COMPARATIVE PERFORMANCE OF SIX CAST TUBE ALLOYS IN AN ETHYLENE PYROLYSIS TEST HEATER

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ABSTRACT

This paper discusses a test program to in-situ evaluate the comparative performance of six centrifugally cast heater tube alloys in an ethylene pyrolysis heater. The unusually high creep growth of conventional HP-40 radiant tubes leading to development of the test program is described, as well as the performance of the test tubes, as measured by post exposure creep growth, carburization behavior, microstructural analysis and time to failure. The performance of an aluminized tube in a separate pyrolysis heater is also described.

Keywords: ethylene pyrolysis heater, heat resistant cast stainless steel alloys, carburization, creep, heater tubes, stainless steels.

INTRODUCTION

Background

In the mid-1970's two ethylene units were brought on stream by a major petrochemical company. The heaters were designed using what was then, conventional, slow-residence-time (SRT) technology. Each heater contained six coil passes arranged in a vertical, serpentine pattern (Figure 1). The initial radiant tube metallurgy was centrifugally cast ACI HK-40, at that time the industry standard alloy for ethylene radiant tubes. All heaters cracked liquid feedstock.

In the 1980's the heaters were modified to allow cracking of gas feedstocks. To adapt to gas cracking, larger diameter outlet pass radiant tubes were installed. The larger diameter tubes permitted longer residence times and lower hydrocarbon partial pressures, altering the cracking selectivity and increasing the value of the cracked products. The outlet passes were retubed with alloy HP-40 modified with 1% niobium. HP-40 was selected based on it being the primary alloy successor upgrade when tube-metal temperatures were expected to exceed those recommended for HK-40 alloy (−982°C/1800°F). In addition to resistance to high temperature oxidation, stress rupture strength was historically the primary criteria for selecting materials for radiant section ethylene cracking service. The HP-40 1Nb alloy was chosen specifically due to improved stress-rupture properties vs. HK-40 and equal or better mechanical properties compared with other modified HP class alloys.

Approximately nine months after installation, several HP-40 tubes in gas cracking service had already elongated from axial creep to the point that they had to be shortened and the U-bends reinstalled to prevent the tubes from interfering with the heater floor. This accelerated creep induced growth was considered highly unusual and initiated an extended effort to learn its cause. The result of that study suggested that carburization and extended decoke times were significant contributors to the...
creep growth. The study culminated in an effort to develop information on relative radiant tube performance in aggressive gas cracking service by installing different tube metallurgies in a designated test heater.

Test Program Design and Implementation

The test program consisted of installing six centrifugally cast tube alloys in the designated test heater. Six alloys were selected as the heaters contained six coils. Two tubes of each alloy were installed in the split outlet pass of the six coils where temperatures were highest and operating conditions most severe. The selected alloys represented state-of-the-art metallurgy and included various HP alloys (25Cr-35Ni) with proprietary additions, except one tube that was a 28Cr-48Ni alloy. An HK-40 tube (25Cr-20Ni) was included as one of the six tested alloys as a "control." Table 1 shows the chemical composition of the six tested alloys. Representative short term and long term mechanical properties for the test alloys are shown in Table 2.

Alloy selection was primarily based on maximizing carburization resistance. Stress rupture and oxidation resistance were secondary considerations if the tube metallurgy and wall thickness combination met 100,000-hour stress-rupture design criteria. All tested tubes were purchased from commercial heats with honed I.D.'s to remove internal casting porosity and surface roughness. Also, tested in a separate gas cracking heater, were two HP-40 alloys that had been aluminized on their O.D. and I.D. surfaces. Aluminizing had shown promise in some studies as a viable method to reduce coking and carburization of pyrolysis heater tubes. 

The test heater was intended to operate in a normal production environment; therefore, no special controls were placed on either cracking or decoking operations. The primary test parameter of interest was time to failure, as measured by gross rupture/cracking or by lack of weld repairability. Initial, outer diameter and wall thickness measurements were taken for post exposure comparison, and weld-to-weld measurements of individual sections making up the welded tube length taken for verifying creep growth along the tube length. A ring from each test tube was also removed for comparison of as-cast and post exposure microstructures. Process outlet and end-of-run tube metal temperatures were measured as was normally done and averaged approximately 843°C/1550°F and 1037°C/1900°F, respectively. Tube metal temperatures during decoking could reach 1093°C/2000°F.

POST SERVICE TUBE EVALUATIONS

Aluminized Tube

The HP-40 aluminized tubes were removed from the heater for metallurgical evaluation after approximately 30 months of service. Two HP-40 non-aluminized tube samples installed in an outlet pass of the heater at the same time were also removed for comparative examination. The heater had cracked both liquid and gas feedstocks during the exposure period. Ring samples approximately six inches long were removed from the tubes at a point immediately above the bottom 180-degree return bend weld. Identification of the samples is as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1</td>
<td>#1 Coil, 7th Pass</td>
<td>HP-40 1%Nb (aluminized)</td>
</tr>
<tr>
<td>No. 2</td>
<td>#1 Coil, 8th Pass</td>
<td>HP-40 1%Nb (aluminized)</td>
</tr>
<tr>
<td>No. 3</td>
<td>#2 Coil, 8th Pass</td>
<td>HP-40 1%Nb (non-aluminized)</td>
</tr>
<tr>
<td>No. 4</td>
<td>#2 Coil, 7th Pass</td>
<td>HP-40 1%Nb (non-aluminized)</td>
</tr>
</tbody>
</table>

Laboratory investigation included visual observations, examination of the tube samples with a "horseshoe" magnet to qualitatively measure magnetic response on I.D. and O.D. surfaces, metallographic examination using mounted and polished specimens and circumferential measurements.

Visual observation showed that all four tube samples were similar in appearance except that the aluminized tube samples exhibited spalling at the I.D. surface that was not observed on the non-aluminized samples. No excessive oxidation or other dimensional non uniformities were observed to either the aluminized or non-aluminized samples.
Examination of the as-received samples with a magnet indicated the following:

- Samples 1, 3, and 4 responded similarly to a magnet at the I.D. The magnetic response was mild, to somewhat aggressive, with the response fairly uniform around the I.D. circumference.

- Sample 2 exhibited a rather weak I.D. magnetic response, but a rather strong response at the O.D. The magnetic area extended approximately 120 degrees around the circumference.

Except for the O.D. response of Sample 2, no significant differences were observed in the magnetic response between the aluminized and non-aluminized samples.

Figure 2 illustrates the circumferential measurements taken on the four samples. Moderate growth has occurred to all samples with the aluminized tubes exhibiting slightly greater axial and circumferential growth than the non-aluminized samples.

Photomicrographs of tube Samples 1, 2, and 4 are shown in Figures 3-8. Pertinent observations concerning the microstructures are summarized below:

An aluminum layer was not apparent on either the I.D. or O.D. surface of Sample 1 at 50X magnification (Figures 3 and 4, respectively). The I.D. (Figure 3) appeared to have experienced some carbon pickup immediately beneath the surface. The O.D. of Sample 1 was decarburized with no visual evidence of an aluminum layer.

The primary carbides in the aluminized Sample 2 were less agglomerated and smaller (Figures 5 and 6) than those in Sample 1(Figure 3). Both the I.D. and O.D. exhibit some residual aluminum, although the layers were discontinuous and appear to be spalling at the aluminized/substrate interface. It appeared that at a specific depth the aluminized layer was oxidized to a greater extent than at other depths and the oxidation promoted spalling. The I.D. and O.D. surfaces were much less oxidized and decarburized than Sample 1.

The microstructure of tube Sample 4 was representative of both non-aluminized tube samples (Figures 7 and 8). The carbide agglomeration and morphology were similar to that observed in Samples 1 and 2 except that the I.D. of Sample 1 exhibited greater carbide agglomeration. Minor decarburization and oxidization had occurred on both I.D. and O.D. surfaces.

Main Test Heater Test Tube Evaluations

Visual Observations. All tube samples were removed from the eighth pass next to the bottom 180-degree return bend, except for alloy C, which was removed from the seventh pass. Visually, alloy F exhibited the greatest O.D. deterioration, with significant bulging and longitudinal and circumferential cracking. Alloy D appeared to be in the next worse condition, based on the extent of cracking. The remaining test tubes were similar in appearance. None of the samples exhibited excessive O.D. oxidation.

The I.D.’s of all samples contained a thin, adherent, red scale. The I.D. surfaces of all samples, except for alloy F, were similar, showing little deterioration. Alloy F experienced significantly greater I.D. deterioration in the form of metal loss than did the other samples.

Metallographic Observations. The microstructures of the six test tube samples, illustrating the original as-cast microstructures and the post exposure structures at the I.D., midwall and O.D., are shown in Figures 9-31. A summary of general observations regarding the microstructures follows:

- The as-cast microstructures of all test samples were similar, containing interdendritic primary carbides with some coring in an austenitic matrix.
Alloy F exhibited the greatest O.D. oxidation (Figure 31). Significant I.D. deterioration was also observed (Figure 29), corresponding to the macroscopic observation of I.D. deterioration.

Alloy D exhibited the greatest carburization, based on the volume fraction of carbides at the I.D. surface (Figure 21). Alloy D also contained the largest, blockiest, primary carbides, perhaps due to a lack of carbide forming additives, which tend to restrict carbide growth. Alloy A exhibited the second greatest carburization (Figure 10) while alloy C exhibited the least carburization (Figure 18).

Alloy B contained noticeably more creep voids than did the other samples (Figures 14-16).

Other than the features discussed above, the microstructures of the test tubes did not show any unusual features differentiating one sample from another. Based on a lack of significant secondary carbides and the large, blocky, primary carbides, all test tubes appeared to have experienced exposure to similar tube metal temperatures, approaching 1037°C/1900°F - 1093°C/2000°F.

**Time-to-Failure.** Figure 32 shows the time-to-failure of the six test tube alloys. A tube "failure" was based on cracking, either during normal service, decoking or during upsets, or an inability to successfully weld it without cracking. Alloy C provided the greatest service life of all tested alloys.

**Dimensional Measurements.** Figure 33 illustrates percent wall-thickness loss and O.D. diametrical expansion measurements taken on the test tube samples. The percent wall loss was minor for alloys A and E and moderate for the other alloys. Circumferential expansion was minor for all alloys except alloy F. The maximum expansion for alloy F was measured at a localized bulge and does not necessarily represent an average expansion as do the other alloys. Of the two measurements, circumferential expansion is considered to be the more relevant in relation to limiting service life.

**Axial Creep Growth.** Other than service life, axial creep extension was considered to be the most important measured test parameter. Figure 34 illustrates the axial creep rate of the tested alloys. Alloy C by far exhibited the lowest creep rate of the six alloys.

**Carburization Measurements.** The greatest influence on creep growth is carburization. Tube sample carburization was measured using three methods: (1) with average and maximum O.D. magnetic permeability measurements using a ferrite gage, (2) with Knoop microhardness profiles and, (3) by chemical etching using a draft procedure developed by NACE Task Group T-5b-11a, "Standard Test Method for Measuring the Carburization of Alloys for Ethylene Cracking Furnace Tubes."

Figure 35 shows magnetic permeability measurements taken at the O.D. of ring samples taken from the test alloys at areas of maximum magnetic response. The measurement results are qualitative numerical values of magnetic response and have no units. The higher the numerical value, the greater the degree of carburization, as measured by magnetic response. Based on the measurements, the six alloys would be ranked in descending order of performance as follows: alloy C, alloy E, alloy F, alloy D, alloy A and alloy B.

Knoop microhardness profiles were taken on mounted and polished specimens using a 1 Kg weight (Figure 36). This method proved more difficult with respect to ranking carburization performance, as the six alloys exhibited different maximum I.D. hardnesses and depth profiles. The relative maximum hardnesses do give some qualitative information regarding the extent of I.D. carbon pickup; however, the correlation with metallographic visual observations is not good. Using a maximum I.D. hardness as a comparison with extent of carbon pickup must be used with caution as, in this case, the alloys had different as-cast levels of carbon. The hardness profile results suggest the following descending performance ranking, based on a qualitative weighting of maximum hardness and depth of carburization, as estimated from the asymptote of the curves: alloy E, alloy B, alloy C, alloy A, alloy D and alloy F.

The extent of carburization was also measured using a chemical etching method proposed by NACE Task Group T-5b-11a. This method involves immersing a test specimen in a solution of nitric and hydrofluoric acid for approximately two hours. The depth of carburization is estimated by the etching contrast between the carburized zone and the unaffected base metal. The test alloy carburization ranking, based on chemical etching, is shown in Figure 37. Using this method the descending performance ranking of the six alloys is as follows: alloy C, alloy E, alloy F, alloy B, alloy A and alloy D. Figures 38
The most obvious and important parameter regarding heater tube reliability is useful service life. Of the metallurgical parameters affecting service life, axial creep and carburization (which affects creep and weldability) are considered the most important. Table 3 shows a simple numerical ranking of the test tube alloys, based on total service life, axial creep and carburization. The test tubes were ranked in each of the three categories from one to six, with one being the best performer in each category. The numbers in each category were then added together to arrive at a total performance related numerical ranking. The test tube with the smallest number was considered the best performer. All categories were given equal weighting.

In the Table 3 ranking, one can see that there is an inconsistency with an alloy's service life ranking compared with its total ranking. However, the agreement between creep elongation and carburization between test alloys is good. Creep elongation and carburization are considered to be more reliable methods for ranking alloys as total service life can be affected by influences outside the control of the test program, i.e., operational and decoking upsets, welding skills, and subjective judgements regarding retirement. Axial growth is particularly important as it establishes the need to shut down a heater to shorten the tube. Failure to shorten tubes before they reached the heater floor resulted in warped and bowed heater coils with consequent, higher tube stresses and creep rates. This situation could potentially result in a failure of the entire coil and an uncontrollable fire.

Figure 44 compares the results of the three methods used to rank the carburization resistance of the test tube alloys. In general, the agreement between the different methods is not good. Of the three methods, the O.D. magnetic response measurements and chemical etching gave closer results compared with knoop hardness measurements. Based on the three carburization test methods used, the chemical etch method is probably the most accurate and useful method of measuring carburization resistance, which agrees with the opinions of the T5B-11a task group.

There does not appear to be an obvious correlation between performance in the evaluated categories with alloy chemistry or mechanical properties, with the exception of alloy C. Alloy C was the superior performer in all of the important categories of service life, carburization resistance and axial creep. The major difference between the chemistry of alloy C and the other test alloys is the higher nickel content. The primary benefit of the higher nickel appears to be increased carburization resistance, with lower axial creep possibly being simply a beneficiary of the increased carburization resistance. Regardless of specific alloy additions or rated stress rupture strength, none of the other alloys distinguished themselves from one another, with the possible exception of alloy B, which was a poor performer in all of the important categories and exhibited greater microstructural creep damage than the other alloys. Significantly, the performance of the generic HK-40 alloy (alloy D), despite its extensive carburization, compared favorably with that of the higher alloyed, more expensive HP-40 alloys.

CONCLUSIONS

The results of the ethylene heater tube test program provided the following results:

1. The best overall performing alloy was alloy C, a 28Cr-48Ni alloy.

2. The generic HK-40 alloy's performance (alloy D) was comparable to that of the higher alloyed, higher priced alloys.

3. No positive correlation could be made between performance, as measured by the evaluated categories, and chemical composition or mechanical properties of the alloys.

4. The reason for retirement of all test tubes was due either to gross fracture or lack of weldability, instead of the more commonly specified stress-rupture strength selection criteria.
References


Figure 1- Test heater coil configuration.

Figure 2- Graph illustrating comparative creep growth of the aluminized tube samples vs. the non-aluminized samples.
Figure 3- I.D. of aluminized tube sample 1.  50X

Figure 4- O.D. of aluminized tube sample 2.  50X
Figure 5- I.D. of aluminized tube sample 2.  50X

Figure 6- O.D. aluminized tube sample 2.  50X
Figure 7- I.D. of non-aluminized tube sample 4.  50X

Figure 8- O.D. of non-aluminized tube sample 4.  50X
Figure 9- As-cast microstructure of alloy A.  100X

Figure 10- Post exposure I.D. of alloy A.  100X
Figure 11- Post exposure mid-wall microstructure of alloy A. 100X

Figure 12- Post exposure O.D. microstructure of alloy A. 100X
Figure 13- As-cast microstructure of alloy B. 100X

Figure 14  Post exposure I.D. microstructure of alloy B. 100X
Figure 15 - Post exposure mid-wall microstructure of alloy B.  100X

Figure 16 - Post exposure O.D. microstructure of alloy B.  100X
Figure 17 - As-cast microstructure of alloy C.  100X

Figure 18 - Post exposure I.D. microstructure of alloy C.  100X
Figure 19- Post exposure mid-wall microstructure of alloy C. 100X

Figure 20 - Post exposure O.D. microstructure of alloy C. 100X
Figure 21- Post exposure I.D. microstructure of alloy D. 100X

Figure 22- Post exposure mid-wall microstructure of alloy D. 100X
Figure 23 - Post exposure O.D. microstructure of alloy D. 100X

Figure 24 - As-cast microstructure of alloy E. 100X
Figure 25- Post exposure I.D. microstructure of alloy E.  100X

Figure 26- Post exposure mid-wall microstructure of alloy E.  100X
Figure 27 - Post-exposure O.D. microstructure of alloy E. 100X

Figure 28 - As-cast microstructure of alloy F. 100X
Figure 29- Post exposure I.D. microstructure of alloy F.  100X

Figure 30- Post exposure mid-wall microstructure of alloy F.  100X
Figure 31- Post exposure O.D. microstructure of alloy F. 100X

Figure 32- Graph illustrating the service life of the six test heater tube alloys.
(1) At localized bulge

Figure 33- Test alloy post exposure O.D. expansion measurements.

Figure 34- Test alloy longitudinal creep rate measurements.
Figure 35- Test alloy O.D. magnetic permeability measurements.

Figure 36- Test alloy Knoop microhardness profile measurements.
Figure 37- Test alloy carburization depth profile by chemical etching.

Figure 38- Alloy A carburization depth by chemical etching. ~3.3X
Figure 39- Test alloy B carburization depth by chemical etching.  ~3.4X

Figure 40- Test alloy C carburization depth by chemical etching.  ~3.6X
Figure 41- Test alloy D carburization depth by chemical etching. ~3.4X

Figure 42- Test alloy E carburization depth by chemical etching. ~3.4X
Figure 43- Test alloy F carburization depth by chemical etching. ~3.4X

Figure 44- Chart comparing the results of different carburization measurement methods.
## TABLE 1
**Test Tube Chemical Compositions**

<table>
<thead>
<tr>
<th>Test Tube</th>
<th>UNS/DIN</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Ti</th>
<th>Nb</th>
<th>W</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>-</td>
<td>0.5</td>
<td>25</td>
<td>38</td>
<td>0.70</td>
<td>1.8</td>
<td>Rem.</td>
<td>0.13</td>
<td>0.28</td>
<td>0.27</td>
<td>*</td>
</tr>
<tr>
<td>Alloy B</td>
<td>-</td>
<td>.35-.45</td>
<td>24-28</td>
<td>34-37</td>
<td>2.0 max.</td>
<td>1.5 max.</td>
<td>Rem.</td>
<td>0.6-1.3</td>
<td>0.7-1.2</td>
<td>-</td>
<td>0.3-0.8 Mo</td>
</tr>
<tr>
<td>Alloy C</td>
<td>G-NiCr28W</td>
<td>0.45</td>
<td>28</td>
<td>48</td>
<td>1.50</td>
<td>1.50</td>
<td>Rem.</td>
<td>-</td>
<td>-</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Alloy D</td>
<td>J94224</td>
<td>0.40</td>
<td>25</td>
<td>20</td>
<td>1.50</td>
<td>1.50</td>
<td>Rem.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alloy E</td>
<td>J95705</td>
<td>0.40</td>
<td>25</td>
<td>35</td>
<td>1.50</td>
<td>1.50</td>
<td>Rem.</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alloy F</td>
<td>-</td>
<td>0.5 max.</td>
<td>20/27</td>
<td>33/40</td>
<td>2 max.</td>
<td>2 max.</td>
<td>Rem.</td>
<td>-</td>
<td>2 max</td>
<td>-</td>
<td>**</td>
</tr>
</tbody>
</table>

(*) Small additions of rare earth metals
(**) Other unspecified elements

## TABLE 2
**TYPICAL MECHANICAL PROPERTIES OF TEST TUBE ALLOYS**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>T.S. (MPa.)</th>
<th>Y. S. (MPa)</th>
<th>Elong. (%)</th>
<th>100,000 hr. S-R. (Mpa) (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>450 min.</td>
<td>250 min.</td>
<td>8</td>
<td>13.0</td>
</tr>
<tr>
<td>Alloy B</td>
<td>440 min.</td>
<td>225 min.</td>
<td>8 min.</td>
<td>6.7</td>
</tr>
<tr>
<td>Alloy C</td>
<td>400 typ.</td>
<td>220 typ.</td>
<td>3 typ.</td>
<td>8.6</td>
</tr>
<tr>
<td>Alloy D</td>
<td>440 min.</td>
<td>220 min.</td>
<td>10 min.</td>
<td>4.5</td>
</tr>
<tr>
<td>Alloy E</td>
<td>440 min.</td>
<td>220 min.</td>
<td>8 min.</td>
<td>7.5</td>
</tr>
<tr>
<td>Alloy F</td>
<td>540 min.</td>
<td>343 min.</td>
<td>3</td>
<td>6.2</td>
</tr>
</tbody>
</table>

(1) at 1000C

**Notes:**
A) Alloy D (HK-40) minimum stress rupture strength taken from API RP-530.
B) All S-R values are minimums.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Service Life</th>
<th>Elongation Rate</th>
<th>Carburization Resistance(1)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy C</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Alloy F</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>9</td>
</tr>
<tr>
<td>Alloy E</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Alloy A</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>Alloy D</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>Alloy B</td>
<td>6</td>
<td>6</td>
<td>4</td>
<td>16</td>
</tr>
</tbody>
</table>

(1) Based on the chemical etch method