Creep performance of carburized 316H stainless steel at 550 °C

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Abstract

The creep behaviour of two ex-service type 316H austenitic stainless steel casts with different Mn contents and austenite grain size, that were pre-carburized for either 8000 h at 550°C or 3000 h at 600°C in simulated CO₂-rich gas environment of UK Advanced Gas-cooled Reactors, was evaluated by uniaxial creep testing at 550°C in air. The low Mn (0.98 wt.%) steel grade with an average austenite grain size of 142±110 µm presents a higher creep deformation rate and creep ductility compared to the high Mn (1.52 wt.%) steel cast with an austenite grain size of 81±67µm. Below an applied stress of 318 MPa, the presence of the sub-surface carburized layer reduces the minimum creep rate, likely due to the significantly modified material properties of the carburized layer and the presence of local compressive stresses. The stress exponent determined for the high Mn steel carburized at 600 °C $(n=9.6)$, and its reference non-carburized microstructure $(n=9.8)$, identifies the dominant creep mechanism to be dislocation climb & glide. However, crack evolution through M₂₃C₆-decorated grain boundaries within the carburized layer was observed in all the tested material’s conditions at creep strains of 0.50%. The average crack length increases with creep strain and attains values close to the carburized layer thickness at creep strains of $\varepsilon \geq 1.00\%$. The prevalence and size of cracking increases with the local hardness carburized layer depth. At applied stresses $\sigma \geq 318$ MPa, cracking on-loading prior to forward creep already occurs in the carburized layer, leading to a sharp increase in minimum creep rates of carburized specimens. These results demonstrate the impact a relatively thin layer of modified material can have on the materials creep performance; emphasises the requirement to consider the effects of the service environment in structural assessment procedures, particularly for high temperature applications including Generation IV and advanced modular reactor designs.
Keywords: Austenitic stainless steel, Creep deformation, Creep cracking, Carburization, Advanced Gas-cooled Reactors

1 Introduction

A large number of structural and boiler components used in the UK’s Advanced Gas-cooled Reactors (AGRs) are made from austenitic stainless steel type 316H, due to its good water corrosion resistance and high-temperature creep strength [1]. The superheater and reheater sections typically operate at ~460-620 °C [2]. These sections are exposed to high purity water/steam in their internal surface and CO₂ primary gas-coolant on the external surface. The CO₂ from the reactor core is at typical pressures of 600 psi (i.e. 4.14 MPa) and contains minor additions of CO, CH₄, H₂O, and H₂, herein referred to as AGR primary gas coolant. The environmental degradation of these boiler components causes simultaneous external surface oxidation and sub-surface carburization, and those time-dependant (sub-)surface processes may impact creep ductility and crack initiation under creep and creep-fatigue conditions [2, 3]. Tolerance to creep deformation becomes a life limiting factor for some structural components in high-temperature nuclear power plants [4]. The effects of a carburized layer on 316H austenitic stainless steel has now been accounted for in the R5 assessment procedure [5], but is simplified and conservative. Such environmental effects are not explicitly accounted for within any international design codes. Therefore, understanding the impact of carburization on the creep behaviour of 316H steel is crucial, to aid both the accuracy and level of conservatism in assessments of component remnant life [2, 3] and design codes.

Experimental creep studies of non-carburized austenitic stainless steels are usually based on short-term tests under relatively high mechanical stresses and temperatures [6, 7]. Empirical equations describing the main creep deformation mechanisms are applied to the minimum
creep rates from those studies [8]. The creep behaviour at lower stress and temperature conditions that are more representative of steels operating in plant, can be evaluated by applying the constitutive equations and extrapolating the creep responses from the shorter creep tests [6, 7]. Inter- or intragranular diffusion creep is typically a dominant creep mechanism up to 90-100 MPa at 550 °C in austenitic stainless steels [9, 10]. At higher temperatures and/or stresses, dislocation glide & climb creep (i.e. power-law creep) is the main deformation mechanism [9-11]. A novel physical based deformation model has been proposed that incorporates the competing mechanisms responsible for the observed creep response [12]. The model has been applied to evaluate the change in creep properties with the evolution of the microstructural state of solution annealed 316H stainless steel [12]. Moreover, thermal ageing of plastically deformed specimens at 550 °C prior to creep testing induces carbide precipitation close to dislocation cores [13-16]. The number density, average particle size and spacing of intra-granular carbides, are reported to influence the high-temperature dislocation dynamics in austenitic stainless steels during creep [11]. Additionally, the creep ductility of 316 steel is also impacted by intergranular precipitation occurring during creep testing itself [17]. Higher creep ductility values are usually observed at shorter testing times; but the ductility reduces at lower stresses with longer testing times (that are generally of more relevance to components operating in plant). This is thought to be associated with the coarsening of intergranular carbides, thus reducing the average carbide spacing and providing effective stress concentration sites for local damage initiation [17].

Only a limited number of studies to date have examined the effect of a sub-surface carburized layer, that has developed beneath a duplex oxide layer, on the creep response of 316H steels. When 316H stainless steel specimens from only a single cast were exposed to an AGR primary gas coolant for 3000 h at 600 °C, their subsequent creep response at 550 °C and
stresses larger than 300 MPa, were characterised by higher minimum creep rates and reduced rupture times as compared to equivalent non-carburized material [2, 3, 18]. This creep behaviour in carburized specimens was attributed to grain boundary embrittlement and cracking throughout the carburized layer, and a consequential loss of load-bearing capacity [18]. Therefore, it is clear that despite these initial results from a single cast of 316H, the effect on the creep behaviour is not understood, when the material possesses small differences in both chemical composition and local microstructure in the carburized layer, as well as subjecting the material to lower and more relevant applied mechanical stresses.

In this work, we have assessed the crack development in two pre-carburized plant 316H steels and its correlation with the creep response of those materials up to 1.5 % creep strain at 550 °C.

2 Experimental

2.1 Pre-conditioning

Two ex-service 316H stainless steels were investigated in this study which possessed different chemical composition (see Table 1) and service histories. The main difference observed in composition was the Mn content. Thus, hereafter the steels will be labelled as ‘Low Mn’ (0.98 wt.% Mn) and ‘High Mn’ (1.52 wt.% Mn). The grain size was determined previously [19] using the linear line intercept method on Electron Backscattered Diffraction (EBSD) maps [20, 21]. Both the ‘Low Mn’ and ‘High Mn’ steels were in the form of pipes with a wall thickness of ~63 mm, which had been in AGR operation within the secondary coolant loop at ~525 °C for ~9×10⁴ h and 1×10⁵ h, respectively, but had not been exposed to AGR primary gas coolant. Uniaxial creep specimens possessing a parallel gauge length of 40 mm and a diameter of 7 mm, were extracted parallel to the longitudinal direction of the ‘as-received’ pipe materials (Fig. 1a). The gauge length of the specimens were mechanically
ground and polished to 0.25 μm colloidal silica surface finish (Fig. 1b) producing a deformation free surface with a surface roughness of 0.01 Ra ± 0.002 Ra [19]. After surface preparation, the creep specimens were inserted into an autoclave for pre-conditioning carburization at either 550 or 600 °C and a pressure of 600 psi (4.14 MPa), in simulated AGR primary gas coolant containing 500 vppm H₂O, 100 vppm H₂, 300 vppm CH₄, and 1 vol.% CO, balanced with CO₂. Additionally, mechanically ground and polished cylindrical bar coupons, were extracted from the same pipe materials and were placed alongside the creep specimens in the autoclave (Fig. 1c). These coupons were removed at selected time intervals, enabling the evaluation of surface oxide formation and the development of the sub-surface carburized layer which have been previously reported [19]. After either 3000 h at 600 °C or 8000 h at 550 °C, the ‘pre-conditioned’ ‘Low Mn’ and ‘High Mn’ creep specimens from were removed from the autoclave and tested mechanically (Fig. 2a-d).

2.2 Tensile & Creep testing

The mechanical properties of the pre-conditioned specimens were evaluated by tensile and creep testing. However, the focus of this work relates to the understanding of creep behaviour and thus the tensile properties have been included as comparative data where relevant. The tensile properties were obtained using a strain rate of 0.004%/s following BS EN ISO 6892-2:2011 [22] on a Zwick screw driven test frame. Uniaxial creep testing was carried out in accordance with BS EN ISO 204:2009 [23] on a standard deadweight beam-loaded test frame. The force on both tensile and creep test frames were calibrated to BS EN ISO 7500-2 [24]. The specimen temperature was measured continuously for the duration of the tensile and creep tests using three calibrated Nicrosil/Nisil (Type N) thermocouples attached to the top, middle, and bottom of the specimen gauge length. All creep and tensile tests were performed at a temperature of 550 ± 3 °C. For creep tests, a high-
temperature drop-leg extensometer was affixed to specimen knife-edge ridges (Fig. 3a) and the
displacement was recorded throughout the creep test using two transducers positioned outside
the furnace. The extensometer and displacement transducers were calibrated to Class 1.0 of
BS EN 9513:2002 [25]. Prior to heating up the creep specimen on the test rig to 550 °C, the
extensometry and transducers were checked by comparing the measured and expected room-
temperature Young’s modulus of both as-received and pre-conditioned creep steel specimens.
Once verified, the creep specimen was heated up to 550 °C in air using a three-zone tubular
furnace, and held at that temperature for 1 h to ensure temperature uniformity and stability.
Following this, the creep specimen was mechanically loaded (hot-loading) to reach the target
ingenring stress of between 200-270 MPa.

For pre-conditioned specimens, the surface duplex oxide layer readily spalls and cracks
easily during, or shortly after, hot loading to the applied test stress. Therefore, it is expected
that from an early stage during creep testing the oxide regions are not load-bearing [18, 26].
Thus, to determine the applied stress, the load-bearing cross-sectional area of the specimens
was assumed to not include the surface oxide layer [19, 26, 27]. A total of 25 creep specimens
were tested to a target engineering creep strain in the range of 0.00-1.50%. Once the creep test
reached the target engineering creep strain, 20% of the applied stress was removed whilst at
550 °C, and subsequently the specimen was cooled down to room temperature before the
remaining load was removed.

The minimum creep strain rate of creep tests that have entered the secondary creep
regime is often regarded as representative of the material’s creep behaviour [10, 11, 28]. The
relationship between the minimum creep rate ($\dot{\epsilon}_c$) and the applied stress ($\sigma$) at a constant
temperature can be represented by the Norton power-law relationship [28]:
\[ \dot{\epsilon}_c = A\sigma^n \]  

where \( A \) is a constant and \( n \) denotes the stress exponent. The latter, along with the minimum creep rates, have been determined using both experimental data from this work and from the literature for this same material (see Table 4).

Post-mortem stereographic images were taken of all creep specimens using an Olympus SZX9 microscope (Fig. 3b-e). After this, the middle gauge length section of the specimen was removed by wire electrical discharge machining (Fig. 3f), mechanically ground, and polished to 0.25 \( \mu \)m colloidal silica surface finish before being examined using an optical BX51M microscope and a FEI Quanta 200 scanning electron microscope. The mean crack depth in each specimen was determined by averaging all measured cracks across two representative sections of the gauge length totalling 20 mm. Additionally, the maximum crack depth observed across the whole specimen gauge length was recorded and compared to the average carburized layer depth.

### 3 Results

#### 3.1 Material pre-conditioning

The main parameters that characterise the as-received microstructure of both steels are shown in Table 2 together with the average thickness of the surface oxide and sub-surface carburized layers, as well as the bulk and peak surface hardness after pre-conditioning summarised from [19]. The carburized depth was characterised using nano hardness and defined as the location in the microstructure where the local hardness value is at 120\% of the bulk hardness [19]. The two materials present an equiaxed austenite grain structure in the as-received condition, with ‘Low Mn’ steel having a larger average grain size of 142 ± 110 \( \mu \)m compared to 81 ± 67 \( \mu \)m for the ‘High Mn’ steel. The coincident site lattice (CSL) boundary
type $\Sigma^3$ accounted for $> 50\%$ of all grain boundaries in both materials. The number density and average area fraction of the inter- and intragranular inclusions ($> 1 \mu m$), measured by large-area optical microscopy, were estimated to be 43 per mm$^2$ and 0.13$\%$ respectively for both materials [19].

Representative cross-sectional optical images of the pre-conditioned microstructures prior to creep testing are presented in Fig. 2e-h. During pre-conditioning, a duplex surface oxide layer developed on both materials at both 550 and 600 $^\circ$C. This duplex oxide comprises an outer magnetite (Fe$_3$O$_4$) layer, and an inner spinel (MCr$_3$O$_4$) layer where M = Ni, Cr [2, 3, 19]. Beneath the duplex oxide, a carburized layer develops during pre-conditioning, where the excess carbon mainly precipitates as inter and intra-granular Cr-rich M$_{23}$C$_6$ carbides [19]. A heavily carburized region is observed directly beneath the duplex oxide layer in both materials pre-conditioned at 600 $^\circ$C (Fig. 2f & h). In contrast, the etched micrographs do not clearly reveal a similar carburized layer for the microstructures pre-conditioned at 550 $^\circ$C. However, the previously reported nano-hardness results indicate a local increase in hardness due to the presence of a less heavily carburized layer [19]. The grain boundaries within the carburized layers in all cases showed a greater degree of carbide decoration than the bulk microstructure when chemically etched. This is due to the preferential carbide formation at grain boundaries during pre-conditioning.

3.2 Mechanical response upon tensile loading

The strain-on-loading behaviour at 550 $^\circ$C prior to forward creep deformation for all specimens of this study is presented in Fig. 4, alongside the conventional tensile behaviour of the as-received and the preconditioned 3000 h 600 $^\circ$C microstructures of each steel. The representative mechanical parameters are collected in Table 3. The 550 $^\circ$C tensile response of the as-received ‘Low Mn’ and ‘High Mn’ steels are shown in Fig. 5a and appear to be
equivalent within the experimental uncertainty up to 280 MPa and 5\% plastic strain. Furthermore, the values of Young’s modulus ($E$) and 0.2\% proof stress ($R_{p0.2}$) are presented in Table 2. As can be seen in Table 2, similar values for both materials were observed, producing average values of $E = 144$ GPa and $R_{p0.2} = 185$ MPa.

When the materials were subjected to the two carburization pre-conditions, there did not appear to be a significant effect of the developed oxide/carburized surface layer thickness on Young’s modulus for both steels (Table 3). The average experimental values for each pre-conditioning gave a range of between $E = 135-141$ GPa and this compared well with the as-received properties previously described. However, there was a noticeable change in the 0.2\% proof stress of the material as a result of carburization pre-conditioning. Pre-conditioning for 8000 h at 550 °C leads to an average proof stress of $R_{p0.2} = 174$ MPa (‘Low Mn’) and $R_{p0.2} = 175$ MPa (‘High Mn’), whereas the average value in both materials after pre-conditioning for 3000 h at 600 °C is $R_{p0.2} = 208$ MPa. This increase in proof stress correlates with the higher values of surface layer thickness and surface hardness after the 600 °C pre-conditioning when compared to 550 °C (see Table 2).

Fig. 6 shows the cross-sectional view of two ‘High Mn’ specimens pre-conditioned for 3000 h at 600 °C, that were loaded up to a stress of $\sigma = 260$ and 320 MPa respectively at 550 °C, and then immediately unloaded after reaching target stress (to ensure no forward creep occurred) and cooled down to room temperature. These results reveal that upon loading up to a stress of $\sigma = 260$ MPa and prior to creep testing, there was cracking in the duplex oxide layer. Significantly more cracking and spallation of the outermost spinel oxide layer was observed when the specimen is loaded up to the higher stress of $\sigma = 320$ MPa. In contrast, no cracking was observed within the sub-surface carburized layer up to a stress of $\sigma = 260$ MPa prior to
forward creep deformation, whilst cracking was detected when loaded up to the higher stress of $\sigma = 320$ MPa (Fig. 6e).

For specimens which had been exposed to forward creep, an average of 48 cracks was observed across each specimen from both ‘Low Mn’ and High Mn’ materials with a minimum of 5 cracks observed in the ‘High Mn’ specimen pre-conditioned for 3000 h at 600 $^\circ$C and tested at the lowest stress of $\sigma = 200$ MPa. Apart from that specimen, the minimum number of cracks measured from the remaining specimens from both materials in the region of interest was 23.

3.3 Creep behaviour

The two ‘as-received’ materials present significant differences in their creep behaviour, with ‘Low Mn’ steel having a higher creep deformation rate and creep ductility compared to ‘High Mn’ steel, see Fig. 5b at 550 $^\circ$C under an applied stress of $\sigma = 280$ MPa.

When considering the effect of the sub-surface carburized layer on creep behaviour, the creep strain response for ‘Low Mn’ and ‘High Mn’ steels in the 8000 h at 550 $^\circ$C and 3000 h at 600 $^\circ$C conditions performed at 200, 220, 240, 260 MPa and 550 $^\circ$C are presented in Fig. 7, together with the creep response for two ‘High Mn’ as-received creep specimens performed at the same temperature and 240 MPa for comparison. When considering the creep deformation behaviour when a stress of $\sigma = 220$ MPa is applied, there is some variability in the creep responses for ‘Low Mn’ for both carburizing pre-conditions (Fig. 7b). This compares to limited variability in the creep strain response of ‘Low Mn’ steel between the 8000 h at 550 $^\circ$C or 3000 h at 600 $^\circ$C pre-conditioned surfaces performed at $\sigma = 240$ MPa (Fig. 7ed). However, for ‘High Mn’ steel, the two carburized conditions and the as-received microstructure, at an applied stress of $\sigma = 240$ MPa, present differing creep deformation behaviour (Fig. 7ed).
Within the primary creep regime, there is a significant increase in creep rate following the 3000 h at 600 °C pre-conditioning and a much greater level of creep strain can be observed, when compared with the ‘as-received’ material (Fig. 7de). When evaluating the 8000 h at 550 °C condition, there is a clear reduction in primary creep rate and level of strain attained, in comparison with both the 3000 h at 600 °C condition and as-received material. At this applied stress and at longer test durations when steady-state creep deformation is reached, the creep rates for the 3000 h 600 °C and 8000 h at 550 °C conditions were similar and were much lower than the as-received material.

The variation of the measured minimum creep strain rate with applied stress is presented in Fig. 8. For this study, specimens were interrupted prior to failure and the minimum creep rates have been obtained from those creep responses that had achieved steady-state creep. The minimum creep rates from this work have been evaluated alongside the minimum creep rates determined from ‘High Mn’ specimens taken to full separation that were reported elsewhere in [18, 27, 29]. The stress exponent, \( n \), was determined by performing a data fit to the behaviour described by eq. (1) for ‘High Mn’ steel only in both the as-received and the 3000 h 600 °C conditions. For ‘Low Mn’ steel, the creep deformation behaviour to the target creep strains in this study was such that a steady-state creep rate was only achieved at an applied stress of 220 MPa as presented in Fig. 8. The minimum creep rate data for the ‘High Mn’ steel, showed a sharp increase at a stress of \( \sigma = 318 \) MPa. Below that critical stress, the data fit yields a value of \( n \sim 9.6 \), which is similar to the \( n \) value of \( \sim 9.8 \) for the as-received material. A step change in minimum creep rate is observed at 318 MPa and as such, only the top data point at 318 MPa was chosen to derive the stress exponent value for applied stresses above 318 MPa. With the single data point at \( \sigma = 318 \) MPa, a value of \( n \sim 5.8 \) was obtained at stress levels \( \sigma > 318 \) MPa. Alternatively, a stress exponent can be obtained from all 6 data points at applied stresses.
\( \sigma > 318 \text{ MPa} \) which is presented in Fig. S1. However, the stress range covered at stress levels \( \sigma > 318 \text{ MPa} \) is limited to tests up to 340 MPa, with significant scatter observed, so the \( n \) values are not reliable.

Representative un-etched cross-sectional optical images of pre-conditioned ‘Low Mn’ steel prior to mechanical testing and at increasing creep strain levels for an applied stress of \( \sigma = 220 \text{ MPa} \) are presented in Fig. 9. The occurrence of cracks can be observed in the carburized layer of specimens tested to 0.50% creep strain and increase in length on average when tested to a higher creep strain. Additionally, cracking is more severe on specimens pre-conditioned for 3000 h at 600 °C, as compared to those in the 8000 h at 550 °C condition. Similar behaviour is also observed in ‘High Mn’ steel with intergranular cracking increasing in length at higher creep strains. The parameters describing the crack development for all interrupted creep specimens are collated in Table 3. The mean crack depth as a function of creep strain for both steel grades and pre-conditioning parameters is shown in Fig. 10. There is an overall increasing trend in mean crack depth with creep strain for both materials in both pre-conditions. In ‘Low Mn’ steel pre-conditioned for 8000 h at 550 °C, the mean crack depth remains below the average carburized layer thickness, whereas in the 3000 h at 600 °C condition, the mean crack depth attains values close to the mean carburized layer thickness at creep strains of \( \geq 1.00\% \). In contrast, in ‘High Mn’ steel after 8000 h at 550 °C pre-conditioning, the mean crack depth is already close to the average carburized depth after 0.50% creep strain but show relatively little variation with creep strain.

Furthermore, there is also a clear increasing trend in maximum crack depth with creep strain, see Fig. 11. In most cases, a creep strain of only 0.50% suffices to induce a maximum crack size close to, or even larger than the average carburized layer thickness. In addition to
this, the relation between mean crack depth and carburized depth was also examined in Fig. 12, for both materials and pre-conditioned states at four increasing creep strain levels. At creep strains of 0.75 % or below, the average crack depth values were observed to be below the mean carburized depth. However, as creep deformation proceeded to creep strains of 1.00 % and above, the average crack depth reached values close or above the mean carburized depth.

4 Discussion

4.1 Pre-conditioned microstructure

The presence of surface duplex oxide and sub-subsurface carburized layers was observed on both materials when exposed to simulated AGR primary gas coolant at either 550 or 600 °C. After pre-conditioning for 8000 h at 550 °C, both materials present similar oxidation kinetics with the average duplex oxide depth measured to be 56 µm and 53 µm for ‘Low Mn’ and ‘High Mn’ steels, respectively. In contrast, the development of the carburized layer was slower for ‘High Mn’ steel with an average carburized depth of 34 µm as compared to 73 µm for ‘Low Mn’ steel (Fig 1) [19]. The slower carburization kinetics of ‘High Mn’ steel at 550 °C was recently attributed to the enhanced stability of the prior Mn-containing chromia layer in ‘High Mn’ steel, and the consequent delay in the ingress of carbon-containing species [19]. The oxidation and carburization kinetics were accelerated in both materials when pre-conditioning at 600 °C compared to 550 °C. After pre-conditioning for 3000 h at 600 °C, the averaged duplex oxide and carburized depths for ‘Low Mn’ steel were measured to be 105 µm and 144 µm, and for ‘High Mn’ steel to be 110 µm and 138 µm. The local (sub-surface) carbon excess precipitates as inter- and intragranular M23C6 carbides in the austenite matrix.

The presence of carbides increases the material hardness in those carburized regions to $H_{\text{peak}} \sim 6.2$ GPa and $H_{\text{peak}} \sim 5.6$ GPa for ‘Low Mn’ and ‘High Mn’ steels respectively after pre-conditioning for 8000 h at 550 °C, with respect to the reference value in the non-carburized
bulk structure for that pre-condition of $H_{\text{bulk}} \sim 3.1$ GPa. The hardness increases are more severe when pre-conditioning for 3000 h at 600 °C, namely $H_{\text{peak}} \sim 8.2$ and $H_{\text{peak}} \sim 7.9$ GPa for ‘Low Mn’ and ‘High Mn’ steels respectively compared to the non-carburized bulk for that pre-condition of $H_{\text{bulk}} \sim 3.5$ GPa [19]. This is consistent with the metallurgical examination of a heavily carburized region in both materials pre-conditioned at 600 °C, but less noticeable after pre-conditioning at 550 °C, see Fig. 2e-h.

The development of duplex oxide and carburized layers occurs after the spallation of a thin chromium film (Cr$_2$O$_3$) that initially protects the steel from further corrosive attack. The formation of this film is controlled by the availability of Cr at the surface. Through repeated spallation and re-passivation of the film due local stresses, thermal cycling, creep or fatigue, the local surface Cr concentration can decrease [30]. Therefore, alloy composition and local surface properties can influence the formation of the chromia film. Compared to polished deformation free surfaces, strained or work hardened surfaces can provide a greater density of high-diffusivity pathways through which Cr can migrate to the surface facilitating the re-passivation of the chromia film [31]. The increased availability of Cr at the surface maintains the ability of the chromia film to protect the underlying metal for increased durations and thus delaying the development of duplex oxide and carburized layers.

4.2 Mechanical behaviour upon loading

In the as-received condition, the two materials show relatively small variations in the tensile behaviour at 550 °C up to 280 MPa (Fig. 5a). Specimens pre-conditioned at 550 °C behave similarly to the as-received specimens under applied tensile deformation at that temperature (Fig. 4), despite the pre-existence of the duplex oxide and especially the sub-surface carburized layer. In contrast, those specimens pre-conditioned at 600 °C for both
materials present a significant increase in 0.2% proof stress at 550 °C (i.e. $R_{p0.2} = 208$ MPa see Table 3), as compared to the value of the as-received material of $R_{p0.2} = 185$ MPa (Table 2), and thereafter a somewhat lower work-hardening rate. This correlates with the fact that carburization is more severe in the 3000 h at 600 °C condition compared to the 8000 h at 550 °C condition, and with the carburized layer being deeper and having a higher surface hardness for both materials pre-conditioned at 600 °C (Table 2). In order to represent this observation, a schematic is presented in Fig. 13, showing the effect of the pre-conditioning at both temperatures on the thickness ($t_c$) of the outer carburized layer of specimens; furthermore, this effect on both the tensile and creep properties of the material in comparison with the as-received material is shown schematically. The tensile properties of mainly the carburized layer have been recently determined by mechanical testing of ‘hollowed’ cylindrical ‘High Mn’ steel specimens pre-conditioned for 3000 h at 600 °C [26]. The hollowing of specimens, enabled the reduction in the volume ratio of bulk material to carburized material and this testing determined the 0.2% proof stress of only the carburized layer to be $R_{p0.2} = 516$ MPa at 550 °C. The increase in 0.2% proof stress of the carburized material compared to the bulk as-received microstructure of 185 MPa shows the 0.2% proof stress is larger with increasing volume of carburized material. This suggests that the subsurface formation of carbides during pre-conditioning, effectively hinders the dislocation motion in plastic flow during monotonic tensile loading.

4.3 Creep performance

When considering creep performance, the two ‘as-received’ materials present vastly different creep deformation rates (Fig. 5b). ‘Low Mn’ steel is the softest of the two materials with a higher creep deformation rate, and creep ductility that is four times larger than in the case of ‘High Mn’ steel.
The pronounced primary creep rate observed in ‘High Mn’ material pre-conditioned for 3000 h at 600 °C (Fig. 13) has been suggested to be as a result of the increase in tensile strength [3]. This increase is solely because of the significantly modified carburized layer microstructure with the inner non-carburized bulk possessing similar tensile properties to the as-received material. Therefore, on loading the inner non-carburized bulk does not attain its usual strain level and has additional work-hardening capacity. Consequently, stress redistribution within the carburized layer combines with the additional work-hardening capacity of the inner non-carburized bulk, leading to an increase in primary creep rate. When evaluating the ‘High Mn’ in the 8000 h at 550 °C condition, the tensile strength is similar to the as-received material and the resultant creep deformation does not present a pronounced primary creep rate, as compared to the 3000 h at 600 °C condition (Fig. 13). This is consistent with the tensile and creep deformation behaviours being influenced by the interactions of load/stress between the carburized layer and inner non-carburized bulk microstructures.

The value of the stress exponent provides an indication to the dominant deformation mechanism operating during creep [28]. A stress exponent of \( n \approx 1.0 \) usually indicates diffusion creep to be the principal mechanism, whereas dislocation glide & climb is suggested to be the dominant mechanism when the stress exponent is \( n \approx 3-7 \) [32]. A higher stress exponent of \( n \approx 9.8 \) obtained for ‘High Mn’ steel in the as-received condition still points to dislocation glide & climb as being the primary creep deformation mechanism. This result is consistent with other creep testing performed at ~550 °C and similar applied stresses on non-carburized 316 stainless steels [27, 33-35].

The minimum creep rates with the applied stress range of 200 - 318 MPa for ‘High Mn’ steel after pre-conditioning for 3000 h at 600 °C, yields a value for the stress exponent of \( n \approx 9.6 \). This correlates closely with the value of \( n \approx 9.8 \) obtained for the as-received ‘High Mn’
material. This similarity implies that the presence of the carburized layer does not alter the 
dominant creep deformation mechanism of dislocation glide & climb. However, the values of 
the minimum creep rates in the ‘High Mn’ steel are consistently lower for the pre-conditioned 
material as compared to the as-received steel. This difference suggests that the thin sub-surface 
carburized layer possesses a higher creep resistance than the non-carburized bulk structure. 
Thus, with the addition of this carburized layer to the bulk material as a consequence of pre-
conditioning, this material synergy results in an overall impact to global creep behaviour, by 
reducing the rate of deformation. The reduction in creep rate of carburized material can be 
attributed to the presence of carbides which precipitated during pre-conditioning, significantly 
modifying the local material properties, including increasing the material strength and the 
materials resistance to creep deformation. Additionally, it is worth mentioning that near-surface 
carburization due to pre-conditioning would induce compressive residual stresses, beneficial 
for the creep resistance of the material, as a consequence of carbon ingress and subsequent 
carbide precipitation [36].

The minimum creep rate behaviour shown in Fig. 8 for the pre-conditioned ‘High Mn’ 
material, clearly shows a sharp increase in minimum creep rate at an applied stress of 
$\sigma = 318$ MPa. The results from previous works in this higher-stress region, revealed that crack 
formation occurred in the carburized layer upon loading to the desired test stress [26, 27]. Such 
cracking phenomenon reduces the load-bearing area of the material and consequently increases 
the stress in the remaining material. This ultimately leads to an increase in the measured creep 
rate for that particular engineering stress and a reduction in the time to failure compared to the 
as-received material condition [18].

Long term exposure of austenitic stainless steels at high temperature service temperature 
such as those in AGRs can have a detrimental influence on the materials creep resistance [17,
It has been shown the creep rates of thermally aged specimens to be faster than comparative solution annealed specimens [37]. Moreover, the creep ductility reduces when testing at lower stresses with longer testing durations, when compared to shorter tests conducted at higher stresses [17]. The decline in creep properties has been suggested to occur as a result of the recovery the dislocation structure and coarsening of the second phases including ferrite and \( \text{M}_{23}\text{C}_6 \) [38]. The formation of second phases promotes the nucleation of creep cavities due to the higher local stresses on the phase boundaries [39, 40]. The creep cavities eventually coalesce to form micro-cracks reducing the load bearing area leading to failure [6]. A study previously investigated the thermal ageing effect from pre-conditioning for 3000 h at 600 °C and showed no change in creep properties [29].

Even though cracking beyond the oxide layer was not observed upon loading the specimens to the target stress in the lower stress region of this experimental study, namely \( \sigma \leq 260 \) MPa, inter-granular cracking within the carburized layer was detected on all creep strained pre-conditioned specimens. The mean and maximum crack sizes for each tested specimen are collected in Fig. 10 & 11, respectively. The cracking data show a clear increase in crack depth with the creep strain for both materials and pre-conditions. Deeper cracks were observed on specimens that were on test for the longest duration and which had attained the higher creep strains, i.e. the average and maximum observed crack depth was observed to be 11% and 13% deeper respectively in ‘Low Mn’ steel under an applied load of \( \sigma = 220 \) MPa, when compared to specimens under a higher applied stress of \( \sigma = 240 \) MPa. At 240 MPa, the creep deformation behaviour of ‘Low Mn’ steel was such that the target creep strains were reached eight times faster than when applying the lower stress of \( \sigma = 220 \) MPa. Similarly, the average and maximum observed crack depth was observed to be 21% and 57% deeper respectively, in ‘High Mn’ steel (\( t = 19118 \) h) compared to ‘Low Mn’ steel (\( t = 1674 \) h), when
testing the same pre-condition, applied stress of $\sigma = 240$ MPa and the same level of creep strain attained at 1.50%. The lower minimum creep rate and creep ductility in the ‘High Mn’ steel compared to the ‘Low Mn’ steel observed in the as-received conditions (Fig. 5b) may contribute to the increased severity of cracking at longer testing durations. Additionally, specimens with a deeper carburized layer and higher surface hardness, i.e. pre-conditioned for 3000 h at 600 °C, were found to present cracking to a greater depth. In plant conditions, open voids such as surface cracks may provide pathways through which carbon may migrate into the bulk microstructure and therefore enhance carburization in those regions [41]. The relationship between the mean crack depth and carburized layer depth is presented in Fig. 12 and shows at creep strains $\geq 1.00\%$ the average crack depth reached values close to the carburized depth, as defined as the location in the microstructure where the local hardness value is at 120% of the bulk hardness. However, a relatively small creep strain of 0.50% suffices to generate cracks to a length similar in magnitude to the average carburized thickness in most tested microstructures. This implies that cracking in pre-carburized steels is significant in the early stages of creep deformation and, despite not altering the main creep deformation mechanisms during secondary creep, their associated impact on the material’s creep performance needs to be incorporated in current creep deformation models and structural assessment procedures of 316H steels in AGR-relevant environments. This shows the significance a relatively thin layer of modified material can have on the creep response. Therefore, creep-environmental interaction must be a consideration for high temperature applications, including future Generation IV and advanced modular reactors systems, which may utilise other gaseous environments, liquid metals or molten salts as primary coolants.
5 Conclusions

We have assessed the creep behaviour at 550 °C of two ex-service type 316H stainless steels that were previously exposed at either 550 °C and 600 °C to simulated CO₂ primary gas-coolant of AGRs, so as to induce different degrees of surface oxidation and sub-surface carburization. Creep of both as-received and carburized specimens occurs primarily via a dislocation glide & climb creep mechanism. However, at applied stresses $\sigma \geq 318$ MPa, cracks are already detected in the carburized layer upon loading to the target stress and prior to forward creep. Consequently, the load-bearing area of the carburized creep specimens is reduced, leading to an increase in the minimum creep rates. At lower stress levels, the minimum creep rate in the carburized specimens was reduced when compared to the as-received materials. This is likely due to the significantly modified material properties of the carburized layer in comparison to the bulk and potentially from the presence of sub-surface compressive stresses generated during carburization. A significant population of subsurface cracks form and propagate through carburized grain boundaries with increasing creep strain. A creep strain of 0.50 % generates a number of cracks as deep as the average carburized layer depth in the tested materials and pre-conditioning states. The average crack length reaches values close to or above the average carburized layer at strains $\geq 1.00$ % in all creep tested specimens. These results show the need to consider creep-environmental interactions in structural assessment procedures for other high temperature applications.

Acknowledgments

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References


Tables

Table 1. Chemical composition (wt.%) of the two 316H stainless steels under investigation.

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Table 2. The history of the 316H stainless steels prior to pre-conditioning. This includes the in-service temperature and time, average grain size, <d>, and standard deviation of the size distribution (StdDev) and frequency of grain boundary types in the austenite matrix, together with the Youngs’s modulus (E) and 0.2% proof stress (R_p0.2), and the pre-conditioning parameters, i.e. measured oxide thickness (t_o), carburized depth (t_c), the bulk surface hardness (H_{bulk}) and peak surface hardness observed within the carburized layer (H_{peak}), for the two carburized conditions of each material. The threshold in misorientation angle from low-angle grain boundary (LAGB) to high-angle grain boundary (HAGB) was taken to be 15°.

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* Test still running
Table 4 Minimum creep rate of the as-received and pre-conditioned microstructures of both 316H stainless steels.

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**Figure captions**

**Fig. 1.** (a) Schematic showing the location from which the coupons and the creep specimens were extracted along the longitudinal direction of the pipe. Polished coupons and (b) creep specimens were inserted into an autoclave (c) where they were pre-conditioned in simulated AGR gas environments (see main text).

**Fig. 2.** (a) – (d) Pre-conditioned creep specimens prior to being creep tested and (e) – (h) illustrative optical images of the pre-conditioned cross-section of the specimens after etching with 10 vol.% Marbles Reagent for ~20 seconds. The cross-section shows the duplex oxide layer and the inner carburized layer produced upon pre-conditioning and prior to creep testing.

**Fig. 3.** (a) Representative creep specimen mounted in the mechanical testing rig, before being loaded to the target applied stress and then interrupted at a range of creep strains; (b) – (e) shows images of ‘Low Mn’ creep specimens tested at 220 MPa with the white arrow denoting the direction of applied stress. (f) After being interrupted, creep specimens were microstructurally examined by removing the middle gauge length section by wire-EDM.

**Fig. 4.** The engineering strain-on-loading response of Low Mn steel and High Mn steel after preconditioning for either 8000 h at 550 °C or 3000 h at 600 °C, presented alongside the tensile response of ‘High Mn’ steel in the as-received and 3000 h at 600 °C conditions. All mechanical tests were performed at 550 °C.

**Fig. 5.** (a) Tensile response of both materials in the as-received condition at 550 °C; together with (b) their creep response to failure at the same temperature and at an applied stress of 280 MPa.
Fig. 6. Illustrative SEM and optical images of 'High Mn' steel pre-conditioned for 3000 h at 600 °C and then (a) – (d) loaded up to 260 MPa (this work), and (e) loaded up to 320 MPa (adapted from ref. [27]) at 550 °C, and subsequently unloaded before creep testing and cooled down to room temperature. The cross-sectional images reveal the presence of cracking in the surface duplex oxide layer across both conditions, whereas cracking in the sub-surface carburized layer was only observed after loading up to 320 MPa.

Fig. 7. Creep strain response of the as-received and pre-conditioned specimens that were tested at 550 °C under an applied engineering stress of $\sigma = 200, 220, 240$ or 260 MPa. These were interrupted at either 0.19, 0.50, 0.75, 1.00, and 1.50 % engineering creep strain, as detailed in Table 3, apart from one specimen in (a) which is still on test as indicated by the arrow and one specimen in the as-received condition in (e) which was taken to failure.

Fig. 8. Variation of the minimum creep strain rate with the applied stress, and also the values of the stress exponent, ‘$n$’, obtained from the data fitting in the region of stresses < 318 MPa (see text). The open symbols correspond to creep tests that were interrupted before reaching the specimen failure. Includes data from previous studies (see Table 4).

Fig. 9. Illustrative un-etched cross-sectional optical images of ‘Low Mn’ steel, with a prior pre-conditioning at either 550 °C for 8000 h or at 600 °C for 3000 h, as a function of engineering creep strain at 550 °C under an applied stress of $\sigma = 220$ MPa. The cross sectional view of the specimens evidence the occurrence of sub-surface cracking as creep strain increases during the test.

Fig. 10. Mean crack depth as a function of engineering creep strain for both steels and pre-conditioning parameters. The standard deviation of the mean crack depth is ~ 50 % of the
calculated value (see Table 3). The dash horizontal line indicates the mean carburized layer thickness prior to creep testing.

**Fig. 11.** Maximum crack depth as a function of *engineering* creep strain for both steels and pre-conditioning parameters. The dash horizontal line indicates the mean carburized layer thickness prior to creep testing.

**Fig. 12.** Mean crack size vs. carburized depth at four increasing *engineering* creep strain levels. The graphs contain data from both steels and pre-conditioning conditions. The dash line denotes mean crack depth values equal to the carburized depth.

**Fig. 13.** Schematic showing the effect of the thickness of the outer carburized layer of specimens on mechanical properties from pre-conditioning (a) for 8000 h at 550 °C; and (b) for 3000 h at 600 °C compared to the as-received condition for ‘High Mn’ steel.
Fig. 1.
Fig. 2.
Fig. 3.
This figure has been replaced to include on the X-axis Engineering Strain and to define in the legend that the triangles are Strain-on-loading increments.
Fig. 5.

This figure has been replaced to include on the axes Engineering Creep Strain and Engineering Stress.
This figure has been replaced to increase the size of the red and orange text “Oxide cracks”.
Fig. 7.
This figure has been replaced to include on the Y-axis Engineering Creep Strain and re-format to make it clearer to follow as per reviewer 2’s comment 4.
This figure has been replaced to include on the X-axis Engineering Stress and include the min creep rate of Low Mn at 280 MPa.
Fig. 9.
This figure has been replaced to include on the X-axis Engineering Creep Strain.
Fig. 11.

This figure has been replaced to include on the X-axis Engineering Creep Strain.
Fig. 12.
Fig. 13. Schematic showing the effect of the thickness of the outer carburized layer of specimens on mechanical properties from pre-conditioning (a) for 8000 h at 550 °C; and (b) for 3000 h at 600 °C compared to the as-received condition for ‘High Mn’ steel.

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