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The Role of Grain Boundary Ferrite Evolution and Thermal Aging on Creep Cavitation of Type 316H Austenitic Stainless Steel

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Abstract

To understand the interaction between microstructural evolution and creep cavitation during stress relaxation at an elevated temperature, an ex-service AISI type 316H stainless steel sample containing both weld metal and heat affected zone (HAZ) from an advanced gas-cooled reactor was studied. Multiple techniques that include secondary electron microscopy, electron backscatter diffraction (EBSD), transmission electron microscopy (TEM) and plasma focused ion beam tomograph were used for microstructure and creep cavities characterisation. Although no creep cavities were observed in the weld metal, the HAZ was extensively creep cavitated. At randomly oriented grain boundaries, creep cavities are present and closely linked with $M_{23}C_6$ and ferrite precipitates formed during thermal aging. Less precipitation (e.g. absence of ferrite) and less creep cavitation were observed at $\Sigma 3$ coincidence

site lattice boundaries. During in-service aging, at random grain boundaries, $M_{23}C_6$ formation and growth cause the local elemental depletion of γ stabilisers and promote a phase transformation from austenite to ferrite. The crystallographic relationship between ferrite and austenite were also studied by EBSD and TEM. Ferrite precipitates formed during aging often grow into the austenite grain not expected by traditional nucleation and growth theory, likely due to physical constraints by the existing carbides at the grain boundaries. The formation and growth of creep cavities is closely associated with the $M_{23}C_6$ and ferrite formed on grain boundaries. This study highlights the importance of considering the effect of thermal aging in accelerating creep cavitation.

Keywords: creep, thermal effects, ferrite, austenitic stainless steels, orientation relationship

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1 Introduction

Austenitic stainless steels are widely used for components operated at a high temperature such as advanced gas cooled nuclear reactors (AGRs) due to their excellent mechanical properties and creep resistance. However, at elevated operating temperatures, creep cavitation can occur in areas of high stresses such as heat affected zones (HAZ) in the thick-walled boiler header [1,2]. Intergranular

creep cavities can nucleate, grow and coalesce during service, leading to cracking in the HAZ. This is driven by the relaxation of residual stresses in the weldment [1], together with the effect of reduced creep ductility in the HAZ at operating conditions [2–4] and the triaxial stress state arising from the weld geometry [5]. However, there is also a link between creep cavitation and local microstructure [2,6], which is complicated by the fact that the microstructure can evolve during service due to thermal aging effects [2,7]. Understanding the relationship between stresses, local microstructure and cavitation is essential to develop a mechanistic understanding of creep cavity nucleation in these materials. Some commonly reported precipitates in ex-service type 316H stainless steel are carbide precipitates (e.g. $M_{23}C_6$), ferrite precipitates and a low volume fraction of G phase [2,6].

It is well known that $M_{23}C_6$ carbides are normally the first precipitates to form during aging of austenitic stainless steel [8–11] due to carbon supersaturation in austenite [11]. It has been reported that a cube-on-cube orientation relationship (OR) is present between $M_{23}C_6$ and neighbouring austenite grains [12–14]. By developing local stress concentrations at grain boundaries [15,16], intergranular $M_{23}C_6$ precipitates have been shown to act as nucleation sites for creep cavitation [16–18].

In austenitic stainless steel, due to non-equilibrium solidification, δ -ferrite can be retained [19,20]. Hong et al [21] reported the effect of δ -ferrite on creep cavitation in 304L stainless steel, claiming that cavities nucleate at the δ -ferrite and austenite interface by local decohesion. However, ferrite can also be formed during thermal aging. The nucleation and growth of ferrite in service is associated with local

chemical variation introduced by $M_{23}C_6$ precipitation [7] and by dissolution of initial $M_{23}C_6$ precipitates [9,10]. Warren et al [6] reported that over 50% of creep cavities investigated in an ex-service type 316H stainless steel were closely linked with δ -ferrite and ferrite formed during aging. However, it remains unclear whether the cavities or the in-service formed ferrite nucleate first [2].

Ferrite phase has a body-centred-cubic (bcc) crystal structure and exhibits some specific low-energy ORs with face-centred-cubic (fcc) austenite [22–24]. These ORs normally lie within 11° of a Bain OR [25], e.g. Kurdjumov-Sachs (KS) and Nishiyama-Wassermann (NW) ORs [26–28]. A hypothesis by Smith [29] suggested that grain boundary precipitates should exhibit a low-energy OR with one of the neighbouring matrix grains and an irrational OR with the other grain, and the precipitates should grow into the matrix grain with which an irrational OR is present due to a higher mobility of an incoherent interface than a coherent interface. This was supported by Ryder et al [25] in studying ferrite precipitates in a Co – 20% Fe alloy. However, a kinetics study of grain boundary ferrite nucleation in Fe – C alloys indicated that a feasible critical nuclei should be made up predominantly by coherent interphase interfaces [30]. It was therefore suggested that grain boundary allotriomorphs should maintain as coherent a boundary as possible with both neighbouring matrix grains during nucleation [31–33]. Understanding the orientation relationship of ferrite formed during thermal aging with the surrounding austenite can give insight to the ferrite formation mechanism, as well as the link to cavity formation during creep.

In this paper, the relationship between the creep cavitation behaviour and grain boundary characteristics, such as secondary phase precipitation and boundary misorientations, is studied in detail in an ex-service austenitic stainless steel specimen extracted from an AGR boiler header. The microstructure is compared between the weld metal and HAZ of the specimen. The microstructural evolution in HAZ during in-service exposure to temperature and stress is described to provide a link between creep cavities and the morphology, orientation and distribution of carbide and ferrite precipitates at the grain boundaries. The implications of these results for the combined effect of thermal aging and creep cavitation, are discussed in Section 4.

2 Material and experimental methods

2.1 Material and sample preparation

The material investigated in this work was an AISI type 316H stainless steel with a chemistry composition as shown in Table 1. A triangular prism sample was cut from a boiler header of an ex-service AGR as shown in Fig. 1a. The header operated at a temperature in the range of 490 °C to 530 °C for 65,000 hours. The triangular prism sample was sectioned into five small pieces to study and compare the microstructure at different locations (see Fig. 1b). Both weld metal and HAZ microstructures were observed in the sectioned specimen, with reheat cracking observed in the HAZ below the fusion boundary.

For conventional 2D characterisation techniques Secondary Electron (SE) image, Focused Ion Beam (FIB) and Electron Backscatter Diffraction (EBSD), the specimens were mechanically ground using silicon carbide papers followed by polishing with diamond paste to a surface finish of 0.25 μm . The specimens were finally vibro-polished in colloidal silica for 10 hours. Transmission electron microscopy (TEM) foils were prepared using a FEI Helios NanoLab 600i Dualbeam station. The foils were milled perpendicular to the austenite grain boundaries and thinned at a voltage of 30 kV with a reduced beam current from 21 nA to 0.28 nA to give a final thickness of less than 100 nm. A low energy polish at a voltage of 5 kV and beam current of 0.15 nA was used to remove the ion beam damage on the foil surfaces. The FIB images were obtained by the FEI Helios NanoLab 600i Dualbeam station after etching the sample surface with XeF_2 gas. As reported by Liu et al [34], the carbide precipitates will become darker after XeF_2 etching as a result of the difference in work function between the carbide and the metal. The FIB XeF_2 etched image can be used to highlight carbide precipitates and study their distribution.

To study the microstructural evolution and creep cavitation of the ex-service sample, the microstructure of the as-received parent metal was examined, as shown in Fig. 2. The EBSD phase map in Fig. 2a shows that the matrix is austenite and there is no ferrite present within the austenite grains and at grain boundaries. The FIB XeF_2 etched image in Fig. 2b indicates the presence of carbide precipitates at the grain boundaries (where the precipitates were highlighted in dark contrast).

Table 1: The chemistry composition of the investigated ex-service AISI type 316H stainless steel
(mass %)

C	Si	Mn	P	S	Cr	Mo	Ni	B	Co	Fe
0.060	0.400	1.980	0.021	0.014	17.170	2.190	11.830	0.005	0.100	66.230

Fig. 1. (a) Image showing the ex-service AGR boiler header component and the triangular prism sample cut from the component as indicated by the black dashed triangle. (b) The triangular prism sample was then sectioned into five pieces as marked in black dashed lines.

Fig. 2. The microstructure of the original parent 316H stainless steel sample. (a) EBSD phase map of a region in the original sample showing no ferrite at the austenite grains and grain boundaries. (b) FIB XeF₂ etched image where carbide precipitates are highlighted in dark contrast at the austenite grain boundaries.

2.2 EBSD maps and analysis

EBSD scanning was performed in a Zeiss SigmaHD FEG-SEM (field-emission gun) equipped with an EBSD detector (DigiView 3) and data was collected by the orientation imaging microscopy (OIM) software (Ametek, Utah, USA). All the EBSD acquisitions were undertaken at a stage tilt of 70° and accelerating voltage of 30 kV to maximise the signal to noise ratio. To identify the orientation of bcc ferrite at the fcc austenite grain boundaries a step size between 0.02 to 0.05 μm was used, while for the largest EBSD scanning for statistics of austenite-austenite grain boundary

misorientation the step size was 0.8 μm . The EBSD data sets were analysed using the software TSL OIM Analysis and MTEX toolbox (developed by Bachmann et al [35]). Data pixels with a confidence index (CI) smaller than 0.1 were removed. These low CI data points can be identified incorrectly in their orientations and phase structures. The OR of ferrite and austenite was determined by selecting a pixel in the centre of the ferrite and a pixel in the austenite at a position near to the ferrite to generate an axis/angle pair to represent the fcc-bcc phase boundary misorientation. The mismatch of an experimentally found OR with KS, NW and Bain OR were calculated respectively and compared (a detailed calculation approach can be found in Appendix A).

2.3 (S)TEM image and diffraction

The scanning transmission electron micrograph (STEM) images were taken in a JEOL 2100F STEM equipped with a field-emission gun operating at an accelerating voltage of 200 kV; the phase chemistry was measured in the same instrument coupled with an energy-dispersive X-ray (EDX) detector. A JEOL JEM-2100 TEM operating at 200kV voltage with a LaB_6 source and a CCD camera was used to perform the TEM bright-field and in-centre dark-field imaging. The selected area electron diffraction patterns (SAED) were recorded with a Orius diffraction camera to identify the ferrite and carbide phase, and to determine the OR between the carbide precipitates and austenite. The SAED patterns were filtered by a Median filter to remove the noise in the background without changing the diffraction spots.

2.4 X-ray Tomography (XRT)

A matchstick XRT sample was cut from the HAZ by electrical discharge machining (EDM) giving a final dimension of approximately 6 mm in length and 0.5 mm in diameter. The sample was then scanned using a Zeiss Xradia 520 Versa X-ray microscope operated at a source voltage of 110 kV with a voxel size of 0.38 μm . The scanning contained a total of 1932 projections with a long exposure time of 25 s to increase the signal to noise ratio.

2.5 Plasma FIB (PFIB) cross-sectioning

A FEI HELIOS PFIB coupled with an Oxford EDX detector was used to cross section a region in the HAZ by Xe^+ ion milling. A 60X faster milling rate of Xe^+ PFIB than conventional Ga^+ ions milling enables a larger sectioning and 3D reconstruction volume with a high resolution [36]. This is particularly important and useful for characterisation, establishing distribution and statistical analysis of small features such as intergranular creep cavities. The ion milling was conducted at a voltage of 30 kV and current of 59 nA to achieve a fast sectioning rate whilst minimising the surface damage. A rocking mill was set to an angle of 5° to reduce the curtaining on the milled surface. A total of 236 serial slices with the slice thickness of 300 nm were obtained, and the SEM image for each slice was collected together with EDX map simultaneously. The SEM image was recorded at 25 kV voltage and 22 nA current with an image resolution of 4096×3536 , and the pixel size in the XY plane of the

sample surface was given 24 nm × 31 nm after the projection correction in the Y direction. The detailed approaches for data processing and 3D reconstruction for the PFIB and XRT data can be found in Appendix A.

3 Results

3.1 Overall microstructure

The triangular prism sample shown in Fig. 1 contains weld metal and the HAZ. Fig. 3a-Fig. 3d show the microstructure of the weld metal and the HAZ. In the HAZ the austenite grain boundaries were creep cavitated (Fig. 3a and Fig. 3b) and these intergranular discontinuous creep cavities had an irregular shape (see the sub-figure in Fig. 3b). In addition, some rod-like inclusions identified by EDX to be manganese sulphide (MnS) were present in the HAZ (as shown in the sub-figures in Fig. 3a).

The weld metal shows a different microstructure as shown in Fig. 3c and Fig. 3d. No inter-granular creep cavities were observed in the weld metal. Compared to the rod-like MnS inclusions in the HAZ, the weld metal contained many spherical inclusions, which EDX (see the sub-figures in Fig. 3d) indicates are likely to be manganese silicates. Fig. 4a is a schematic diagram showing the relation and arrangement of the weld metal, HAZ and parent of the ex-service sample, with Fig. 4b showing cracking observed at the HAZ close to the fusion zone.

Fig. 3. (a) and (b) microstructure of the HAZ showing inclusions and intergranular creep cavities. The sub-figures in (a) show the elemental maps of manganese and sulphur of a rod-shaped inclusion in HAZ. The sub-figure in (b) shows the morphology of creep cavities where the grain boundaries were highlighted in white dashed lines; (c) and (d) microstructure of weld metal showing inclusions and absence of grain-boundary cavities. The sub-figures in (d) were the elemental maps of manganese and silicon of spherical-shaped inclusions in the weld metal.

Fig. 4. (a) a schematic diagram shows the weld metal, reheat-cracking, HAZ and the parent of the ex-service sample; (b) SEM secondary electron image shows the cracking at the HAZ.

3.2 Heat-affected zone

The EBSD Inverse Pole Figure (IPF) map of a region in the HAZ is shown in Fig. 5 where the crystallographic orientation of each austenite grain is shown in different colour. The grain boundary misorientation was gained based on the orientation of neighbouring grains. Random grain boundaries are shown in blue lines. In this paper, the random grain boundaries are defined as the grain boundaries with Σ values larger than 49 and/or deviations from the exact coincidence larger than $\Delta\theta_m$, where $\Delta\theta_m = 15^\circ \Sigma^{-1/2}$ (Brandon criterion described in [37]). The frequency of coincidence site lattice (CSL) boundaries with different Σ values (see Fig. B.1 in Appendix B) was

calculated based on the misorientation of each Σ value listed in [38], where different misorientations with the same Σ value were combined together, e.g. 49a, 49b and 49c. A total fraction of 40% were identified to be $\Sigma 3$ CSL boundaries (i.e. a rotation of 60 degrees around $\langle 111 \rangle$ direction) as shown in black lines in Fig. 5, while $\Sigma 5$ to $\Sigma 49$ occupied a total of 10% of grain boundary (red lines). After merging these $\Sigma 3$ CSL boundaries within the austenite grains, the average grain diameter in the HAZ was determined to be around 150 μm .

Fig. 5. EBSD IPF map of HAZ shows crystallographic orientation of each grain and grain boundaries. The random grain boundaries are highlighted in blue while $\Sigma 3$ CSL boundaries are shown in black and $\Sigma 5$ - $\Sigma 49$ in red.

3.2.1 3D reconstruction

Fig. 6a-Fig. 6g shows a typical SEM frame of the HAZ obtained by plasma FIB cross sectioning and the corresponding elemental maps. There are three features to be noted, namely (i) inclusions, (ii) voids linked with clusters of precipitates and (iii) intergranular creep cavities. The rod-like inclusion in Fig. 6b to Fig. 6g is enriched in Mn and S but depleted in other alloy elements (i.e. Cr, Fe, Ni), corresponding with manganese sulphide. The second feature is a cluster of precipitates in the centre of the image. EDX elemental maps show that the composition of the region is chromium dominated and contains manganese but is depleted in iron and nickel. Such regions have been reported by Warren et al [39] as chromium-enriched regions retained during fabrication, which contain multiple precipitates (e.g. ferrite and $M_{23}C_6$). Voids are present within these precipitate cluster regions and at the interface between the cluster region and matrix. There are Mn and S signals from inside the larger voids, suggesting that manganese sulphide inclusions have promoted the growth of voids under stress. To distinguish voids in these precipitate cluster regions from those in the HAZ at grain boundaries, we define the damage at the austenite grain boundaries as cavities. The EDX maps (see Fig. 6b and 6c) show that the austenite grain boundaries are chromium enriched and iron depleted, which results from the presence of carbide precipitates at the grain boundaries.

Fig. 6h shows the 3D reconstructed tomography of these three features, namely inclusions, intergranular cavities, and voids linked with the precipitate cluster region, based on the PFIB cross-sectioning slices. The voids within the precipitate cluster

region marked in blue have irregular shapes, and their size varies significantly. By comparison, the grain boundary creep cavities are distributed along the curved grain boundaries with relatively even spacing. In addition, the intergranular cavities have irregular geometries and a more even size variation.

Fig. 6. Plasma FIB cross sectioning. (a) a typical SEM slice of the cross sectioning. (b)-(g) EDX maps showing the elemental compositions of this slice. (h) 3D reconstruction of the inclusions, intergranular creep cavities and voids linked with precipitates cluster region based on the cross-sectioning slices.

The statistics of the inclusions (based on XRT), voids linked with the precipitates cluster regions and intergranular creep cavities (based on Plasma FIB) is compared and shown in Fig. 7. Due to their irregular shapes, the equivalent spherical diameter was used to quantify their average size, as shown in Fig. 7a. The equivalent mean diameter of inclusions in the HAZ is 7.5 μm , much larger than voids and cavities. The mean size of voids and cavities of 0.67 and 0.64 μm respectively are similar to each other, but their size distributions are different (see Fig. 7b). The size range of the intergranular cavities is relatively narrow, with over 65 percent of cavities within this cross sectioned volume in the HAZ being 0.5-0.9 μm in diameter. The absence of large creep cavities (i.e. larger than 1.3 μm in diameter) may indicate that the growth of intergranular cavities could be constrained by the austenite grains, where only the grain boundary itself is a favourable growth path. Conversely, the sizes of voids linked with the precipitates cluster regions were shown to vary considerably - most of these voids are smaller than 0.5 μm in diameter and these smaller voids were distributed at the interface of the cluster region and austenite grain. However, large voids (i.e. over 1.3 μm diameter) are also observed within the cluster regions.

Fig. 7. (a) comparisons of equivalent mean diameter of inclusions, voids linked with precipitates cluster region and intergranular creep cavities. (b) comparisons of size distributions of voids and cavities.

3.2.2 Characterisation of precipitates

Fig. 8 shows FIB XeF₂ images of three regions in the HAZ containing austenite grain boundaries. In the original parent sample, only carbide precipitates were observed at the austenite grain boundary. The grain boundary in the ex-service material contains a number of additional features not present in the original parent sample. Several features with different contrast were present at the grain boundary in the HAZ after in-service aging: black contrast cavities, dark contrast carbide precipitates and bright contrast precipitate features. Smaller, dark contrast intra-granular carbide precipitates were also observed. In Fig. 8c, a $\Sigma 3$ CSL boundary is highlighted by the white dashed line. Only carbide precipitates were observed at this $\Sigma 3$ boundary and the carbide precipitates had a plate-shaped morphology compared to an irregular

shape on random grain boundaries. On random grain boundaries, the bright contrast features were seen to grow into the austenite on either side, and the cavities are closely linked with both these bright precipitates features and the grain boundary carbide precipitates.

To further identify and study these features, STEM EDX and TEM diffraction were performed, as shown in Fig. 9. A TEM thin foil was lifted out by FIB from an austenite grain boundary and the STEM dark-field image is shown in Fig. 9a. EDX maps of the same region are shown in Fig. 9b-Fig. 9h. The grain boundary carbide precipitates marked by black arrows in Fig. 9a are enriched in chromium, manganese, molybdenum and carbon but depleted in nickel and iron, consistent with $M_{23}C_6$ carbide precipitates as reported in [2,11,17]. In addition, the intra-granular precipitates with well-defined geometries indicated by white arrows have a similar chemical composition as the grain boundary carbide precipitates. As shown in the FIB XeF_2 images (see Fig. 8), bright contrast features at the grain boundaries were observed to grow into the adjacent austenite grains. These can be seen in Fig. 9a, namely α_1 and α_2 . The $[01\bar{2}]$ SAED pattern of α_1 is shown in Fig. 9i, from which a bcc crystal structure with a lattice parameter of 2.93 Å was identified, corresponding to ferrite. The ferrite is enriched in iron but depleted in other alloy elements such as chromium, nickel, and manganese (see Fig. 9b-Fig. 9h), and $M_{23}C_6$ carbide is present at the ferrite-austenite interface. It is interesting to note the presence of a creep cavity linked with the ferrite and $M_{23}C_6$ at the grain boundary and growing into the austenite that opposes the ferrite. At the edge of the cavity and at the ferrite-

austenite interface, silicon enriched precipitates are present which are also enriched in nickel and molybdenum. The silicon enriched precipitates are consistent with phases reported and identified by Slater et al [40], Warren et al [39] and Burnett et al [2] to be G phase. In addition, there are higher concentrations of nickel and depletion of chromium at the austenite grain boundaries.

Fig. 8. (a), (b) and (c) FIB XeF₂ etched images showing cavities, highlighted grain boundary precipitates and intra-granular precipitates in HAZ.

Fig. 9. Austenite grain boundary and austenite grain by STEM and TEM. (a) STEM dark-field (DF) image showing cavity, ferrite, silicon-enriched precipitates, grain boundary $M_{23}C_6$ and intra-granular $M_{23}C_6$. The two ferrite precipitates were marked as α_1 and α_2 respectively. Black arrows indicate grain boundary $M_{23}C_6$ while white arrow indicates intra-granular $M_{23}C_6$. The silicon-enriched precipitates were marked by red arrow and the austenite grain boundary was highlighted by the white dashed line. (b)-(h) EDX elemental maps of the same region showing the chemical composition of these phases and the grain boundary chemical segregation. (i) TEM $[01\bar{2}]$ zone pattern of α_1 .

Although the chemical compositions of both the grain boundary and intra-granular carbide precipitates suggest they were $M_{23}C_6$, this was further confirmed by TEM diffraction. Two grain boundary carbide precipitates in another similar ex-service sample were identified to be $M_{23}C_6$ based on their crystal structure and lattice parameter (approximately 10.70 $\text{\AA}$).

Fig. 10a shows a bright-field (BF) image of the intra-granular carbide precipitates distributed within the austenite grain with faceted geometries, and a mean size of 0.07 μm . Two zone-axis SAED patterns of the austenite (i.e. $[\bar{1}12]$ and $[001]$ zone-axis patterns) are shown in Fig. 10c and Fig. 10d. The superlattice reflections (e.g. $\frac{1}{3}(220)_\gamma$, $\frac{1}{3}(311)_\gamma$, etc.) are indicated by the white rectangles. The $\frac{1}{3}(220)_\gamma$ superlattice reflection as indicated in Fig. 10d by the white circle were used to generate the in-centre dark-field image, as shown in Fig. 10b where the intra-granular carbides were shown in bright contrast confirming that these superlattice reflections were from these intra-granular carbide precipitates with three times larger d-spacings than the austenite matrix. Simulated diffraction patterns corresponding to the two zone axis are shown in Fig. 10e and Fig. 10f respectively, where the black spots are from austenite and red spots from Cr_{23}C_6 . From the patterns, the lattice parameter of the carbide precipitates was determined to be approximately 10.77 Å which corresponds with M_{23}C_6 type carbide. It is also clear that a cube-on-cube OR is present between the intragranular M_{23}C_6 and austenite, which is consistent with [11,13]. The cube-on-cube OR explains the well-defined arrangements and faceted geometries of the carbides in the TEM BF image.

A total of 3945 intragranular carbides and 130 grain boundary carbides were examined by FIB XeF_2 etching to study their size distribution, as shown in Fig. 11. The size of the intragranular M_{23}C_6 (see Fig. 11a) vary significantly from 0.02 to 0.35 μm , and most intra-granular M_{23}C_6 have a diameter of 0.10 - 0.13 μm , while the mean size is 0.11 μm with a standard deviation of around 0.05 μm . Although the

morphologies of the grain boundary $M_{23}C_6$ vary at different misoriented grain boundaries, they tend to be continuous at the grain boundaries with the longest axis nearly parallel to the boundaries. The lengths of the longest axis of the carbide precipitates were therefore used to estimate their size distribution (see Fig. 11b). The majority of the grain boundary $M_{23}C_6$ have a length of approximately 0.50 μm . The mean length is 0.63 μm with a standard deviation of around 0.43 μm , whereas the mean width is approximately 0.25 μm with a standard deviation of 0.11 μm .

Fig. 10. (a) TEM bright-field image showing intra-granular $M_{23}C_6$. (b) In-centre dark-field image from (220) reflection of the $M_{23}C_6$. (c) and (d) correspond to $[\bar{1}12]$ and $[001]$ zone-axis SAED patterns of the austenite showing superlattice reflections from the intra-granular $M_{23}C_6$, where the bigger and brighter spots are from the austenite matrix as indicated in larger rectangles, while the smaller and darker spots are from the $M_{23}C_6$ as indicated in smaller rectangles. The white circle in the zone $[001]$

pattern indicates the superlattice reflection used to generate the dark-field image. (e) and (f) are the simulated SAED patterns for the superimposed zone axis $\bar{1}\bar{1}2$ and $[001]$ respectively, where the black dots indicate the diffraction pattern expected for the austenite while red dots indicate the expected pattern for Cr_{23}C_6 .

Fig. 11. The size distribution of (a) the intra-granular M_{23}C_6 and (b) the grain boundary M_{23}C_6 in the HAZ by XeF_2 FIB etching.

3.2.3 Ferrite characterisation

In Fig. 9a, the two allotriomorphic ferrite precipitates (α_1 and α_2) grow into the same austenite grain with a nearly parallel growth direction. The OR of the ferrite with the parent austenite was investigated by EBSD. Fig. 12 show the EBSD image quality combined with ferrite phase maps as well as orientation maps of both austenite and ferrite in the HAZ. The austenite grain boundaries and creep cavities (marked by blue arrows) were shown in black due to a lower Kikuchi pattern quality. Fig. 12a-

Fig. 12c reveals that the allotriomorphic ferrite (in green) can grow into either side of the austenite grain or distribute at the grain boundaries with no clear growth direction. Although creep cavitation on random grain boundaries is extensive in this specimen, no ferrite or cavities were observed at the coherent $\Sigma 3$ CSL boundaries, as illustrated in Fig. 12b and Fig. 12c. However it is interesting to note the presence of a cavity (black circle marked in Fig. 12b) at the junction of the $\Sigma 3$ boundary and the random grain boundary.

Fig. 12d-Fig. 12f show the orientation maps corresponding to the same regions in the HAZ as in Fig. 12a-Fig. 12c. Since there is no meaningful mechanical reference (e.g. rolling and transverse direction, etc.) for the ex-service sample, the orientation maps here represent the orientation of the ferrite and austenite with respect to the reference of the sample frame direction. It is clear that some ferrite precipitates at the same austenite grain boundary can exhibit a near-parallel crystallographic orientation with one another (as marked in black arrows in Fig. 12d and Fig. 12f, where the ferrite show similar IPF colours). Ferrite with similar orientation at the same grain boundary can grow into the austenite either side of the grain boundary. Although often ferrites growing into one side of the boundary share a similar orientation, this is not always the case, such as in Fig. 12d where α_1 and α_2 have different orientations to other ferrite at the boundary.

However, when a change in ferrite orientation occurs, a carbide precipitate is typically present between the ferrite precipitates which had different orientations. Fig. 12a and Fig. 12d show the EBSD scans that correspond to the same area as in the

FIB XeF_2 etched image in Fig. 8a, showing that the bright contrast features previously observed at the grain boundary growing into austenite grain on the FIB image correspond to these ferrite precipitates in the EBSD. By comparing the EBSD orientation map with the FIB etched image, it is of interest to note the presence of a carbide precipitate in between two ferrite precipitates which have a small orientation deviation with each other, e.g. α_1 and α_2 in Fig. 12d have a misorientation of 4° where a carbide precipitate is present at the boundary between the two ferrite (see Fig. 8a).

Fig. 12. Grain boundary and ferrite characterisation by EBSD. (a)-(c) EBSD image quality adding ferrite phase maps where the green colour ferrite, and black colour cavities (indicated in blue arrows) can be seen at the austenite matrix grain boundaries. (d)-(f) EBSD orientation maps showing the orientation of austenite and ferrite of the same region that corresponds to (a)-(c). The black arrows indicate those ferrites showing an example of near-parallel crystallographic orientation between them.

The ORs between the ferrite and austenite grains were examined for total of 50 ferrite precipitates, which generated 105 misorientations (i.e. rotation matrix) with neighbouring austenite grains. Each ferrite generated two misorientation data sets with both neighbouring austenite grains, with the exception of five ferrite precipitates which were in a triple junction contacting with three austenite grains. The 105 misorientation data sets are shown in Fig. 13a by projecting the {001} plane normal of ferrite onto the {111} of austenite together with the simulated exact bcc-fcc ORs (i.e. Bain, NW, KS) [28,41]. The three Bain clusters which are equivalent in crystallography due to the 3-fold symmetry around $\langle 111 \rangle$ of austenite can be seen and the experimental misorientations were noted to distribute surrounding and outside the Bain clusters. The detailed examination indicates that except one ferrite precipitate, all the other 49 ferrites had at least one misorientation with a neighbouring austenite grain that was within $\pm 5^\circ$ of a Bain cluster. As the Bain cluster is defined as 11 degrees from the Bain OR [25,41], a $6\text{--}16^\circ$ Bain mismatch is considered to be a feasible range for rational ORs in this study. These ferrite-austenite misorientation data sets were shown in Fig. 13b, where the strong rational ORs can be seen surrounding the Bain clusters.

The ORs of ferrite precipitates (excluding those at a triple junction) and austenite grains were linked with the growth direction for ferrite by plotting the stereographic projections (see Fig. 13c-Fig. 13e). Fig. 13c shows the misorientation projection of ferrite with the austenite grain it grows into and the green colour misorientation data points in surrounding the Bain clusters indicated a strong rational OR between these

ferrites and the austenite it grows into. However, it should also be noted that not all of the ferrite precipitates studied had a rational OR with the austenite it grows into, since some scattered data points deviated far from the Bain clusters (i.e. irrational ORs). For comparison, Fig. 13d was the projection of the ferrite orientation onto the austenite which was on the other side of the ferrite growth, from which the same conclusion can be determined, i.e. some ferrite had a rational OR with the austenite opposite to it while others did not have such a rational OR. In addition to these ferrites whose growth direction can be clearly distinguished, 9 ferrites did not have a clear growth direction into either of the neighbouring austenite grains, and these are shown in Fig. 13e. The stereographic projection was drawn by plotting the misorientation of ferrite with both neighbouring austenite grains (18 rotation matrices in total). Again, some misorientation data points surround the Bain clusters while others are scattered outside, which indicates that whilst the association is less clear, these ferrite precipitates still have a rational OR with one side of the austenite grain rather than both austenite grains.

For the ferrite and austenite exhibiting the rational ORs shown in Fig. 13b, the mismatch calculations (see Fig. 14) between the experimental misorientations and exact theoretical ORs were performed to study whether NW or KS within a Bain cluster was closer to the ferrite-austenite OR in the ex-service sample. These misorientation data points were within 6-16° Bain mismatch and the red points indicate the KS mismatch, which is smaller than the NW mismatch for most of the data points. The mean mismatch for the three ORs were compared in the sub-figure

where the average mismatch for KS was 3.4° , smaller than the 5.2° mismatch observed for NW.

There were however 15 ferrites which exhibited rational ORs with both neighbouring austenite grains. This is the so-called 'dual orientation ferrite' as reported in [22,23] which is expected to be favoured on low index CSL boundary (e.g. Σ from 3 to 21). Table B.1 in Appendix B shows the misorientation of grain boundaries exhibiting dual orientation ferrite in this study with the exact low index Σ CSL boundaries. It should be noted that only one of these boundaries is a low-angle grain boundary which is therefore supposed to form dual orientation ferrite. All the other boundaries which had dual OR ferrite did not correspond to any $\Sigma 3 - 21$ CSL boundaries based on a comparison of γ - γ misorientations and exact CSL with Brandon criteria (i.e. $\Delta\theta_m = 15^\circ \Sigma^{-1/2}$) [37].

Fig. 13. Stereographic projections show the misorientation and OR between the ferrite and austenite where the green spots indicate the $\{001\}$ of ferrite projecting on the $\{111\}$ plane of austenite. The simulated exact theoretical ORs between bcc and fcc crystal, namely KS, NW and Bain were also included and are indicated in blue, red and black respectively. (a) The projection of $\{001\}_\alpha$ on $\{111\}_\gamma$

for a total of 50 ferrite precipitates studied by EBSD (a total of 105 axis/angle pair misorientation data sets). (b) The projection of those ferrite-austenite misorientations that were in the range 6-16° of the Bain mismatch (i.e. $\pm 5^\circ$ around a Bain cluster). (c) The projection of misorientation of the ferrite with the austenite it grew into. (d) The projection of misorientation of the ferrite with the austenite that was opposite to the grain it grew into. (e) The projection of misorientation of ferrites where no clear growth direction into the austenite grains could be distinguished.

Fig. 14. The mismatch between exact theoretical ORs (i.e. Bain, NW, KS) and the experimentally found OR for 49 ferrite precipitates. The sub figure indicates the comparison of average mismatch of the three ORs.

Fig. 15 shows TEM image of a ferrite that has grown into both austenite grains, where the longest axis of growth of the ferrite in the top austenite grain (γ_1) is nearly perpendicular, while in the lower austenite grain (γ_2) the ferrite has grown parallel to the grain boundary. The TEM BF image was taken at the $[1\bar{1}1]$ zone axis of the ferrite shown in Fig. 15b. The grain boundary is highlighted by the white dashed line. Two faceted interfaces were noted in the ferrite with respect to γ_1 and γ_2 , which are marked as plane A and plane B with red lines, indicating some extent of interphase boundary coherency. The trace of plane A was nearly parallel with $[\bar{2}31]_\alpha$ while plane B was parallel with $[\bar{3}14]_\alpha$. In addition, evidence of ledge growth (as marked by the blue arrow) was observed at the α - γ interface [42]. Note that there are several $M_{23}C_6$ precipitates at the grain boundary between the two regions of the ferrite, the presence of which have affected the growth behaviour of the two regions of ferrite growth.

Fig. 15. TEM image and SAED patterns showing a ferrite at the grain boundary between two austenite grains (γ_1 and γ_2), where the ferrite has grown into both austenite grains. (a) TEM bright-field image in zone $[1\bar{1}1]$ of the ferrite. The austenite grain boundary was marked as a white dashed line. The red lines indicate the traces of two planar interfaces of the ferrite on two sides of the grain boundary, plane A and plane B respectively. Ledge growth at the α - γ interface is marked by a blue arrow; (b) zone $[1\bar{1}1]$ SAED pattern of the ferrite. (c) zone $[1\bar{1}0]$ pattern of the ferrite.

Fig. 16 shows EBSD phase maps that depict the four main types of ferrite growth and OR behaviour observed in this specimen. 80% of ferrite precipitates grow into one adjacent austenite grain, as shown in Fig. 16a, b and c. Of these single growth

direction ferrites, 31% grow into the austenite grain with which the ferrite has a rational OR present, as in Fig. 16a where α_1 and α_2 both have a rational OR with γ_2 . 40% of ferrite precipitates grow into the austenite grain that they have an irrational OR with, as shown in Fig. 16b. Straight interfaces were observed (marked by red lines) in the four ferrite precipitates in Fig. 16b although no rational OR is present between the individual ferrites α_1 , α_2 , α_3 , α_4 and γ_1 . 29% of ferrite precipitates grow into one grain but have a rational OR with both adjacent austenite grains (see Fig. 16c). In addition, there are limited numbers of ferrite precipitates at grain boundaries that have no clear growth direction identified at the 'macroscopic' scale by EBSD as shown in Fig. 16d. These ferrite precipitates can have a rational OR with either of the adjacent matrix grains or with both grains.

Fig. 16. EBSD phase maps showing the growth behaviours of ferrite observed in the ex-service sample. (a) ferrite grew into the neighbouring austenite grain with which the ferrite has a rational OR; (b) ferrite grew into the austenite grain with an irrational OR (c) ferrite that has grown into one austenite grain and has a rational OR with both adjacent austenite grains; (d) ferrite at austenite grain boundary with no clear growth direction.

4 Discussion

The combination of temperature, stress and the underlying microstructure all play significant roles in controlling creep cavitation. As a consequence, it is important to understand how the microstructure of a material subject to long term exposure to creep conditions evolves and subsequently influences the formation of creep cavitation damage at grain boundaries that leads to interlinkage and cracking. Understanding this behaviour should enable a more accurate predication of creep life of the components used at an elevated service temperature. It is well established that 316H steel headers used for AGR boilers are subject to reheat (creep damaged) cracking in the HAZ close to weldments. This study has characterised the microstructure of an ex-service 316H boiler header steel close to a weld after 65,000 hours at temperatures between 490 °C to 530 °C in service to understand the evolution of grain boundary cavitation.

Comparing the original type 316H stainless steel parent sample to the ex-service sample shows microstructural changes have occurred during in-service aging. In the original parent material, only grain boundary $M_{23}C_6$ carbide precipitates are present (see Fig. 2), whereas in the ex-service material both grain boundary and intra-granular carbide precipitates are observed, as well as ferrite precipitates and creep cavities at the grain boundaries. The grain boundary carbide precipitates in the original sample can be retained from the cast and will continue to grow during in-service aging, whilst carbide precipitates also nucleate at high energy sites and fast diffusion paths such as grain boundaries, incoherent-twin boundaries and to a lesser

extent coherent twin boundaries [11]. Intra-granular carbide precipitates with a cube-on-cube OR will then nucleate at the defects within the austenite grains such as dislocations. Additional dislocations due to residual strain from welding may contribute to the formation of these intra-granular carbides in the ex-service specimen. The high population of these fine (mean diameter 0.11 μm) dispersed semi-coherent [12] intra-granular carbide precipitates may have a significant effect on the creep deformation rate by inhibiting dislocation movement.

The evolution of ferrite in the ex-service specimen is of significant interest. The iron/chromium/nickel ternary phase diagram at elevated temperature is sensitive to local changes in composition, and rapid M_{23}C_6 precipitation at grain boundaries can move the system across the $\gamma/\gamma+\alpha$ phase boundary, causing ferrite formation [7]. In addition, nickel (Ni) and manganese (Mn) are austenite stabilisers [8,43,44], and the STEM EDX in Fig. 9 shows an enrichment of Ni at the grain boundary and of Mn in the M_{23}C_6 precipitates, which will lead to a local depletion of these elements in the surrounding austenite. We propose that the formation and growth of additional M_{23}C_6 at the austenite grain boundaries during thermal ageing promotes nucleation of ferrite from these localised depletion regions of austenite. The ferrite precipitates nucleate with an OR close to KS (i.e. the close-packed plane and close-packed direction of the two phases are parallel) to minimize the interphase interface energy during nucleation [32,45].

As shown in Fig. 16a, a relatively high proportion (over 30%) of ferrite precipitates that have a rational OR to only one adjacent austenite grain grow into the austenite

grain with which they have a rational OR. This is in conflict with Smith's hypothesis [29] and studies of Ayers and Joy [46] and Ryder et al [25]. Ryder et al [25] found that in the Co - 20% Fe system, the ferrite precipitates which have a rational OR with only one matrix grain always grow into the matrix where the rational OR is absent. The link between OR and growth behaviours of ferrite precipitates in 316H has not previously been reported in such detail. In the ex-service specimen in this study, a portion of partially coherent α - γ interface is maintained on both adjacent austenite grains during the ferrite precipitates growth, as shown by the faceted planes A and B in Fig. 15, and the faceted interfaces in Fig. 16b. This implies that the ferrite precipitates will maintain some extent of interface coherency even with the irrationally oriented austenite grain. This is in agreement with the behaviour of allotriomorphs studied in other alloys [31,33]. Although interphase boundary coherency minimizes total interfacial energy during nucleation [32], it can restrain ferrite growth in the perpendicular directions (see Fig. 15) due to immobility [46,47] which can be overcome by a ledge growth mechanism [32,42,47]. In addition, in the ex-service 316H stainless steel, the ferrite growth direction may also be influenced by the presence of grain boundary $M_{23}C_6$ precipitates. As reported in [12,48], the formation of $M_{23}C_6$ can cause asymmetric chemistry concentration profiles across grain boundaries. This will provide an asymmetric driving force in the adjacent austenite grains affecting the ferrite growth direction. The $M_{23}C_6$ precipitates at the grain boundary promote the nucleation and growth of ferrite due to the local elemental depletion of austenite stabilisers, but they can also act as physical

obstacles to limit the extent of ferrite growth in certain directions, as in the case of the ferrite shown in Fig. 15.

As expected for a material with this stacking fault energy, a high frequency of $\Sigma 3$ CSL boundaries were observed in the sample, but very few displayed evidence of cavitation. It was reported by Lim and Raj [49] and Don and Majumdar [50] that CSL boundaries with low Σ values, e.g. $\Sigma 3$ boundaries, show less cavitation than random grain boundaries. When considering the local response to creep, the misorientation of grain boundaries is important both due to grain boundary interaction with the stress and because the morphology of precipitates depends on the grain boundary misorientation. Hong et al [51] found that grain boundary misorientation can be responsible for the carbide morphology due to minimum interfacial energy selection. For example, a random high-angle grain boundary tends to have triangular-shaped carbides, while $\Sigma 3$ CSL boundaries have plate-shaped carbides, which has been observed and shown in Fig. 8c. Kim et al [52] claimed that creep cavity nucleation can be linked with the carbide morphology, i.e. carbides with a plate-shaped morphology have a lower interfacial energy (i.e. low energy $\{111\}$ interfaces on both sides of the carbide) and so are less likely to nucleate a cavity compared to a triangular-shaped morphology (i.e. $\{111\}$ interface present on only one side). This morphology dependence, higher coherency, as well as the proportionally lower precipitation (absence of ferrite) offer reasons for the higher creep cavitation resistance of a $\Sigma 3$ CSL boundary compared to a random grain boundary.

Depletion of austenite stabilisers as carbide grows during thermal ageing in service leads to formation of ferrite phase at the grain boundary. The combination of carbide and ferrite precipitates on the boundary subsequently act as nucleation sites for creep cavities. In Fig. 12b and 12e, the ferrite marked in red arrow has a rational OR with austenite grain γ_1 and an irrational OR with γ_2 , whilst a cavity is present between the ferrite and γ_1 - i.e. there is no physical contact between the ferrite and γ_1 . This strongly implies that this ferrite is likely to have formed from γ_1 before the presence of the cavity, since the orientation of the precipitate should be determined at the nucleation stage rather than the subsequent growth [45,53]. This suggests that ferrite forms in this specimen at least in part prior to the cavity nucleation process.

It is well known that carbide precipitates (e.g. $M_{23}C_6$) can promote creep cavity initiation. However, in aging materials in high temperature plants, such as this ex-service 316H stainless steel, the ferrite precipitates play an important role for intergranular creep cavitation by adding more nucleation sites. There is a strong difference in the mechanical properties of the austenite, ferrite and carbide phases, with the ferrite expected to be more ductile, and the carbide harder and brittle [54,55]. This combination of phase behaviour will lead to higher local stress concentrations at boundaries where both precipitates are present [19,56], potentially increasing the chances of nucleation of a cavity at the interface of these phases. After the formation of ferrite at the grain boundaries, the proportion of creep cavitation is accelerated. Cavities may be nucleated under local stress by the decohesion of α - γ and α - $M_{23}C_6$ interface and of α - $M_{23}C_6$ - γ triple junction (see Fig. 8b and 8c) due to strain

incompatibility. In addition, strain energy resulted from volume change (based on the lattice parameters measured by electron diffraction in Fig. 10c and Fig. 9i the lattice mismatch between austenite and ferrite is around 22 pct) and constrained shape change after the γ - α phase transformation [42] might be relaxed by the formation of creep cavities at the γ - α interphase boundaries.

Fig. 17. The proposed potential sequence for ferrite formation and creep cavitation during the in-service creep where the microstructure evolution at different stage was shown on a general creep curve.

The proposed overall precipitation and creep cavitation sequences during in-service aging are summarised in Fig. 17. Thermal ageing leads to additional carbide precipitates at the grain boundaries. The formation and growth of these carbide precipitates causes the local depletion of austenite stabilisers, leading to ferrite precipitation at grain boundaries that then act as additional nucleation sites for cavities, accelerating the cavitation process. This study shows that when considering

creep cavitation in steels at high temperature, the evolution of secondary phases can significantly modify the degradation process.

Conclusions

The microstructure of weld metal and the HAZ of an ex-service type 316H stainless steel have been characterised by multiple techniques to understand the phase evolution and creep cavitation behaviour during in-service creep exposure. The main conclusions can be summarised as follows:

1. After in-service aging at 490 °C to 530 °C for 65,000 hours, no cavities were observed in the weld metal.
2. The random grain boundaries in the HAZ were extensively creep cavitated during aging.
3. The local elemental depletion of austenite stabilisers caused by the formation and growth of grain boundary $M_{23}C_6$ and the associated elemental redistribution promotes the transformation of austenite into grain boundary ferrite with a near KS OR.
4. The ferrite formed during aging has a rational OR with at least one neighbouring austenite grain, but can grow into either neighbouring austenite grain, whether they possess a rational or irrational OR. Faceted interfaces (i.e. some extent of interfacial coherency) can exhibit even when growing into an austenite that have an irrational OR with the ferrite.

5. A high fraction (40 percent) of $\Sigma 3$ CSL boundaries were observed in the ex-service sample, and compared to the random grain boundaries, the $\Sigma 3$ CSL boundaries show an absence of creep cavities. This can be explained by the plate-shaped carbide and absence of ferrite at the $\Sigma 3$ CSL boundaries.
6. The formation of ferrite at the grain boundaries will, together with carbide precipitates, promote the nucleation of creep cavities. The decohesion of interphase interfaces under stress is likely to nucleate cavities. The presence of the ferrite and carbide formed during thermal aging accelerates the creep cavitation process.

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Appendix A

Orientation relationship and CSL mismatch calculation approach

The formal definition of an orientation relationship (OR) (between fcc and bcc phases), Q , is $\vec{a}_i^{bcc} = \vec{a}_j^{fcc} Q_{ji}$. The lattices fcc and bcc have point group symmetries R_{ji} , where R_{ji} uses the standard repeated index summation convention for latin subscripts running from 1 to 3, defined by the invariance of the metric tensor ($\mathbf{g}_{ij} = \vec{a}_i \cdot \vec{a}_j$) as $R_{ik} \mathbf{g}_{ij} R_{jl} = \mathbf{g}_{kl}$. By considering the symmetries of the metric tensor, a general definition for cubically equivalent ORs, $\tilde{Q}$, can be made from any pair of symmetry operators, R, S belonging to the point group O_h :

$$\tilde{Q} = RQS \quad (1)$$

This definition for equivalent rotation matrices is in agreement with the definition used by Grimmer to find the rotation matrices corresponding to CSL [57]. Grimmer also proved that the set of equivalent rotation matrices necessarily included the inverse of Q i.e. $\tilde{Q} = RQ^{-1}S$.

The set of equivalent rotation matrices whose rotation axis is within the standard stereographic triangle, and with smallest rotation angle has been named disorientation [57]. Formally we define the disorientation angle, ψ_Q , as:

$$1 + 2\cos\psi_Q = \text{Max Tr } \tilde{Q}, \text{ where Tr is the trace of a matrix} \quad (2)$$

The formulation for disorientation can be applied to finding the minimum angular deviation rotation matrix, Δ , between two ORs i.e. mismatch between two ORs from

Q_1 to Q_2 . The corresponding disorientation, which can be found from the minimum angle condition for ψ_Δ is then:

$$\tilde{\Delta} = \tilde{Q}_2 \tilde{Q}_1^{-1} \text{ with } 1 + 2\cos\psi_\Delta = \text{Max Tr } \tilde{\Delta} \quad (3)$$

The mismatch between exact Bain, NW or KS and an experimental OR can be calculated with the procedures above by setting Q_1 to the Bain, NW or KS and Q_2 to the experimentally found rotation matrix. For clarity, we write explicitly the Bain, NW, and KS ORs below.

1. Bain: $(001)_{\text{fcc}} || (001)_{\text{bcc}}$ and $[110]_{\text{fcc}} || [111]_{\text{bcc}}$

$$Q_{\text{Bain}} = \begin{pmatrix} \frac{1}{2} + \frac{\sqrt{3}}{2\sqrt{2}} & -\frac{1}{2} + \frac{\sqrt{3}}{2\sqrt{2}} & 0 \\ -\frac{1}{2} + \frac{\sqrt{3}}{2\sqrt{2}} & \frac{1}{2} + \frac{\sqrt{3}}{2\sqrt{2}} & 0 \\ -\frac{1}{2} & -\frac{1}{2} & 1 \end{pmatrix}$$

2. NW: $(111)_{\text{fcc}} || (110)_{\text{bcc}}$ and $[\bar{1}\bar{1}0]_{\text{fcc}} || [001]_{\text{bcc}}$

$$Q_{\text{NW}} = \begin{pmatrix} 0 & -\frac{1}{\sqrt{3}} + \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} + \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{2}} & \frac{1}{2\sqrt{3}} + \frac{1}{\sqrt{6}} & -\frac{1}{2\sqrt{3}} + \frac{1}{\sqrt{6}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{2\sqrt{3}} + \frac{1}{\sqrt{6}} & -\frac{1}{2\sqrt{3}} + \frac{1}{\sqrt{6}} \end{pmatrix}$$

3. KS: $(111)_{\text{fcc}} || (110)_{\text{bcc}}$ and $[011]_{\text{fcc}} || [111]_{\text{bcc}}$

$$Q_{KS} = \begin{pmatrix} \frac{1}{6} & \frac{1}{6}(1 + 2\sqrt{6}) & \frac{1}{6}(-2 + \sqrt{6}) \\ \frac{1}{6}(1 - 2\sqrt{6}) & \frac{1}{6} & -\frac{1}{6}(2 + \sqrt{6}) \\ -\frac{1}{6}(2 + \sqrt{6}) & \frac{1}{6}(-2 + \sqrt{6}) & \frac{2}{3} \end{pmatrix}$$

The ORs for CSL for fcc and bcc are the same as for the primitive cubic lattice when these are expressed in the orthogonal coordinate system. Grimmer has found an algorithm for computing the CSL matrices [38], and listed the orientations for some Σ values. The mismatch between two fcc crystals and CSL ORs can be found from the formalism described above by choosing Q_1 to any CSL and Q_2 to the experimentally found rotation matrix between two fcc crystals.

XRT and PFIB reconstruction procedures

The software Avizo 9.7.0 version was used to perform the data processing and 3D reconstruction for the XRT data as well as for the Xe⁺ Plasma FIB (PFIB) cross sectioning data. The XRT data was processed by applying an edge-preserving smoothing filter to reduce noise. A watershed tool was then used to remove the background. A simple global greyscale threshold combined with a 'top hat' tool was performed to segment the inclusions from the material. Finally, the segmented features smaller than 5 μm in diameter were removed to distinguish inclusions from smaller features.

The PFIB data were aligned manually. A fast Fourier transform filter was applied to remove curtaining on the milled surface. An unsharp masking filter was performed to eliminate blurring. An edge-preserving smoothing was undertaken before the final segmentation. The segmentation of voids, grain boundary cavities and inclusions together were completed by greyscale threshold and 'top hat' tool with limited manual work. However, due to their similar contrast, these features were identified and distinguished from one another manually.

Appendix B

Fig. B.1. The frequency of different CSL boundary from $\Sigma=3$ to 49 in the ex-service sample based on Brandon Criterion. The axis/angle pair description of each Σ value was shown in [38].

Table B.1: The mismatch between the γ - γ misorientation and exact CSL boundary misorientations

γ - γ GBs	$\Delta\Sigma 3(^{\circ})$	$\Delta\Sigma 5(^{\circ})$	$\Delta\Sigma 7(^{\circ})$	$\Delta\Sigma 9(^{\circ})$	$\Delta\Sigma 11(^{\circ})$	$\Delta\Sigma 13a(^{\circ})$	$\Delta\Sigma 13b(^{\circ})$
$46^{\circ}\langle -0.663, 0.573, -0.481 \rangle$	15.45	34.42	9.41	21.94	20.94	35.1	18.76
$38.1^{\circ}\langle 0.129, 0.764, -0.632 \rangle$	31.56	25.37	18.33	6.1	14.14	25.27	18.78
$22.9^{\circ}\langle 0.005, -0.335, 0.942 \rangle$	45.48	17.05	26.08	20.65	31.28	7.7	18.71
$55.3^{\circ}\langle -0.382, 0.704, -0.599 \rangle$	13.74	38.66	20.04	24.28	14.74	42.29	28.94
$55.6^{\circ}\langle -0.652, 0.151, 0.743 \rangle$	17.86	36.84	25.29	18.25	9.85	41.43	33.06
$3.3^{\circ}\langle -0.384, -0.249, -0.889 \rangle$	57.12	33.97	35.35	36	47.53	19.74	24.94
$56.5^{\circ}\langle 0.148, 0.622, 0.769 \rangle$	17.76	36.1	23.24	19.41	11.12	41.49	31.31

γ - γ GBs	$\Delta\Sigma 15(^{\circ})$	$\Delta\Sigma 17a(^{\circ})$	$\Delta\Sigma 17b(^{\circ})$	$\Delta\Sigma 19a(^{\circ})$	$\Delta\Sigma 19b(^{\circ})$	$\Delta\Sigma 21a(^{\circ})$	$\Delta\Sigma 21b(^{\circ})$
$46^{\circ}\langle -0.663, 0.573, -0.481 \rangle$	19.6	34.17	18.3	26.02	5.88	24.55	10.55
$38.1^{\circ}\langle 0.129, 0.764, -0.632 \rangle$	14.86	24.36	26.16	12.61	22.01	21.46	15.88
$22.9^{\circ}\langle 0.005, -0.335, 0.942 \rangle$	25.6	10	43.88	11.36	33.41	16.05	25.4
$55.3^{\circ}\langle -0.382, 0.704, -0.599 \rangle$	19.36	40.37	8.37	32.42	14.3	34.45	15.27
$55.6^{\circ}\langle -0.652, 0.151, 0.743 \rangle$	16.57	39.15	10.07	29.73	20.01	37.36	16.44
$3.3^{\circ}\langle -0.384, -0.249, -0.889 \rangle$	45.01	25.18	58.86	23.6	43.95	18.95	41.17
$56.5^{\circ}\langle 0.148, 0.622, 0.769 \rangle$	15.57	38.92	10.55	30.76	18.4	36.51	14.52

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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Figure Captions

Fig. 1. (a) Image showing the ex-service AGR boiler header component and the triangular prism sample cut from the component as indicated by the black dashed triangle. (b) The triangular prism sample was then sectioned into five pieces as marked in black dashed lines.

Fig. 2. The microstructure of the original parent 316H stainless steel sample. (a) EBSD phase map of a region in the original sample showing no ferrite at the austenite grains and grain boundaries. (b) FIB XeF_2 etched image where carbide precipitates are highlighted in dark contrast at the austenite grain boundaries.

Fig. 3. (a) and (b) microstructure of the HAZ showing inclusions and intergranular creep cavities. The sub-figures in (a) show the elemental maps of manganese and sulphur of a rod-shaped inclusion in HAZ. The sub-figure in (b) shows the morphology of creep cavities where the grain boundaries were highlighted in white dashed lines; (c) and (d) microstructure of weld metal showing inclusions and absence of grain-boundary cavities. The sub-figures in (d) were the elemental maps of manganese and silicon of spherical-shaped inclusions in the weld metal.

Fig. 4. (a) a schematic diagram shows the weld metal, reheat-cracking, HAZ and the parent of the ex-service sample; (b) SEM secondary electron image shows the cracking at the HAZ.

Fig. 5. EBSD IPF map of HAZ shows crystallographic orientation of each grain and grain boundaries. The random grain boundaries are highlighted in blue while $\Sigma 3$ CSL boundaries are shown in black and $\Sigma 5$ - $\Sigma 49$ in red.

Fig. 6. Plasma FIB cross sectioning. (a) a typical SEM slice of the cross sectioning. (b)-(g) EDX maps showing the elemental compositions of this slice. (h) 3D reconstruction of the inclusions, intergranular creep cavities and voids linked with precipitates cluster region based on the cross-sectioning slices.

Fig. 7. (a) comparisons of equivalent mean diameter of inclusions, voids linked with precipitates cluster region and intergranular creep cavities. (b) comparisons of size distributions of voids and cavities.

Fig. 8. (a), (b) and (c) FIB XeF_2 etched images showing cavities, highlighted grain boundary precipitates and intra-granular precipitates in HAZ.

Fig. 9. Austenite grain boundary and austenite grain by STEM and TEM. (a) STEM dark-field (DF) image showing cavity, ferrite, silicon-enriched precipitates, grain boundary M_{23}C_6 and intra-granular M_{23}C_6 . The two ferrite precipitates were marked as α_1 and α_2 respectively. Black arrows indicate grain boundary M_{23}C_6 while white arrow indicates intra-granular M_{23}C_6 . The silicon-enriched precipitates were marked by red arrow and the austenite grain boundary was highlighted by the white dashed line. (b)-(h) EDX elemental maps of the same region showing the chemical composition of these phases and the grain boundary chemical segregation. (i) TEM $[01\bar{2}]$ zone pattern of α_1 .

Fig. 10. (a) TEM bright-field image showing intra-granular M_{23}C_6 . (b) In-centre dark-field image from (220) reflection of the M_{23}C_6 . (c) and (d) correspond to $[\bar{1}12]$ and $[001]$ zone-axis SAED patterns of the austenite showing superlattice reflections from the intra-granular M_{23}C_6 , where the bigger and brighter spots are from the austenite matrix as indicated in larger rectangles, while the smaller and darker spots are from the M_{23}C_6 as indicated in smaller rectangles. The white circle in the zone $[001]$ pattern indicates the superlattice reflection used to generate the dark-field image. (e) and (f) are the simulated SAED patterns for the superimposed zone axis $[\bar{1}12]$ and $[001]$ respectively, where the black dots indicate the diffraction pattern expected for the austenite while red dots indicate the expected pattern for Cr_{23}C_6 .

Fig. 11. The size distribution of (a) the intra-granular M_{23}C_6 and (b) the grain boundary M_{23}C_6 in the HAZ by XeF_2 FIB etching.

Fig. 12. Grain boundary and ferrite characterisation by EBSD. (a)-(c) EBSD image quality adding ferrite phase maps where the green colour ferrite, and black colour cavities (indicated in blue arrows) can be seen at the austenite matrix grain boundaries. (d)-(f) EBSD orientation maps showing the orientation of austenite and ferrite of the same region that corresponds to (a)-(c). The black arrows indicate those ferrites showing an example of near-parallel crystallographic orientation between them.

Fig. 13. Stereographic projections show the misorientation and OR between the ferrite and austenite where the green spots indicate the $\{001\}$ of ferrite projecting on the $\{111\}$ plane of austenite. The simulated exact theoretical ORs between bcc and fcc crystal, namely KS, NW and Bain were also included and are indicated in blue, red and black respectively. (a) The projection of $\{001\}_\alpha$ on $\{111\}_\gamma$ for a total of 50 ferrite precipitates studied by EBSD (a total of 105 axis/angle pair misorientation data sets). (b) The projection of those ferrite-austenite misorientations that were in the range $6-16^\circ$ of the Bain mismatch (i.e. $\pm 5^\circ$ around a Bain cluster). (c) The projection of misorientation of the ferrite with the austenite it grew into. (d) The projection of misorientation of the ferrite with the austenite that was opposite to the grain it grew into. (e) The projection of misorientation of ferrites where no clear growth direction into the austenite grains could be distinguished.

Fig. 14. The mismatch between exact theoretical ORs (i.e. Bain, NW, KS) and the experimentally found OR for 49 ferrite precipitates. The sub figure indicates the comparison of average mismatch of the three ORs.

Fig. 15. TEM image and SAED patterns showing a ferrite at the grain boundary between two austenite grains (γ_1 and γ_2), where the ferrite has grown into both austenite grains. (a) TEM bright-field image in zone $[1\bar{1}1]$ of the ferrite. The austenite grain boundary was marked as a white dashed line. The red lines indicate the traces of two planar interfaces of the ferrite on two sides of the grain boundary, plane A and plane B respectively. Ledge growth at the α - γ interface is marked by a blue arrow; (b) zone $[1\bar{1}1]$ SAED pattern of the ferrite. (c) zone $[1\bar{1}0]$ pattern of the ferrite.

Fig. 16. EBSD phase maps showing the growth behaviours of ferrite observed in the ex-service sample. (a) ferrite grew into the neighbouring austenite grain with which the ferrite has a rational OR; (b) ferrite grew into the austenite grain with an irrational OR (c) ferrite that has grown into one austenite grain and has a rational OR with both adjacent austenite grains; (d) ferrite at austenite grain boundary with no clear growth direction.

Fig. 17. The proposed potential sequence for ferrite formation and creep cavitation during the in-service creep where the microstructure evolution at different stage was shown on a general creep curve.

Fig. B.1. The frequency of different CSL boundary from $\Sigma=3$ to 49 in the ex-service sample based on Brandon Criterion. The axis/angle pair description of each Σ value was shown in [38].