The weld material and the weld joints have been evaluated by the Notified Body (TÜV).

**BENEFITS OF CENTRALLOY® G 4852 MICRO R**

The lifetime of the tubes operated within the typical steam reformer environment, is determined by the available creep rupture strength of the material, which in turn determines the minimum sound tube wall thickness (MSW) necessary to design a tube.

Standards have been established that a design life of 100,000 hours (approx. 11 years) was reasonable and therefore one has to establish the stress which an alloy can withstand at given design temperature and pressure for 100,000 hours without failure.

Naturally, the 100,000 hour design value is theoretical. It assumes constant non-stop operation of the furnace always within the predetermined design conditions. Furthermore, the effects of any interruptions are not considered, even though it is well known that each shut-down of a furnace will shorten the tube life.

The most popular method is the equation proposed in the American standard API RP 530:
\[
\text{MSW} = \frac{\text{OD} \times P}{2 \text{Sa} + P} \quad \text{(with fixed OD)}
\]
\[
\text{MSW} = \frac{\text{ID} \times P}{2 \text{Sa} - P} \quad \text{(with fixed ID)}
\]

where:
- OD / ID = tube size (mm);
- P = design pressure (MPa);
- Sa = allowable 100,000 stress rupture value (lower limit of the scatter band, 95% confidence interval).

Nevertheless, this 100,000-hour design basis works well. Sufficient compensations are built into the various calculations with the result that the theoretical continuous life of 11 years is close to the life actually achieved in normal operation. When the furnace is operated within the limits of the pre-determined design conditions, the service life can even be significantly extended.

The characteristic Larson Miller curve (parametric stress rupture strength) for the alloy Centralloy® G 4852 Micro and the recently improved material Centralloy® G 4852 Micro R is shown in Fig. 3.

This improved alloy Centralloy® G 4852 Micro R was introduced and put into service in several operating plants in 2005, and has been commercially available since 2007. Over the past few years, S+C has supplied reformer tubes in Centralloy® G 4852 Micro R material for many major projects around the world, with the thinnest tube wall possible. Longer tube life and more reliable performance under adverse conditions (such as a high number of start-up/shut-downs, overheating, hot spots due to catalyst performance, etc.) are expected.

The material offers customers a range of benefits or combinations of benefits from which to choose. These include:

- **Increased lifetime**
  By retaining the existing tube design, (dimensional parameters) and operating conditions, this alloy substantially increases the lifetime of the tubes.

- **Process improvements**
  By maintaining the existing reformer tube outside diameter in combination with the higher strength of this alloy, it is possible to reduce the MSW. This subsequently increases the tube inside diameter, which allows additional process gains through increased catalyst volume and improved heat transfer. Results of exemplary calculations are given in Table 2. The reduced MSW results additionally in an increased resistance to thermal shock.

<table>
<thead>
<tr>
<th>Centralloy® G</th>
<th>Min. stress to rupture at 100,000 h (MPa)</th>
<th>MSW (mm)</th>
<th>ID (mm)</th>
<th>Catalyst volume</th>
<th>Tube weight (kg/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4852</td>
<td>18.3</td>
<td>11.2</td>
<td>101.0</td>
<td>Reference</td>
<td>33.9</td>
</tr>
<tr>
<td>4852 Micro</td>
<td>21.2</td>
<td>9.8</td>
<td>103.8</td>
<td>+ 5.6%</td>
<td>30.3</td>
</tr>
<tr>
<td>4852 Micro R</td>
<td>24.6</td>
<td>8.5</td>
<td>106.4</td>
<td>+10.8%</td>
<td>26.9</td>
</tr>
</tbody>
</table>

Alternatively, if tube dimensions remain unchanged and the design remains based on the standard 100,000 hours, the higher creep strength of Centralloy® G 4852 Micro R allows an increase of more than 20°C in operating temperature, which will result in significant capacity gains.

The thinner wall of tubes in Centralloy® G 4852 Micro R means less weight and less cost, providing a commercial advantage, especially when nickel prices are high.

**CONCLUSIONS**

Operators of steam reforming furnaces can utilise the latest material developments, especially the significantly improved creep rupture strength of Centralloy® G 4852 Micro R, to fully optimise their operation. This
advanced material with optimal balanced chemical composition can either be incorporated in revamps on existing units to increase capacity and raise unit profitability or can be used in new units to reduce the number of tubes. Additional benefits include improved heat transfer, reduced tube skin temperature and lower fuel consumption.

References


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