RESEARCH NOTE

CREEP LIFE ASSESSMENT OF PRIMARY REFORMER HP40-NB MODIFIED STEEL TUBE OF AN AMMONIA PLANT

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Abstract Assessment of creep damage and residual creep life of a cast HP 40 Nb Mod. reformer tube was performed, wherein the experimental Larson-Miller diagram and area fraction of creep voids were adopted. The state of damage of the tube in service was metallographically analyzed by using light and electron microscopy. Samples from the serviced reformer furnace tube were cut and prepared for void examination and creep test at 940°C-1000°C under 20-30 MPa stress. Microstructural examination was carried out with an Scanning electron microscope with secondary and backscattered electron detectors. Inter-granular voids in the microstructure of the worked tube as a result of a creep phenomenon are ranked relating to the remaining life.

Key Words Creep Life Assessment, Ammonia Plant, HP40 Nb Modified Steel Tube

1. INTRODUCTION

A major aspect of plant life management is estimating the remaining life of high-temperature components, which have a finite life due to creep. Methods based on post-service evaluations of the actual component material and direct estimation of the remaining creep life has gained popularity in the last decades. This is mainly because the results of such methods are expected to be more accurate in view of the fact that no assumption needs to be assumed regarding the materials properties or the past history of the component [1]. In this research the post - service evaluation of an HP-40 Nb modified reformer tube was done based on the accelerated, uniaxial stress rupture testing of samples excised from the tube.

In tubes, which are filled with supported nickel catalyst, methane reacts with steam, carbon dioxide and oxygen into the synthesis gas. Reformers are the heart of the fertilizer industry and any failure in this section of the plant results in premature shutdown leading to huge losses in terms of damage to the equipment, production losses and safety hazard [2].

2. ALLOY DEVELOPMENT

Since the catalyst tube assembly can amount to 25% of total cost of the furnace, there is a great incentive to optimize its design from chemical, thermal, and mechanical points of views. In the 80s, HP (25Cr/35Ni) modified alloys were developed by using certain metals, such as,
Designation and Composition of HP Alloy [3].

<table>
<thead>
<tr>
<th>ACI designation</th>
<th>UNS number</th>
<th>ASTM specification</th>
<th>Composition wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP</td>
<td>NO8705</td>
<td>A297</td>
<td>%C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.35-0.75</td>
</tr>
</tbody>
</table>

TABLE 2. Characteristic of As Cast HP Alloy [4].

<table>
<thead>
<tr>
<th>Melting point</th>
<th>Density kg/dm³</th>
<th>Coefficient of expansion mm/mm/°C</th>
<th>Thermal conductivity W/m°C/°C</th>
<th>El%</th>
<th>0.2% proof stress (MNm⁻²)</th>
<th>UTS MNm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1350°C</td>
<td>8.02</td>
<td>10⁸×18.5</td>
<td>At 1050°C</td>
<td>8, 6</td>
<td>250</td>
<td>450</td>
</tr>
</tbody>
</table>

* For centrifugally cast pipes 8 and for static castings 6

Figure 1. Shows the relation between wall thickness and amount cyclic that is an important consideration tube life [5].

molybdenum, niobium, tungsten and titanium. Designation and composition of the HP alloy are shown in Tables 1 and 2 [1,2,3].

The requirements of a cost effective reformer design are maximum reliability, operating stability and high thermal efficiency. The materials used must have a high creep strength confirmed with good strain relation, good weld ability, and excellent oxidation resistance and, after aging, good ductility and good weld ability [5].

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Figure 2. Minimum creep rupture stress versus temperature for a period of 100,000 h [5].

In retrofit or revamp design, the HP-40 Nb Mod. allows two possibilities. First, with the outside diameter fixed because of existing inlet and outlet manifolds, make the tubes thinner. This improves the rate of heat transfer and increases 30% to 40% production capacity. With the thinner...
3. MATERIALS AND EXPERIMENTS

Due to carbon formation and catalyst break up in a HP40 Nb modified tube in Razi Petrochemical Complex [7], it is deduced that the consume of the heat flux was locally stopped. Therefore, local overheating occurs which caused the failure of the tube after 12350 hr of its operation. Due to this overheating the tube and all of the catalyst were replaced, see Figure 4.

Many test samples were prepared for creep life assessment and metallographic analysis from a region far from the failed part of the tube (four meter). The creep rupture test was preformed according to ASTM-E139-83. The results are shown in Table 3.

For micro-structural evaluation, standard metallographic preparation techniques were used. The metallographic specimens were etched in glyceregia (40 parts glycerol, 40 part hydrochloric acid and 20 part nitric acid). The microstructure was examined using optical and scanning electron microscopy.

The phases observed were analyzed for chemical composition by using an energy dispersive x-ray analyzer system (EDX) in conjunction with a SEM.

The damage assessment of reformer furnace tube is based on Larson Miller parameter (LMP) and on the metallographic analysis of a serviced individual tube. Although this tube is not the real representative of the complete furnace tubes but it is important note that destroying a large number of the tubes is not practical, in addition this tube is the most damaged one. Therefore the extent of damage is the highest and its remaining life is the lowest.
3.1 Damage Assessment  The most important mechanism for damage and life extinction of the tubes is creep. The extent of the damage can be calculated by using temperature compensating time parameters or by evaluating the range of microstructural deterioration [2].

3.2 Larson-Miller Parameter  The standard method used to interpret creep stress-to-rupture data is the parametric expressions such as the one which developed by Larson and Miller [8-10] that is defined by the following equation:

\[ LMP = \frac{T}{1000} (\log t + C) \]

where; \( T \) is the service temperature (K), \( t \) time to rupture (hr), and \( C \) is a constant.

To find the maximum value of the constant \( C \) in the Larson-Miller equation, or in other words, to assess the minimum remaining life of the tubes the following data are used:

\[ LMP = T \log t + C \]

\[ LMP = constant \]

\[ LMP(1) = (938 + 273)(\log 108.3 + C) \]
\[ LMP(2) = (995 + 273)(\log 14.4 + C) \]

At stress 30Mpa \( LMP(1) = LMP(2) \)

\[(938 + 273)(\log 108.3 + C) = (995 + 273)(\log 14.4 + C) \rightarrow C = 17.459 \]
Figure 6. (a) SEM micrograph shows massive primary carbides in an austenitic matrix and fine secondary carbides within the austenite grain upon exposure to elevated temperature, (b) SEM micrograph shows the damage part of the tube which due to high temperature, secondary carbides were reduced and the inter-dendritic carbides had undergone significant agglomeration and coarsening and (c) light micrograph shows random creep voids.

The stress state in the material is complex, but it is clear that stress due to internal pressure plays a leading role in damage accumulation. As the internal pressure varies little along the tubes, damage concentrates in the hotter section [11,12]. Therefore, in the present work the average stress in the tubes or the effective stress was used for calculation.

The following data and equations were used for finding the effective stress in the tubes, [13].

\[ r_i = 41 \text{ mm}, \quad r_o = 54 \text{ mm}, \]
\[ P_i = 33.35 \text{ bar} = 3.34 \text{ MPa} \]
\[ \sigma_f = -3.34, \quad \text{MPa} = \sigma_3 \]
Figure 7. Classification of the damage in a reformer furnace tube, as indicated after metallographic preparation [15].

\[ \sigma_H = 12.43 \text{ MPa} = \sigma_2 \]

\[ \sigma_{ox} = 4.5 \text{ MPa} = \sigma_1 \text{, by using VonMises equation; } \]

\[ \bar{\sigma} = \frac{1}{\sqrt{2}} \sum \left[ (\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + \right. \]

\[ \left. (\sigma_2 - \sigma_3)^2 \right]^{\frac{1}{2}} \]

\[ \bar{\sigma} = 13.4 \text{ MPa} \]

By using data in Table 3 and the highest value of the constant C according to the creep data, the (LMP)s values were determined for various stresses and temperatures as below;

\[ \text{LMP}(1) = (930 + 273)(\log 108.3 + 17.459)10^{-3} = 23.607 \]

\[ \text{LMP}(2) = (995 + 273)(\log 14.4 + 17.459)10^{-3} = 23.606 \]

\[ \text{LMP}(3) = (1000 + 273)(\log 42.1 + 17.459)10^{-3} = 24.294 \]

\[ \text{LMP}(4) = (1041 + 273)(\log 25.2 + 17.459)10^{-3} = 24.481 \]

\[ \text{LMP}(5) = (1016 + 273)(\log 71.3 + 17.459)10^{-3} = 24.893 \]

Using the results of the creep rupture tests (Table 3), the plot of the stress versus Larson Miller parameter (master curve) was drawn in Figure 5.

By extrapolating the master curve to the calculated effective stress experienced in the tubes (13.4 MPa), the Larson-Miller parameter at the effective tube stress was deduced to be 25.56. By using this value of \((\text{LMP} = 25.56)\), the remaining life of the tubes at the service temperature (870°C) was calculated as follow.

From Figure 5, the line equation is:

\[ \text{Stress} = -8.505 \text{ LMP} + 230.88 \]

At stress 13.4 MPa \( \text{LMP} = 25.559 \)

\[ 25.559 = (870 + 273)(\log t + 17.459)10^{-3} \]

\[ t = \frac{79860}{9.2} \text{ year} \]

3.3 Micro-Structural Deterioration Creep damage starts in the wall as round voids randomly distributed on dendritic boundaries figure 6. Their preferred formation is on boundaries perpendicular to the tensile stress.

The structure consists of massive primary carbides in an austenitic matrix (Figure 6a) in addition; fine secondary carbides were precipitated within the austenite grain upon exposure to elevated temperatures. In serviced material removed from the damaged part of the tube (Figure 6b), temperature was high and the number of...
secondary carbides was reduced and the inter-dendritic carbides had undergone a significant agglomeration and coarsening. EDX analysis of these inter-granular carbides shows that they are chromium and niobium rich carbides [6].

Figure 6c shows the result of the light metallurgical survey along the tube illustrating random distribution of voids.

With regard to references [11 and 14] and by five level damage characterization approach of I. Le May [15] (Figure 7), in which damage was classified as level A or having no detectable voids, level B as displaying isolated cavities, level C having oriented cavities, level D having micro-cracks and level E having macro-cracks, the damage was revealed to be in the end range of level B. This means the approximate remained life is something around seventy percent of the designed life (which is generally 100,000 hr).

4. CONCLUSIONS

1. The remaining life of primary reformer tubes was predicted to be about 9 years. This was done by utilization stress and temperature assisted acceleration that involves the use of Larson – Miller parameter.

2. Calculations based on the stress-rupture test results showed that the Larson-Miller Constant (C) for 12350 hr serviced HP-Nb modified reformer steel tube was about 25.56.

3. On the basis of the metallographic, damage that have been observed in the microstructure of the serviced tube and its comparison with the classification of the damage in the reformer tubes it was indicated that around seventy percent of the designed life (~70,000 hr = 8.1 years)) was remained.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


