

Condition Assessment Strategies in Centrifugally Cast HP Steam Reformer Tube Alloys

David Knowles+, Karl Buchanan#, Milo Kral#

+Shell Global Solutions International, PO Box 38000, 1030 BN Amsterdam

#Dept Mechanical Engineering, Private Bag 4800, Christchurch 8140, New Zealand

Abstract

In steam methane reforming one of the key reliability aspects relates to ensuring the integrity and reliable operation of the catalyst filled radiant tubes. The tubes experience temperatures beyond 900°C for a considerable length of time, which makes creep the prime mode of failure. Predicting and assessing creep damage rates is challenging for a number of reasons: the alloys are not subject to any international specifications, the tubes are cast and their microstructures evolve substantially in service. These factors are known to lead to considerable scatter in creep life, strain and ductility response.

This paper describes the initial steps of a current approach to managing tube life and outlines the early stages of a study aimed at development of a methodology to utilise appropriate inspection in combination with judicious creep strain/rupture testing to provide an effective strategy for long-term assessment and management of reformer tube integrity. The work involves creep testing and microstructural characterisation of service-exposed material to incorporate the influences of material changes

Keywords: Centrifugally cast alloys, creep strain, microstructure

1. Introduction

In steam methane reforming one of the key reliability aspects relates to ensuring the integrity and reliable operation of the catalyst filled radiant tubes. These tubes are generally exposed to metal temperatures beyond 900°C for a considerable length of time, which makes creep the prime mode of failure. Generally non-standardised materials with a range of chemistries are employed, the tubes being fabricated by centrifugal casting. This cast structure along with in-service aging is known to lead to substantial variations in creep strain/life response. Furthermore the variation in local metal temperature along the length of individual tubes are known to be significant so that the remnant life of the tube is very sensitive to the location at which any inspection measurements are made.

Temperature estimates using radiation thermometry plays a key role in day-to-day management of the furnace, but this is a specialist technique and is subject to a number of potential errors; generally it does not capture the long-term trends in temperature at local regions along the tube length. At the present time there are a number of complementary inspection techniques that can be adopted during routine outages to assess the condition of the tubes, of which measuring diametral growth is a widely adopted technique often in parallel with ultrasonic or eddy current inspection.

This paper describes the initial outline of a study aimed at development of a methodology to utilise appropriate inspection measurements in combination with judicious creep strain/rupture

testing to provide an effective strategy for long-term assessment and management of reformer tube integrity. The work involves creep testing and microstructural characterisation of service-exposed material to incorporate the influences of material changes.

2. Inspection Techniques

2.1 Material inspection

If one considers a controlled failure process in a reformer tube, the prime ‘damage’ mechanisms relate to microstructural modification and creep. To date a non-destructive, volumetric measure of microstructural change (as opposed to surface replication) has not been adopted in general use. In relation to bulk creep damage assessment a number of techniques have evolved over recent decades and have been utilised with mixed success. To better understand the applicability of these techniques it is important to keep in mind the general nature of a typical strain/time plot in the creep regime, Figure 1

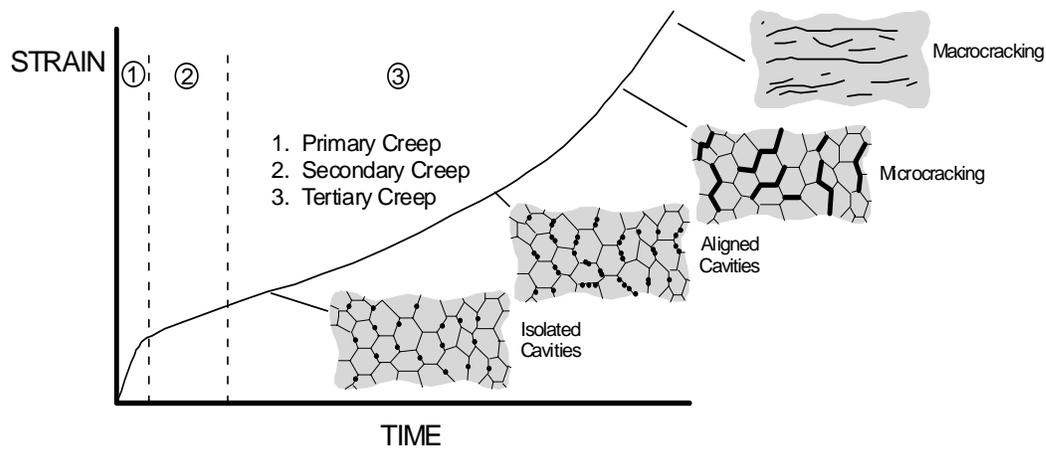


Figure 1. Typical creep strain versus time curve for a metallic material.

Generally the initial primary creep regime (1) can be ignored as it does not play a role in the damage process and its influence on dimensional changes in actual cast tubes is limited. In regions (2/3) strain evolves and damage accumulates due to a number of processes – multiplication of dislocations, intergranular stress generation, grain boundary cavity formation, cavity linkage, micro and macro cracking to name a few. Most inspection techniques aim to measure changes at a material microstructural level and focus on these damage processes beginning with cavity formation. However it is important to recognise that the early stages of cavity formation are difficult to measure and this manifestation of damage is rarely observed in the first 1/3rd of a component’s life.

Typical non-destructive inspection techniques fall into three general categories (often used in combination):

1. Measurement of strain—principally through diametric growth in the cast tubes
2. Eddy current inspection
3. Ultrasonic inspection

Given the complex cast microstructure in these tubes, consisting of extensive regions of columnar grains and a varying extent of more equiaxed grains on the inner surface, for the latter two processes it is acknowledged that successful application requires both a validated procedure and well informed interpretation/understanding of the results.

The eddy current technique has been found to be particularly useful at finding more extensive defects in tubes that are in the final stages of life (and hence not suitable for a further campaign), but the interpretation of the output from the inspection is subjective. Uncertainties can be reduced substantially by implementing baseline inspection on the tubes prior to their entering service.

The perceived advantage of the strain-based approach is that, in principle, it can be used to monitor the earlier stage of creep damage (strain) accumulation, which is complementary to the aforementioned measures. For improved accuracy it is desirable to measure changes in the internal diameter along the whole length of each tube using laser profilometry. The benefits to this technique stem from the fact that the internal surface of the tubes is bored and not subject to any corrosion in service. If no prior inspections have been carried out then the growth in any region of the tube can be compared to a base line from the cold section of the tube outside the radiant box. The main draw back of internal inspection is simply that access is only available during a catalyst change-out and hence the opportunity for inspection can be very limited.

External dimension profiling can be carried out rapidly during any planned shutdown, but its accuracy is more limited owing to:

- Variation in the outer diameter of the tubes owing to the measurement being on the as-cast surface (no final machining) and
- The potential for surface oxidation

In practice this latter concern is not significant; primarily the initial surface wall loss is due to oxidation of the rough surface cast finish. The substantial variation in external diameter negates the ability to compare tube growth, using cold regions as a benchmark. Owing to this fact, base lining of the tubes either prior to entering service, or early in life, is seen as a critical step and considered as best practice. Regular inspection then allows a clear measure of strain evolution to be recorded for every tube as a function of any position along their length i.e., effective mapping of strain evolution throughout the radiant box can be undertaken.

2.2 Temperature

A final inspection technique, which warrants mention, is that of temperature, a critical parameter in any reformer tube life assessment study. Temperature measurement is normally achieved using radiation thermometry. While this can provide accurate results it is known to be prone to a number of large potential sources of error, if not applied with insight, including:

- Emissivity errors,
- Reflection errors– from furnace wall and neighbouring tubes,
- Size of source effects,
- Adsorption and emission errors.

These issues are described in depth by Saunders [1], which provides excellent background on the subject.

A less well recognised advantage of regular measurement of diametral growth is that, to a first approximation, it provides a time-averaged measure of the thermal exposure along the length of the reformer tube which is an alternative and often more accurate indicator of the non uniformity of the temperature profile within the furnace. This is clearly indicated in Figure 2 where an inspection has highlighted the extremely localised nature of accelerated tube growth in the coffin section (towards the outlet of the tube). In this case the location of concern could not be monitored with optical pyrometry, owing to difficult access, but allowed appropriate selection of the location from which to take creep specimens.

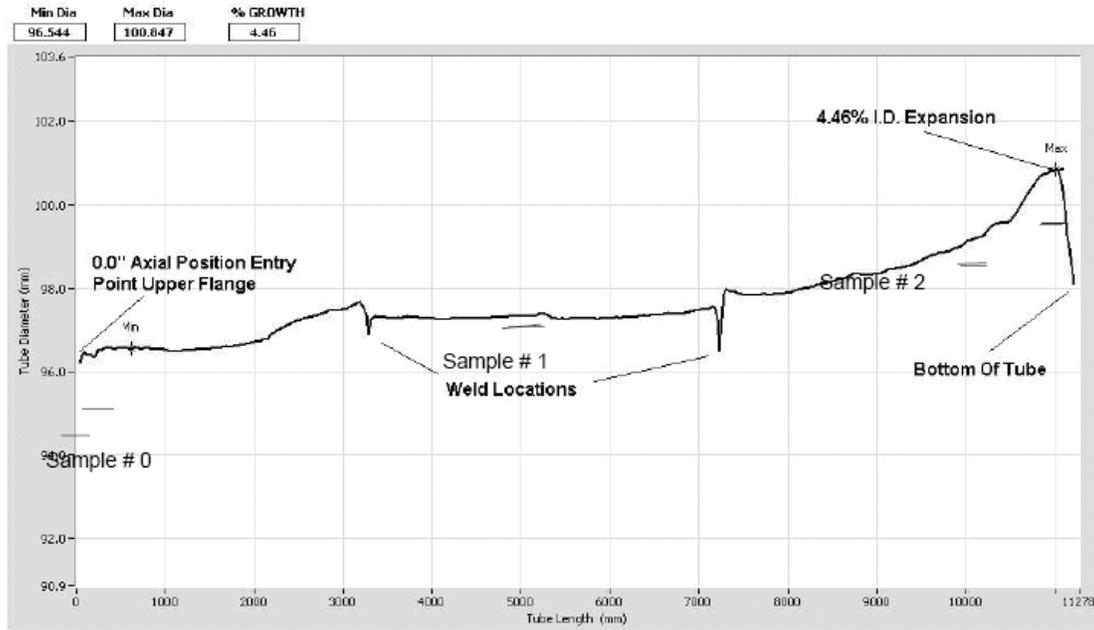


Figure 2. Internal laser profilometry from a service exposed reformer tube. Clearly marked are the weld locations and the region of highest diametral growth, which, in this instance is in the ‘coffin’ section of the furnace.

3. Strain/Life Interpretation

The traditional approach to reformer tube design life assessment has followed the approach as described in API 530 [2] whereby the Larson-Miller Parameter is used as a time-temperature parameter to allow prediction of the required rupture life when the tube wall is subjected to specific combination of stress and temperature.

$$LMP = f(\sigma) = (T + 273)[C + \log(t_R)]$$

where σ is stress, T is temperature ($^{\circ}\text{C}$), t_R is time to rupture, and C is a constant. In principle this approach can be used to determine accumulated tube life; a Robinson life-fraction summation technique can be applied if one has access to regular and accurate temperature measurement. Larson-Miller Parameter data is generally available from the tube supplier which can be used for

this purpose. However this approach should be treated with some caution as it is acknowledged that there are a number of significant drawbacks:

1. Remnant life estimates are based on tube metal temperatures and primary hoop stress but do not consider the secondary through-wall stresses generated due to temperature gradients.
2. Aside from temperature measurement the previously mentioned inspection techniques provide no input to the assessment process and hence the opportunity does not exist to optimise life consumption estimates.
3. Larson Miller data is based on relatively short-term testing (rarely beyond 1 year) and microstructural modifications (in-service aging) in long-term exposure are known to modify significantly the creep performance [3].

In older generation HK alloys, due to the reduced high temperature strength, thicker walled tubes were employed, and the through-wall stresses were known to contribute significantly to life consumption via creep relaxation. In thinner tubes fabricated using HP alloys it is generally acknowledged that this effect is reduced substantially. Its influence is, obviously, very dependent upon the number of cycles which a unit will see and the manner in which the unit is shut down/started up. Thomas et al [4] have described a strain based approach, centred on the ductility exhaustion method in R5 [5] which discusses this topic in some detail. For ductile materials it has been found that the contribution of these cycles to life reduction is minor, though further consideration of this aspect is warranted.

Strain-based approaches to creep life assessment has not historically gained much attention in the petrochemical/refining sector, but the introduction of the Omega method in API 579 [6] has changed this position somewhat in recent years. In terms of uniaxial stress the Omega method is simply described by:

$$\dot{\varepsilon} = \dot{\varepsilon}_o \exp[-\Omega \varepsilon_c]$$

where $\dot{\varepsilon}_o$ is the starting creep rate, ε_c is the accumulated creep strain at the given stress and Ω is a stress/temperature dependent material parameter which describes the shape of the creep curve. This approach is essentially a specific continuum damage mechanics formulation as discussed in detail in many texts such as Penny and Marriott [7], damage (D) being related to an acceleration in creep strain rate via the relation:

$$D = 1 - \frac{\dot{\varepsilon}_o}{\dot{\varepsilon}} = 1 - e^{-\Omega \varepsilon_c}$$

If one ignores the initial region of primary creep then this form of relation can easily be fitted to a typical creep strain curve as illustrated in Figure 3 and, in principle, measurement of diametral growth (given stress, time and temperature) can then directly be related to a position on the creep curve, hence current life consumption can be calculated. If temperature and stress vary then integration of strain increments can be achieved by use of the strain rate acceleration factor, which is represented in the above description of damage. From a material perspective a significant drawback in the model is that it cannot consider time related development of microstructure. While this isn't a major concern when testing thermally stabilised wrought alloys it is an important consideration in these centrifugally cast materials, which see much higher temperatures.

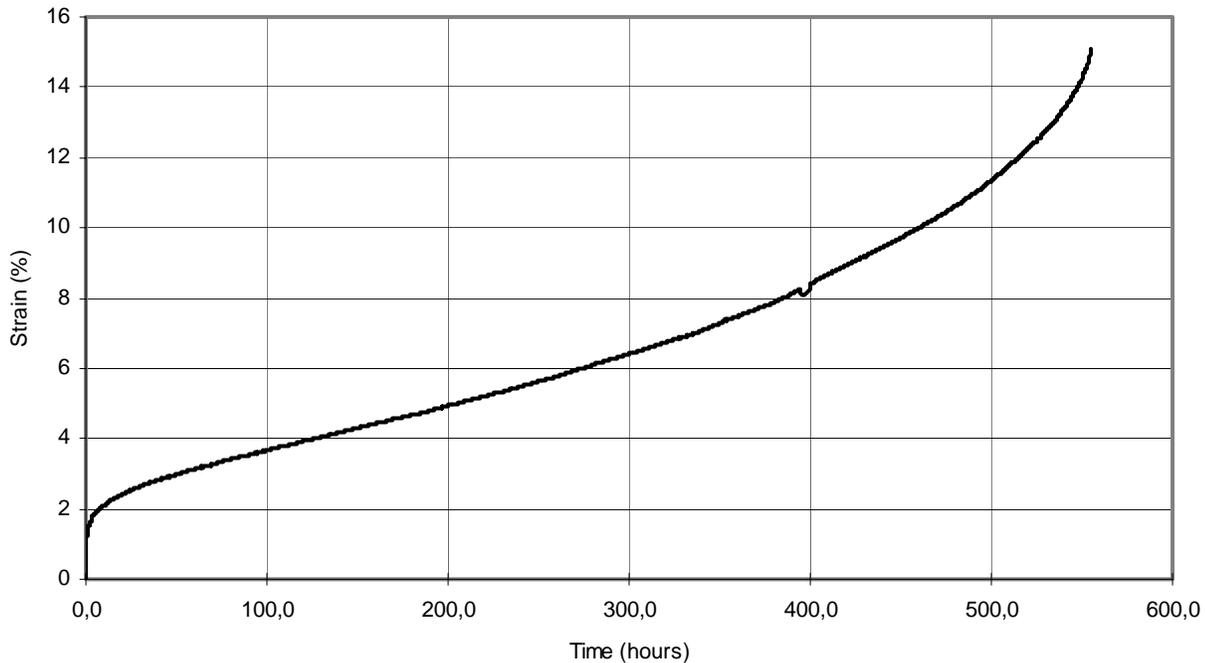


Figure 3. Short-term creep strain vs. time curve for typical 25/35 microalloyed ex service tube (alloy A) tested at 1000deg C. Note ductility at failure greater than 14%.

In practice a wide range of creep models could be adopted to fit the general form of the creep strain curve and hence make better use of in-situ diametric growth measurement, but it is important to ensure these do not over model the situation! A major factor is that the alloys we are trying to assess are somewhat unique to each supplier, they have additions of a range of microalloying additions, and are cast, and hence any parameters used to describe their creep strain response are subject to substantial variation. Compounding this is the need to recognise that the time/temperature evolution of the microstructure in service will further modify the form of the creep curve and the rate of damage evolution. In practice this means that the mechanical response of any given tube in service is very sensitive to how the tubes are thermally exposed and hence aging is a parameter that requires careful consideration in any creep modelling.

4. Role of Material Aging

To graphically illustrate the influence of microstructural condition one should compare the results of Figure 3 with Figure 4. These tests are from two different ex-service materials. In both instances the tubes had experienced minimal in-service creep damage as measured by strain, however while the 1065 °C test gave the expected life and ductility, the tube tested at 1000 °C failed at less than 50% of the expected life with a ductility lower than 1%.

As a first consideration there appear to be two major parameters that influence this variability in creep. Gaining a better understanding of these influences can provide a dual benefit:

- Opportunity for improved specification in procuring new tubes which are less prone to degradation in ductility
- Refinement in prediction of the creep strain response i.e. optimisation of the creep strain versus life relation.

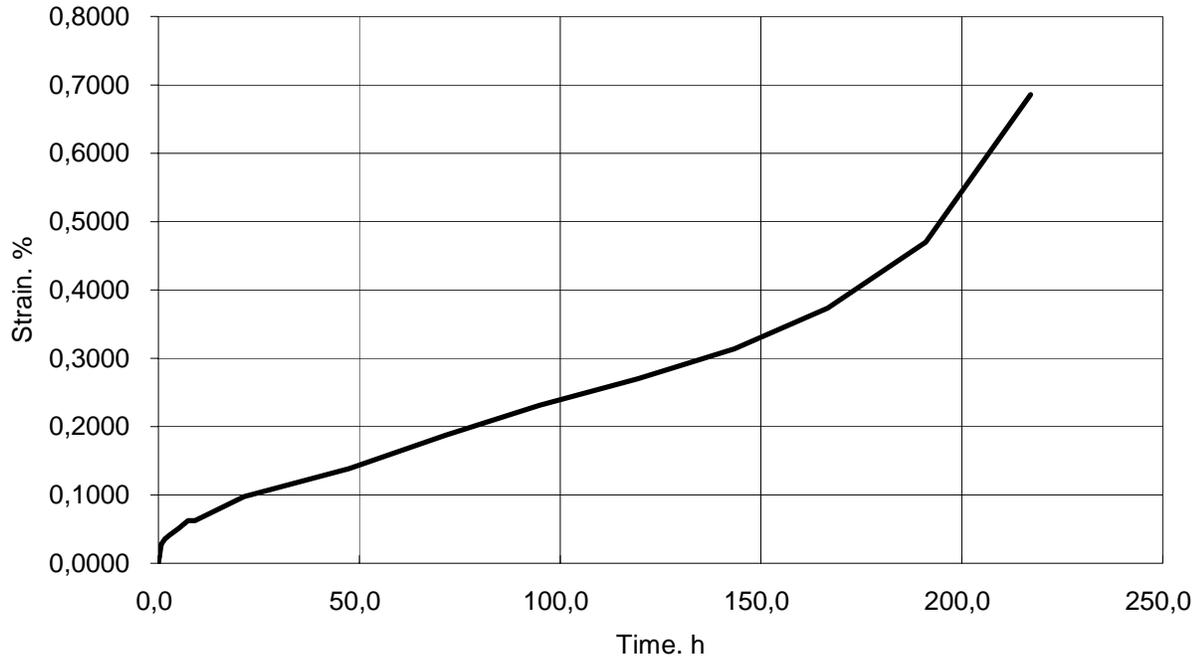


Figure 4. Short-term creep strain vs. time curve for ex service 25/35 microalloyed tube (alloy B) tested at 1065 deg C. Note ductility at failure less than 1.0%.

The book, Atlas of Microstructures [8] has provided an informative review of microstructures that can be generated in this genre of alloys as a function of thermal exposure, but does not make a clear link to mechanical response. In the current study we are aiming to use a combination of service exposed materials and limited laboratory pre-aged HP niobium modified and HP microalloyed material to gain a better understanding of the relations between microstructure versus creep response in both the as received and service aged conditions.

At the current time only limited work has been undertaken, but to illustrate the approach we use can consider alloys A and B, with creep responses shown in Figure 3 and Figure 4 respectively, and where more detailed investigation of the microstructure using optical, scanning electron and transmission electron microscopy techniques has been initiated. Table 1 gives the chemical composition of the investigated alloys.

Table 1. Material composition (wt%).

	C	Cr	Ni	Nb	Mn	Si	Ti	W
Alloy A*	0.34 0.35-	25.78	34.39	0.84	1.09	1.11	0.02	0.46**
Alloy B	0.4	23-28	33-38	N/A	1.0-1..5	1.0-2.0	+	+

OES,** XRF ,Balance: Fe

+For alloy B manufacturer's compositions provided. Ti and W are deliberate alloying additions, with undefined compositions

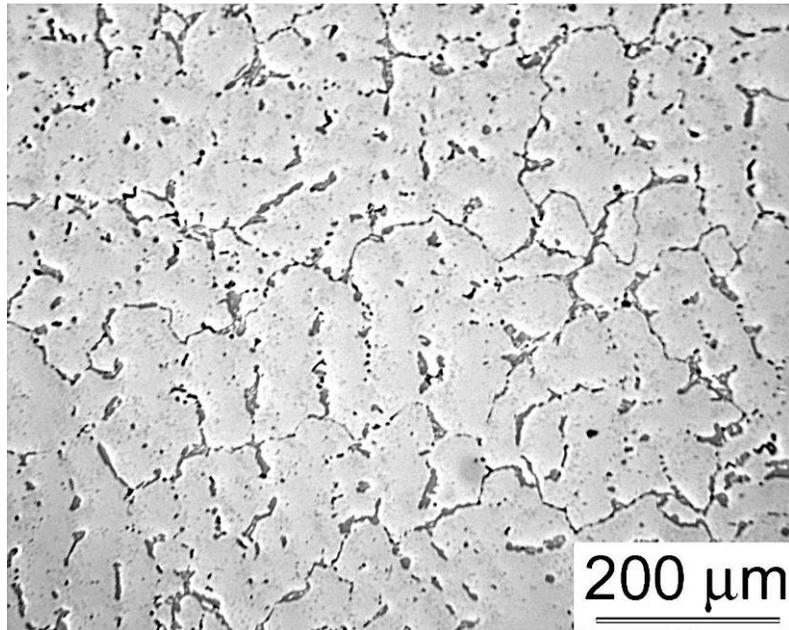
Figure 5 shows low magnification optical micrographs of the two alloys, both taken from the mid-wall location in the tube. Both alloys show the typical dendritic microstructure characteristic of these cast materials. In comparison, alloy B's microstructure has a smaller dendrite arm spacing, and the primary carbide network is much more continuous.

Higher magnification optical images in Figure 6 reveal several differences. In alloy B, the primary carbides are mainly chromium carbides. Cuboidal titanium carbides, revealed as the dark grey phase in Figure 6a, ranging in size from 3-8 microns are also present. However, the volume fraction of these titanium carbides in alloy B appears to be much less than the (NbTi)C precipitates (dark grey phase in Figure 6b) in the A alloy and they are less integral to the primary carbide network. Further the B alloy intragranular (secondary) precipitate population is strikingly more refined than in the A alloy.

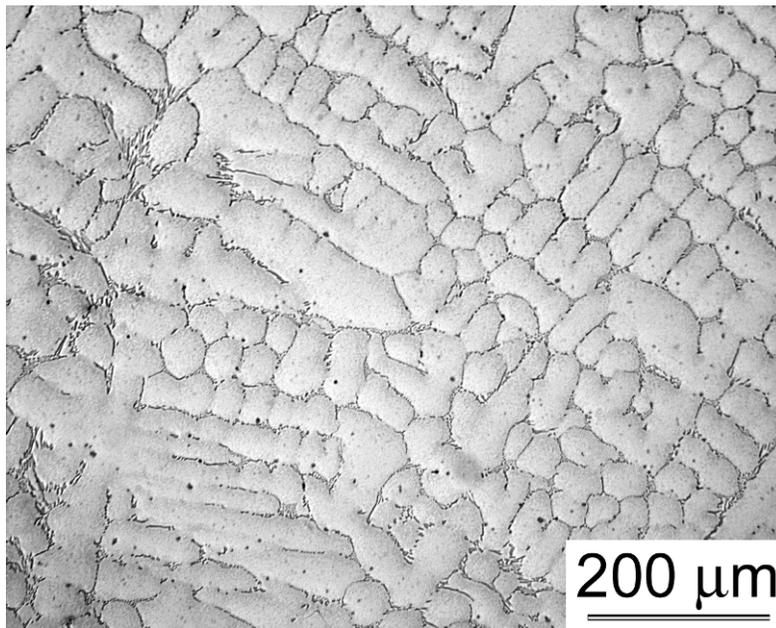
Figure 7 shows SEM micrographs of the alloys. The primary carbide network of the B alloy retains its original lamellar/acicular appearance, while the A alloy primary carbides are relatively coarse and blocky. The secondary precipitate distribution in the B alloy is significantly refined in comparison the higher ductility material as noted in the optical micrographs. The white phase in the A alloy is (Ti,Nb)C carbides.

Based upon the preliminary microstructural differences observed, the relatively low ductility of the B alloy is thought to be mainly due to the continuous, acicular/lamellar primary carbide network and the higher density of finely distributed carbides in the matrix which would render the matrix more resistant to shape change during creep. This more creep resistant matrix would impart large stresses at the interdendritic regions which may then be forced to deform locally to accommodate shape change, reducing overall macroscopic ductility.

Clearly these initial findings are only related to two specific examples, but the aim is to generate sufficient creep strain and microstructural information to allow categorisation of a typical range of alloys into subgroups for which suitable creep strain vs. life parameters can be derived. What is apparent from this work is that relatively minor changes in microstructure can impart significant differences in the alloy's ductility

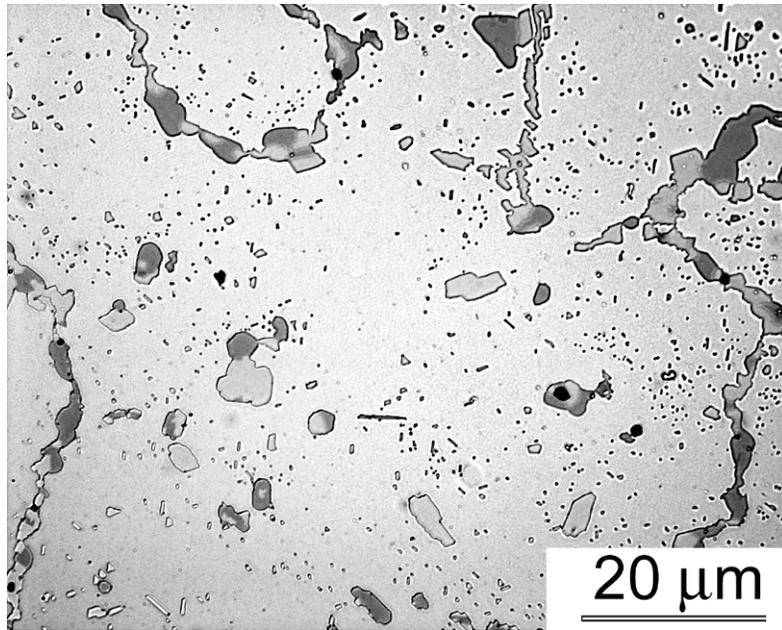


(a) Alloy A

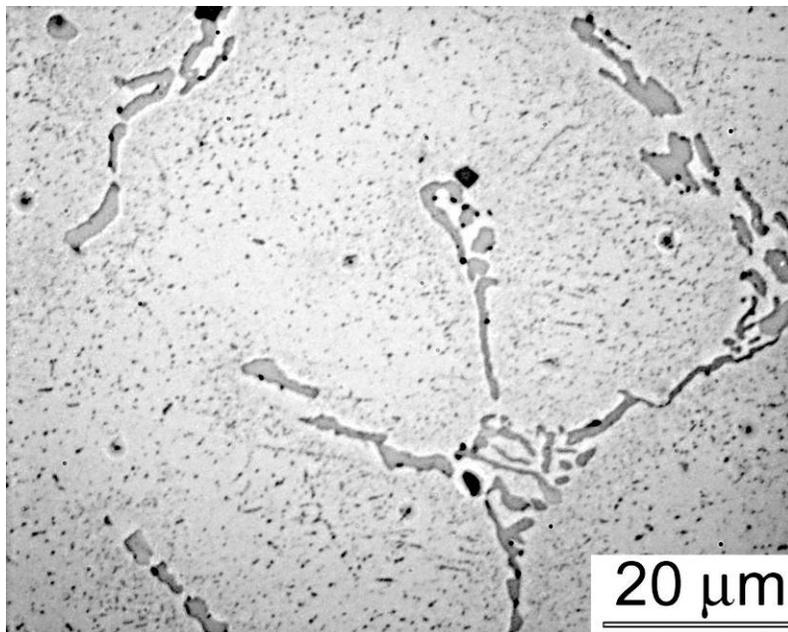


(b) Alloy B.

Figure 5. Optical micrographs. Etched with glyceresia, 100x original magnification.

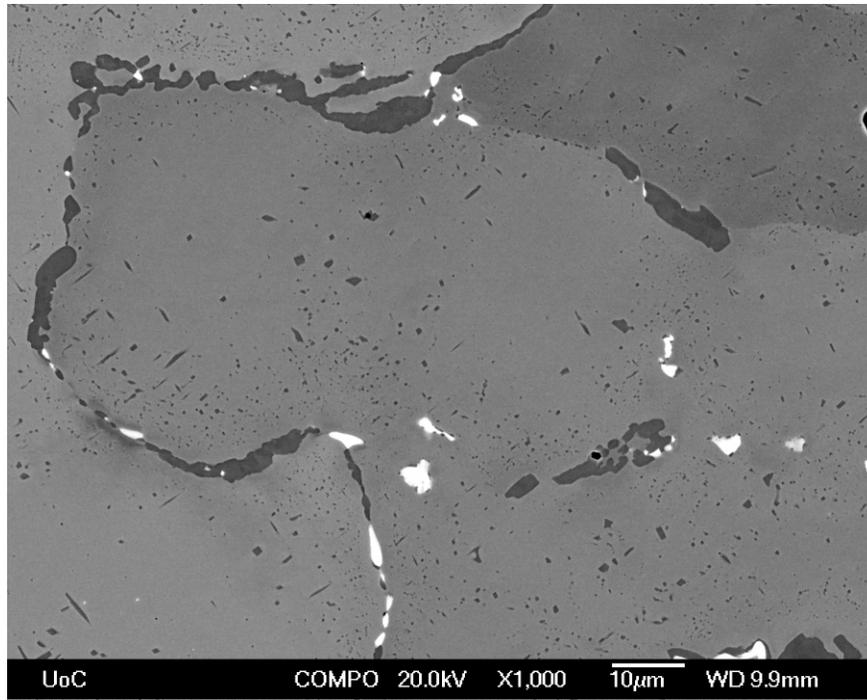


(a) Alloy A

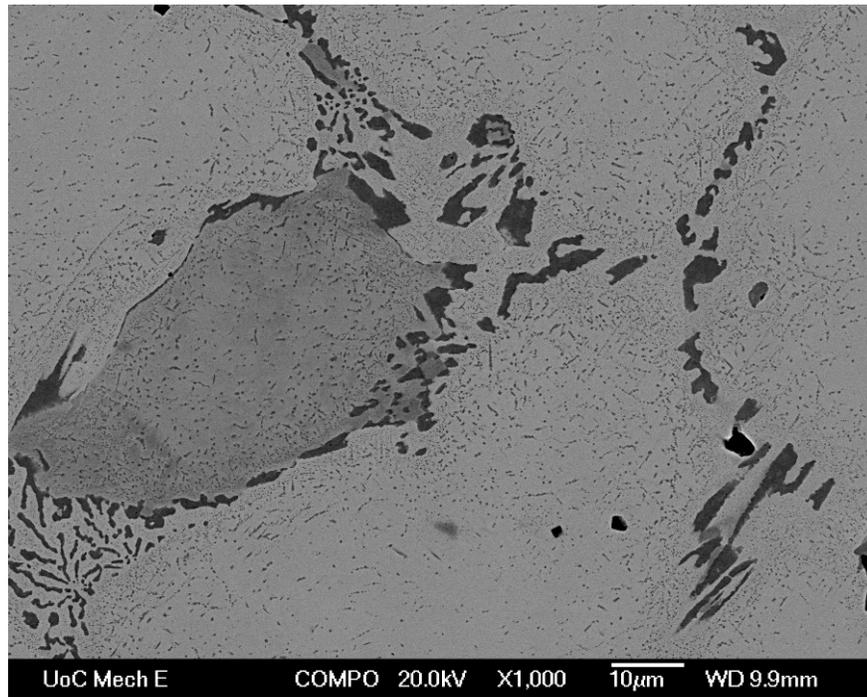


(b) Alloy B

Figure 6. Optical micrographs. Etched with glyceresia, 1000x original magnification.



(a) A alloy



(b) B alloy

Figure 7. Backscattered scanning electron images, as-polished.

5. Tube life management

The brief observations and comparisons of microstructure vs. creep strain response described above illustrate clearly the uncertainty that faces the current operator of such tubes. Without further information (which will arise from better understanding of the materials) a pragmatic approach to life assessment has to be adopted which combines the best features of a number of inspection and life assessment techniques. The combination of these will depend somewhat on the manner in which the furnace is operated. However for a typical hydrogen manufacturing unit the following could be considered as a measured approach to optimise reliability while avoiding unnecessary replacement.

1. The tubes should be base-lined by suitable inspection (particularly diametric growth) prior to first use—this is particularly recommended if regular external dimension profiling is to be undertaken. Careful consideration should be given to associating which tubes relate to individual heats at the foundry (recognising that elements such as Ti are added separately to each individual casting)
2. At a predefined (relatively low) strain, during a turn around inspection, the worst tube can be removed from service and undergo accelerated (strain based) creep testing. If necessary one tube from each heat of the furnace tube sets could be selected.
3. Based on the outcome of creep testing a remnant life estimate can be made, a refined creep strain/life model employed and an upper creep ductility defined (based on microstructure and creep results on the actual tube) which will allow much more accurate tube condition assessment.
4. Regular temperature measurement and strain monitoring (when allowable) continues
5. Tubes are finally removed at the recalculated strain (ideally supported by a second inspection method which can identify the later stages of creep damage)

The main advantage of this approach are that one can set lower bound expectations on tube performance, monitor the early stages of creep damage (using strain) and then, by sample removal, obtain an actual sample (s) of service exposed material (s) on which to base the expected creep strain and rupture ductility for the remaining tube set. Generally a single tube will, along its length, contain a range of material thermal exposure and strain, hence a comprehensive set of testing from different locations on a single tube could provide considerable information in relation to the condition of the remaining tube set in the furnace. A further refinement could be to split the tubes into individual heats for consideration if this is thought necessary. Of course accurate thermography throughout life is paramount to identifying anomalies in operation and significant temperature excursions that may modify the material microstructure.

Finally it should be remembered that short – term creep testing using methods such as Omega remain dependent upon applicability of the models to extrapolate from short-term testing to long-term life. Given the limitations and complexity required to address the role of microstructural aging it still remains necessary to ensure that representative databases to describe the behaviour of thermal aged cast alloys are available.

6. Conclusion

A short summary of available inspection techniques to monitor condition in steam methane reformers has been made. Owing to its ability to monitor the early stages of creep evolution strain measurement, in the form of diametric growth is seen as providing information that complements the other common techniques.

At the present time the lack of understanding in terms of the microstructure/creep property relation for this genre of cast alloys, where some low ductility failures are known to occur, precludes gaining the perceived value from accurate and regular strain measurement. A significant body of research is still required to address this shortfall, both in terms of microstructural understanding and in creep strain related data base generation (for a range of alloy aged conditions).

At the present time the most satisfactory approach to life management of a tube set is to use a combination of appropriate inspection techniques, accurate temperature measurement and sample removal and creep testing.

Acknowledgements.

The authors are grateful to Shell Global Solutions International for permission to publish this paper.

References

¹ P. Saunders, Radiation Thermometry, Fundamentals and Applications in the Petrochemical Industry, SPIE press.

² API STD 530, Calculation of Heater Tube Thickness in Petroleum Industries, American Petroleum Institute, Washington DC, 2004.

³ C. Thomas, The effect of Aging on the Strength of Reformer Tube Materials, 51st Annual Ammonia Safety Symposium, AIChE Technical Manual, vol 47 pp 35 to 45, 2006.

⁴ C.W.Thomas, A.J.Tack and N. Briggs , International Journal of Pressure Vessel and Piping, 70, pp 59-68 1997.

⁵ British Energy R5 code, Assessment procedure for the high temperature response of structures.

⁶ API Recommended Practice 579, Fitness For Service, American Petroleum Institute, Washington DC, 2000.

⁷ R.K. Penny and D. L. Marriott Design for Creep, Chapman and Hall, 2nd Edition 1995

⁸ E. Berghof-Hasselbacher, P Gawenda, M Schorr, M. Schutze and J. Hoffman, Atlas of Microstructures, Dechema, Materials Technology Institute.