The Effect of Sodium Hydroxide on Niobium Carbide Precipitates in Thermally Sensitised 20Cr-25Ni-Nb Austenitic Stainless Steel

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1. Abstract (100 words only)

Niobium-stabilised austenitic stainless steel (20Cr-25Ni-Nb) has been immersed in sodium hydroxide, which is used as a corrosion inhibitor. The work shows how NbC precipitates may be degraded by use of pH 13 NaOH. Initial electrochemical measurements indicate that there is no benefit to this pretreatment as regards long-term corrosion inhibition, and post corrosion imaging shows the initiation of pitting corrosion at Nb-rich precipitates still present in the microstructure.

2. Introduction

Advanced gas-cooled reactor (AGR) oxide fuel is clad in a 20Cr-25Ni-Nb austenitic stainless steel. Spent fuel elements have historically been stored in well-controlled cooling ponds typically containing either demineralised water with low concentration of chloride (≤0.1 ppm chloride ([Cl-])), or in sodium hydroxide (NaOH) dosed cooling ponds with up to 2 ppm [Cl-] [1] [2] [3] [4]. Going forward, pond chemistry of <0.1 ppm [Cl-] with pH 11.5 NaOH is planned. The NaOH pH-moderation of these ponds is used to inhibit corrosion of the stainless steel cladding. The 20Cr-25Ni-Nb alloy is stabilised by ~0.6% niobium (Nb) which precipitates as niobium carbide (NbC) during the manufacturing process [5]. Despite Nb stabilisation, during reactor operation a small proportion of fuel cladding can become sensitised through an alternative mechanism, known as radiation induced segregation (RIS), which leads to a redistribution of alloying elements at the microstructural level (notably, Cr diffusion away from grain boundaries), rendering the alloy sensitised [5] [6] [7]. The alloy can also be sensitised through the use of a two-stage heat treatment which causes Cr depletion at grain boundaries by the formation of Cr carbide precipitates [5] [8] [9] [10].

Whilst NbC precipitates play an important part in stabilising the free carbon content within this alloy; investigators have also sought to improve the fundamental mechanistic understanding by both identifying and characterising the sites where corrosion initiates in relation to these precipitates [5] [11] [12] [13] [14]. Phuah et al [14], during post corrosion imaging, using scanning electron microscopy (SEM), noted the presence of pits and crevices adjacent to NbC precipitates in thermally sensitised 20Cr-25Ni-Nb when polarised in a Cl- environment. This led to the hypothesis that the NbC phase forms a galvanic couple with the austenite matrix leading to preferential dissolution of the austenite, predicted to be less noble. Chan et al [11]

also witnessed similar features at NbC precipitates, grain boundaries and triple junctions on thermally sensitised 20Cr-25Ni-Nb following corrosion experiments.

Clark et al [5] utilised scanning Kelvin probe force microscopy (SKPFM) to map the nobility of microstructural phases within the thermally sensitised 20Cr-25Ni-Nb alloy, which indicated that the NbC phases were up to 30 mV more noble than the matrix. Thermally sensitised 20Cr-25Ni-Nb grain boundaries (containing Cr carbide precipitates) were up to 65 mV less noble than the matrix, although it was noted that these negative Volta potentials appeared localised along areas of the grain boundaries, possibly an indication of low sensitisation. Clark et al [5] also showed that NbC phases play a significant role in the corrosion of the 20Cr-25Ni-Nb alloy. At the microstructural length-scale, the use of in-situ electrochemical atomic force microscopy (EC-AFM) showed that several intergranular (IG) pits initiated at sensitised grain boundaries. In addition, initiation was observed at a precipitate, thought to be NbC, present on a triple point grain boundary. At the larger length-scale, IG pits were found to be present at locations where a high number density of NbC precipitates were present.

Ahmedabadi et al [15] did not observe corrosion around NbC precipitates following a double loop electrochemical potentiokinetic reactivation (DL-EPR) test for sensitisation on a proton irradiated Nb-stabilised AISI 347 (EN 1.4550, UNS S34700) austenitic stainless steel. They did, however, observe the presence of pits at large clusters of smaller sized NbC precipitates (~300 nm), indicating that the NbC precipitates create strained regions within the matrix; pointing to past work on oversized elements limiting Cr depletion (from RIS) [16] and other works on thermal sensitisation [17]. This observation led to the notion that the precipitate-matrix interface can act as a sink for excess point defects generated from irradiation processes. Proton irradiation of 20Cr-25Ni-Nb stainless steel has also been conducted by Alshater et al [18], though in the published work such voids were not observed at either the Bragg peak, the NbC precipitates nor the NbC-matrix interface. Ahmedabadi et al [15] suggest another reason for the pitting around NbC clusters may be due to Cr depletion at the precipitate-precipitate interface. However, if this were to be the case, then NbC interfaces would show a similar microchemistry to a RIS sensitised grain boundary for instance: Cr depletion and Ni enrichment. The pitting corrosion Ahmedabadi et al [15] witnessed around NbC clusters, said to be from an excess of defects, would differ from that exhibited in thermally sensitised 20Cr-25Ni-Nb as the material was proton irradiated through the RIS sensitisation mechanism.

NaOH has been successfully implemented as a corrosion inhibitor for spent AGR fuel since 1983 [19] [20]. Much of the work undertaken by industry surrounding the use of this inhibitor has been summarised by Hambley [19]. Both the oxygen reduction reaction and hydrogen peroxide-water reduction reactions are pH dependant, and NaOH inhibits corrosion by decreasing the free corrosion potential (E_{corr}). Hambley [19] gives additional reasons for the use of NaOH, in that it not only makes local acidification difficult, but also: (a) supresses the formation of radiolytically generated hydrogen peroxide (H_2O_2, the formation of which would serve to increase E_{corr}), and (b) competes with Cl^- for electromigration at corrosion sites. At a higher pH the local breakdown potential (E_b) for sensitised grain boundaries is sufficiently more positive of E_{corr}, and as such IGC initiation is inhibited. Chan et al [11] showed that E_{corr} of 20Cr-25Ni-Nb in 500 ppm [Cl^-] can be supressed by up to ~250 mV by NaOH (pH 11.5) in thermally sensitised conditions. Additionally there appeared to be a decrease in E_b by ~50 mV, whereas in the 'Nb-stabilised' condition there was a small increase in E_{corr}. During post corrosion characterisation of thermally sensitised and Nb-stabilised 20Cr-25Ni-Nb Chan et al

[11] observed a modification of the NbC phases, which appeared fractured. Does this apparent modification of NbC precipitates in NaOH witnessed by Chan et al play a role in improved corrosion resistance, and additionally, is this effect due to the elevated pH or something else, such as a Cl⁻ induced effect? A survey of the literature reveals little information on the corrosion of NbC in NaOH environments; though there is evidence that metallic Nb has very poor resistance to alkaline environments [21] [22] [23] [24].

The work in this paper aims to provide insight into the behaviour of NbC precipitates in pH moderated wet storage conditions. Electrochemical techniques have been used to assess the influence of pH on the corrosion behaviour of 20Cr-25Ni-Nb stainless steel in the presence of Cl⁻. Changes in the NbC precipitate morphology (and eventual dissolution) can lead to changes in the susceptibility of the alloy to undergo localised corrosion.

3. Experimental

Two different 20Cr-25Ni-Nb austenitic stainless steel geometries were used in this study, tube material and end cap strips (obtained from Westinghouse). The composition of the sample materials was determined through third party chemical analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) and is summarised in Table 1[1]. The end cap, as a flat strip, (350 x 25 x 0.8 mm) was cut to ~150 mm lengths by hacksaw. All specimens were solution annealed at 1150°C for 0.5 hours in an Ar atmosphere, water quenched, and then aged in air at 600°C for 2 weeks, unless otherwise stated. The end cap stabilisation ratio for our alloy composition was 4:1 ([Nb] / [C] + [N]), which according to Powell et al [8], should result in the formation of $M_{23}C_6$ and NbC upon aging. In comparison, the stabilisation ratio for our tube composition was 10:1, which should result in the formation of M_6C and NbC during aging, according to Powell et al [8]. Sample material was cut into 15 x 15 x 0.8 mm (W x L x T) specimens by hand guillotine or cutting wheel.

The 20Cr-25Ni-Nb tube specimens were supplied in 900 mm lengths[2], cut to ~150 mm length by hacksaw, then solution annealed at 1200°C in Ar for 0.6 hours, and then aged in air at 600°C for 2 weeks. Tube samples were longitudinally cut into 7 x 5 mm strips by cutting wheel (~36° curvature), and the helical ribs removed by grinding. Copper wire was spot welded to the back of the tube specimen and the exposed area masked with non-conductive lacquer.

All types of 20Cr-25Ni-Nb specimen were ground using SiC paper, then polished using diamond suspension to a 1 µm finish and rinsed with ethanol.

A flow diagram describing the main experiments and associated characterisation at each step is shown in Figure 1.

3.1.   Immersion Experiments

Immersion experiments were conducted on both tube and end cap specimens, each thermally sensitised according to the information outlined previously. Tube specimens were immersed in pH 11.5 NaOH for 3 days, analysed by scanning electron microscopy (SEM), re-immersed for a further 4 days, and then subsequently re-analysed by SEM. Additional specimens were

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[1] AGR tube and end cap cladding have slight differences in composition to facilitate machining and welding respectively

[2] Inner diameter 14.6 mm, outer diameter 16.1 mm (including helical ribs)

immersed in pH 13 NaOH for 7 days and 28 days in 100 ml pH 13 NaOH solution. Parafilm was used to cover the beakers to limit neutralisation which can occur because of atmospheric CO_2 uptake. Beakers were stored at room temperature throughout the experiment. Additionally an electrolytic etch was performed on a thermally sensitised 20Cr-25Ni-Nb tube specimen (6 V polarisation for 30 seconds) in a solution of pH 14.7 NaOH solution to accelerate NbC dissolution.

Time-lapse microscopy (TLM) experiments were carried out using a saturated calomel electrode (SCE) as a reference electrode, with data collected every 10 seconds. The 20Cr-25Ni-Nb end cap electrode was prepared by first spot welding a wire to provide an electrical connection, then mounting the specimen in cold set resin (Struers Durocit), followed by grinding and polishing. A Meiji MT8000 optical microscope was used with an Infinity 2-5C camera. A waterproof shroud was used to protect the 20x objective lens as this was immersed in the electrolyte. Once the area of interest was identified (a set of three precipitates over a ~20 μm^2 area) the specimen was immersed in NaOH at pH 11.4 (Aldrich, ≥98%, ≤1% Na_2CO_3) and the focus adjusted. The pH 11.4 electrolyte was then removed, dosed to pH 13, and then re-used. Images were captured at 10 minute intervals.

3.2.   Electrochemistry

Potentiodynamic polarisation experiments were carried out using a three-electrode cell configuration (SCE as reference electrode and platinum gauze as a counter electrode). Depending on the experiment, either a 20Cr-25Ni-Nb end cap specimen or NbC sputtering target specimens were used as working electrodes. 20Cr-25Ni-Nb end cap working electrodes were housed in a bespoke PTFE electrode holder which provided an electrical connection to the potentiostat. The NbC sputtering target sample material was obtained from Mi-net (50 x 20 x 10 mm, 99.5% purity) and cut into 10 x 10 x 0.3 mm specimens by electric discharge machining (EDM). NbC specimens were polished using neutral colloidal silica to avoid any breakdown/dissolution effects (typically this is basic). Prior to the start of the potentiodynamic experiment, specimens were immersed in the electrolyte, and the open circuit potentials (OCP) recorded for 1 hour. Experiments using the NbC specimens were conducted in 500 ppm [Cl⁻] (as NaCl). NaOH and sulphuric acid (H_2SO_4) were used to adjust the pH of the exposure environment. The scan rate was 0.5 mVs⁻¹, and polarisation range -300 to +1200 mV vs OCP. Experiments using 20Cr-25Ni-Nb end cap specimens were conducted in NaCl electrolytes (0, 1, 10, 100, 1000, 10000 ppm [Cl⁻]) with and without NaOH pH 11.4 inhibitor. The scan rate was 0.5 mVs⁻¹, and polarisation range -150 mV vs OCP to +2000 mV vs Ref. Potentiodynamic experiments were performed once.

Galvanic corrosion experiments were conducted using a zero resistance ammeter (ZRA) between NbC specimens and AISI 304 austenitic stainless steel (EN 1.4301, UNS30453). Given that 20Cr-25Ni-Nb stainless steel contains NbC precipitates, AISI 304 stainless steel was used as a working electrode. The AISI 304 stainless steel working electrode was coupled with an NbC specimen connected to ground (surface area ratio of 1:1).

Electrochemical impedance spectroscopy (EIS) was performed at frequencies between 10⁻³ and 10⁺⁵ Hz with 10 mV polarisation. EIS was performed using a three electrode cell configuration as described above, except that a wire was attached to the back of 20Cr-25Ni-Nb end cap specimens using silver epoxy, and then encapsulated in cold set resin (Struers Claracit). Three separate experiments were initiated simultaneously using separate

potentiostats in (a) ultra-pure water used as a control, (b) pH 11.4 NaOH to study corrosion inhibition, and (c) pH 13 NaOH as a 'pretreatment'. All electrochemical cells were covered with parafilm as best possible, to minimise acidification over the 15 day exposure period. The cells were kept at room temperature. The 15 day period of immersion in pH 13 NaOH is referred to henceforth as the 'pretreatment'. To determine if the pH 13 NaOH pretreatment was beneficial, potentiodynamic polarisation experiments were performed (0.5 mVs^{-1}, -250 to +1900 mV vs OCP) and experiments were repeated three times.

3.3.   Characterisation

Where required, specimens were sputter coated with gold using an Edwards Scancoat Six instrument for post corrosion observation using SEM (this denoted in the figure caption where this occurred). A number of different SEMs were used to characterise specimens, which included: JEOL JSM-6010 PLUS/LA, Zeiss Evo50, FEI Quanta 650 and Zeiss Sigma VP with energy dispersive X-ray spectroscopy (EDS) capability. For topology and Volta potential measurement a JPK Instruments Nanowizard 3 atomic force microscope (AFM) was used (FM50 Pointprobe tip, 512 x 512 px, 0.6 Hz scan rate) with a typical lift height of 50 nm. Volta potentials were inverted according to convention (brighter areas more noble). For cross sectioning microstructural features, a focussed ion beam SEM (FIB-SEM, FEI Helios NanoLab 600 "dualbeam") instrument was used where required to mill trenches, such that sub-surface imaging could be conducted. A bespoke secondary ion mass spectrometry (SIMS) instrument (utilising a FEI SD gallium LMIS EVA focussing column and Vacuum Generators model 7035 double focussing magnetic sector mass analyser) was used to provide further characterisation of precipitates.

4. Results
4.1.   Immersion Experiments
4.1.1.   Sodium Hydroxide (pH 11.5)

Immersion experiments were conducted on the 20Cr-25Ni-Nb tube material at pH 11.5 to observe the effect of NaOH without any applied polarisation. Figure 2(i) shows an NbC precipitate following 3 days of immersion, and Figure 2(ii) shows a different precipitate from the same specimen following 4 days of further immersion (total of 7 days). Both images were taken using the backscatter electron detector, thus heavier elements, such as Nb, appear brighter than the matrix. EDS analysis confirmed the presence of Si at the dark regions shown in Figure 2(i, ii). It is possible that, rather than this being simply segregation of Si within the NbC precipitate, that the presence of Si is due to the formation of a non-metallic Si inclusion which formed during cooling after the heat treatment. The precipitate appeared to show some signs of dissolution around the outer periphery after 3 days immersion (Figure 2(i)). At the end of the experiment (7 days) precipitates appeared sponge-like (Figure 2(ii)).

4.1.2.   Sodium Hydroxide (pH 13)

Separate end-cap specimens were immersed in pH 13 NaOH for a period of 4 days and 28 days. After 4 days of immersion, Figure 3(i) shows an image of precipitates which appeared to have been dissolved. A trench was milled across the precipitates pictured in Figure 3(ii) with the FIB, such that a cross section through the precipitate could be obtained. Despite the appearance from the surface, the cross section revealed that a large proportion of the NbC

precipitate was still present sub-surface. EDS analysis confirmed that Nb was still present (map shown in Figure 3(iii)).

Further characterisation was undertaken using a FIB-SEM following 28 days immersion in pH 13 NaOH with Figure 4(i) and Figure 4(iii) showing two different precipitate morphologies. Both show far more pronounced NbC dissolution than after 4 days immersion. Figure 4(i) revealed a lamellar-like network. AFM and SKPFM were conducted after 4 days immersion (Figure 5(i)), which resembled what had been observed in Figure 4(i, ii). FIB cross sectioning (Figure 4(ii)) showed that a limited volume of the precipitate remained present below the surface. In Figure 4(iii) another dissolution morphology was observed, with the precipitate appearing friable and flake-like. Cross sectioning (Figure 4(iv)) and EDS analysis of the precipitate following FIB milling (Figure 4(v)) indicated Nb segregation at the large flakes within the precipitate, but not in other parts of the feature, indicating partial removal of NbC.

As an additional experiment to accelerate the effect of NbC dissolution, a 20Cr-25Ni-Nb end cap specimen was electrolytically etched (6 V polarisation for 30 seconds) in a solution of pH 14.7 NaOH. Such an electrolytic etching method is used to test for the presence of both delta ferrite and sigma phase in steels [25]. SEM imaging of the precipitates following this experiment are shown in Figure 6, indicating similar lamellar-like structures to those witnessed previously in Figure 4 and Figure 5.

4.2.   Time Lapse Microscopy

A set of three precipitates were located and imaged over a set time interval, alongside simultaneous recording of open circuit potential (Figure 7). The open circuit potential recorded during immersion in pH 11.4 NaOH showed an increase in potential within the first 4 hours from -340 mV SCE to -185 mV SCE. Subsequently, the potential decreased up to 11 hours of immersion, which was then followed by a sharp increase in potential from -260 mV SCE to 115 mV SCE for the next 22 hours. The potential was then observed to decrease until a steady potential was reached at approximately -200 mV SCE after 60 hours.

The precipitates on the specimen surface, shown in Figure 8(i), were initially immersed in pH 11.4 NaOH for 95 hours, which showed no visual changes. Following this the electrolyte was dosed to pH 13 for a period of 26 hours, and during this time, modification of the precipitates was observed. By working backwards through the TLM images an approximate time for modification could be calculated. The precipitates showed a colour change after 103 hours total immersion time, shown in Figure 8(i) and Figure 8(ii), corresponding to approximately 8 hours immersion in the higher pH 13 environment. The potential dropped after 85 hours of immersion and subsequently increased to steady potential after 116 hours (~110 mV SCE). The OCP measurement did not show a change in potential at the same time corresponding to the darkening of precipitates observed in Figure 8(i) and Figure 8(ii). Following the experiment, the same region of interest was located and imaged using SEM (Figure 8(iii)). EDS analysis confirmed the presence of Nb within each of the precipitates (Figure 8(iv)). As the precipitates appeared roughened, the specimen underwent further characterisation using AFM to confirm the surface roughening (Figure 9).

4.3   Electrochemistry

4.3.1   NbC Bulk Material

To further understand the effect of NaOH on NbC precipitates, potentiodynamic polarisation experiments were conducted on a bulk sample of NbC material (a sputtering target). Figure 10 shows polarisation curves for NbC specimens immersed in 500 ppm [Cl⁻] in acidic (pH 2), neutral (pH 7) and basic pH (pH 9 and 11.5). The results from the experiment are tabulated in Table 2. Figure 11 shows the surface of the NbC specimen following polarisation in pH 11.5 with 500 ppm [Cl⁻], which shows locations in which grains have been removed.

In order to understand if there was any influence of galvanic coupling between the NbC precipitates and the matrix, NbC and 304 stainless steel specimens were electrically coupled and immersed in 500 ppm [Cl⁻] at neutral pH. Figure 12 shows the galvanic current of the coupled electrodes and the coupled potential. The pH of the electrolyte was increased to pH 11.5, using NaOH, after ~7 hours). This resulted in a potential drop from +20 mV SCE to -220 mV SCE, and a corresponding increase in galvanic current, which indicated that corrosion had occurred.

4.3.2 Effect of Sodium Hydroxide on the 20Cr-25Ni-Nb Alloy

Figure 13(i) and Figure 13(ii) show polarisation curves from experiments in [Cl⁻] ranging from 0 to 10,000 ppm, with and without pH 11.4 NaOH pH adjustment respectively. In both cases there was a general trend toward less positive values for the E_b with increasing [Cl⁻], however in both cases E_{corr} also varied.

In a separate experiment 20Cr-25Ni-Nb specimens were immersed in 50 ppm [Cl⁻] electrolyte at pH 9 and pH 11.5 (NaOH) at 50°C and 60°C. Table 3 shows the passive potential range ($\Delta E = E_b - E_{corr}$) calculated for each environment. At pH 11.5 ΔE was approximately 100 mV greater than that for pH 9 at both 50°C, and even greater at 60°C. This indicates that the sensitised 20Cr-25Ni-Nb specimen is passive over a larger range of potentials at higher pH.

4.3.3 Impact of High pH Pretreatment

To evaluate the effect of NaOH on NbC precipitates with time, EIS measurements were recorded for 20Cr-25Ni-Nb end cap specimens immersed in pH 11.4 NaOH, pH 13 NaOH, and ultra-pure water. Nyquist and Bode plots for specimens in pH 11.4 and pH 13 NaOH are shown in Figure 14. The Nyquist plots show one time constant for each of the curves in each environment. A larger Z'' was measured in the pH 11.4 environment compared to the pH 13 environment. After 200 hours immersion in pH 11.4, Z'' drops from ~-1E7 Ω to ~-1.25E6 Ω at 300 hours. A similar drop is observed in the pH 13 environment, but the effect is minimal, owing to the smaller measured Z''. It is not known why a decrease was observed. Carbonation of the electrolyte is likely to have occurred over the 15 day timeframe (given that the cells were not fully covered) which would have led to an increase in solution resistance as the solution conductivity drops. The Bode plots however show only a very small increase in IZI at the low frequency (corresponding to solution resistance) at 300 hours, so the decrease in Z'' is considered to be a result of another factor.

EIS data was fitted to a simple Randles cell (an R(RC) circuit), commonly used for bare metals (a capacitor was used instead of a constant phase element). By fitting an equivalent circuit the charge transfer resistance (R_{ct}) was obtained (plotted in Figure 15 for the pH 11.4 and pH 13

NaOH experiments). Error bars are present on both curves, but the error is much smaller for the pH 13 environment.

Following immersion for 15 days in pH 13 NaOH (the 'pretreatment') potentiodynamic polarisation experiments were undertaken in 1, 100 and 1000 ppm [Cl⁻] at near-neutral pH. The results of potentiodynamic polarisation are shown in Figure 16, allowing a comparison to be made between specimens with and without high pH pretreatment. Scanning electron microscopy was used to characterise the specimens following the corrosion experiments in 100 ppm [Cl⁻] (Figure 17). Imaging of the control specimen showed the presence of IG pitting corrosion, with initiation sites centred around intergranular Nb-rich precipitates (Figure 17(i, ii)).

4.3.   Additional Characterisation of Nb-rich Precipitates

Further analysis of Nb-rich precipitates was conducted using a combination of SIMS and SEM-EDS to evaluate if these precipitates were true carbides (NbC), or predominantly metallic Nb. The SIMS results conducted on the thermally sensitised 20Cr-25Ni-Nb alloy are shown in Figure 18(i), and Figure 18(ii). Bright areas in these figures show locations where Nb and C are in abundance. These have been annotated with black arrows to show some of the locations where there is both Nb and C enrichment (i.e. indicating the presence of NbC). Figure 19 shows an SEM image, and associated EDS mapping analysis of a precipitate on the thermally sensitised alloy following milling by FIB-SEM, this showed that the precipitate was rich in Nb and C. EDS point analysis undertaken on the thermally sensitised alloy in a recent publication by the current author [5], again following FIB milling, is shown in Figure 20. The SEM image (in secondary electron mode) is shown in Figure 20(i), along with the EDS spectrum (Figure 20(ii)) and composition from EDS (Table 4). The EDS spectrum shows the large Nb peak, along with the C peak at ~0.3 KeV.

5. Discussion

In this paper NbC precipitates are shown to be susceptible to limited dissolution in high pH NaOH, both though immersion experiments, and through electrochemical acceleration (polarisation). Immersion in NaOH resulted in the partial modification to the Nb-rich precipitate, and multiple EDS analyses still showed the presence of Nb at precipitate sites following immersion. Some of the low C signals observed during EDS mapping is likely a result of C contamination of the surface, leading to a higher-than-normal C reading (Figure 8(v)). Additional analyses have shown the presence of Nb and C at these precipitates, indicating they are most likely NbC (Figure 18-20).

AFM imaging confirmed that the precipitates were still present following immersion in pH 13 NaOH and appeared modified, with lamellar strand-like structures. AFM analysis conducted following the TLM NaOH experiment showed that the majority of troughs within the precipitates were ~60 nm deep, and partial dissolution of the precipitate appears to have followed scratch marks on the metal surface. It is likely that the specimen preparation process caused some small surface scratches along the precipitates. Darkening of the precipitates was observed during the TLM experiment, and thus modification of the precipitates must be attributed to the change in chemistry from pH 11.4 to pH 13 NaOH. This occurred at the small surface scratches which must have been present before immersion, and not solely because the prior mechanical preparation alone. It is postulated that dissolution first occurs along surface

scratches present on the NbC, and then onto areas of the NbC precipitate that are perhaps less resistant, leaving behind a lamellar bridge-like network. Volta potential mapping of NbC precipitates and the surrounding matrix using SKPFM (Figure 5(ii)), indicated that some locations of the precipitate were up to 20 mV more noble than the surrounding matrix, in line with past work by Clark et al [5].

Reviews [26] [27] of the C-Nb system indicate two stable phases, cubic NbC and hexagonal Nb_2C. The NbC phase, which is stable at temperatures below 3600°C (at ~40-50 At % C), starts a phase transformation upon cooling from the cubic to trigonal structure at 1050°C, forming Nb_6C_5. At this temperature there is an order-disorder transformation where atomic planes are stacked alternatively with and without defects. This could help to explain the evolution in surface modification; given that the alloy was solution annealed at a similar temperature (1150°C). Transmission electron microscopy, combined with electron diffraction, or electron backscatter diffraction using an SEM, would allow the crystal phase of the precipitates to be determined [28] [29]. Such diffraction techniques were not available to the authors of the present work, and, as such, could be explored as part of a follow-on investigation.

A survey of the literature has shown no links to the use of NaOH as an etchant for NbC; and neither has there been any known reports of the accelerated NbC dissolution / modification in NaOH at pH 13, other than that reported here. Greenwood and Earnshaw [30] indicate that NbC, an interstitial carbide, should have the general formula Nb_2C (Smith et al [27] and Cuppari and Santos [26] indicate that the C-Nb system can take two stable phases: NbC and Nb_2C). Those authors allude that the majority of interstitial carbides are highly inert and insoluble with water[3], compared to transition element carbides which are more reactive, being rapidly hydrolysed in dilute acids and in some cases even water. Despite being more reactive than interstitial carbides, Warren [31] reported no reaction of transition metal carbides (TiC, ZrC and SiC) with boiling pH 14.6 NaOH. A book of metal etchants [32], indicated that the NbC system may be slowly etched by use of hot H_2SO_4, (despite elemental Nb being passive in this environment [21]). Alternatively etching by use of HF was recommended, which slowly etches the material. Sulphamic acid (20%) or buffered HF[4] solution for light removal of NbC was also suggested. Given the information from the references on NbC, Nb_2C and other transition metal carbides, one would not expect dissolution, which in the work described here is greatly accelerated at pH 13 compared to pH 11.4. Therefore, the observed behaviour might suggest that the characteristics of these Nb-rich precipitates reflect the behaviour of metallic Nb rather than the carbide. Lyon discussed the corrosion of Nb and its alloys in [21], with only little literature on the electrochemistry of Nb other than in extreme environments, Lyon concluded that the element is possibly passive in most environments. Elemental Nb spontaneously forms a very stable passive oxide film (Nb_2O_5) allowing it to passivate in almost all environments at standard temperature and pressure, giving exceptional corrosion resistance. It has very good corrosion resistance in salt solutions but is not resistant to strong bases where the niobium pentoxide (Nb_2O_5) and niobate / metaniobate (NbO_3^-) are stable species, which causes activation of the metal through passive film dissolution (reformation and dissolution of the passive film). In NaOH, Lyon states that Nb becomes active at concentrations above 10% (pH 14.4), at temperatures above 25°C, forming NbO_3^-. Robin [24]

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[3] Greenwood and Earnshaw [26] do note that most interstitial carbides show degradation in HF and concentrated HNO_3 environments
[4] This is also known as a buffered oxide etch

studied the corrosion of commercially pure Nb in bases, as a function of temperature and concentration. The study found that the element underwent corrosion at the free corrosion potential in NaOH at 10 wt% (pH 14.4). The original Pourbaix atlas provides an insight into the metallic Nb-water system at 25°C [33]. Pourbaix predicted passivity in basic conditions, forming niobium pentoxide (Nb_2O_5). Pourbaix also indicated that Nb metal is resistant to corrosion to common acids stating that "caustic alkalis are without action", and therefore Nb_2O_5 must act as a protective oxide. Due to the lack of thermodynamic data at the time of publication by Pourbaix, only a rough guide could be given for dissolved species, suggesting the presence of NbO_3^- and Nb_2O_5 ions at high pH (pH 12 and above). In 2007 Asselin et al [22] provided an update to the metallic Nb-water system, showing a domain above pH 6.5 where soluble NbO_3^- is the dominant species. That said, Asellin et al said it was not likely for soluble NbO_3^- to form in most environments, and that there is evidence that Nb_2O_5 becomes soluble if exposed to strong bases [23]. Dulski [34] also provided evidence that Nb is soluble in NaOH solutions for elemental separation purposes.

In order for the precipitates to be predominantly metallic Nb with a small mix of NbC or Nb_xC_y phases, an excess of unreacted Nb would have to be present as solid solution within the steel matrix, in this case enabling metallic Nb to precipitate at NbC/Nb_xC_y sites. If this were to happen one would expect: (i) very low C in the steel matrix (given the high affinity of Nb for C), and (ii) the presence of elevated Nb levels within the steel matrix (because the steel matrix would be saturated with Nb), (iii) metallic Nb precipitates. The EDS analyses performed in this work have not shown elevated levels of Nb in the steel matrix, and SIMS has confirmed the presence of C at Nb precipitate sites (Figure 18-20). Therefore on the basis of the available characterisation performed, one must conclude that these precipitates are most likely NbC or Nb_xC_y phases. More advanced chemical mapping such as atom probe tomography (APT), nanoscale secondary ion mass spectrometry (NanoSIMS), or nanoscale electron spectroscopy for chemical analysis (NanoESCA) would give further insight into the composition of the Nb_xC_y phases. In particular NanoESCA would allow the different bonding states to be observed following pretreatment. This would allow identification of other Nb-rich phases (if present), which may be more or less resistant to NaOH. A comparison could then be made with irradiated material to determine if the same phases are present.

An investigation using NbC sputtering target material was undertaken. The greatest current densities were observed in an acidic environment (HCl, pH 2), which was approximately two orders of magnitude greater than in the neutral (pH 7) and basic (pH 11.5) environment. OCP in the pH 2 environment was more negative than in the neutral and basic environments (pH 2 was -245 mV, pH 11.5 was -210 mV relative to the OCP measured at pH 7). The transpassive current density at pH 11.5 was slightly greater than in the neutral environment. The pH 11.5 environment was the only one in which a distinct breakdown potential (E_b) was observed (E_b was defined as a sharp and continuous increase in current density). Imaging undertaken following the experiment (Figure 10) indicated that the corrosion mechanism for NbC in pH 11.5 is either intergranular or via dissolution of the binder phase (often used for producing sputtering targets). Potentiodynamic polarisation of 20Cr-25Ni-Nb in low [Cl^-] (0, 1, 10 ppm [Cl^-]) showed that E_{corr} was stable at -100 mV SCE in neutral conditions, compared to -300 mV SCE when dosed to pH 11.4 using NaOH. An increase in current density through the transpassive region with increasing [Cl^-] was observed in neutral environments, but in pH 11.4 NaOH the current density measured at E_b (in neutral pH) showed no sharp increase until [Cl^-] reached 100 ppm, the threshold concentration for pitting to occur. Experiments conducted in

pH 11.4 NaOH showed both a greater transpassive current density and greater current density at E_b. Importantly the current density in the transpassive region does not increase with [Cl⁻], as it is shown to in the neutral environment.

EIS measurements conducted on specimens during a pretreatment period (2 weeks immersion) showed that R_{ct} was greatest in the pH 11.4 environment (interestingly, R_{ct} was lower for the pH 13 environment). R_{ct} showed a gradual increase with time for the pH 13 environment, starting at <1 MΩ, then stabilising at 2 MΩ (~200 hours), however after ~340 hours R_{ct} decreased. In comparison, the pH 11.4 environment showed a much greater increase in R_{ct}, starting at 2 MΩ, then after ~50 hours immersion increased to 10 MΩ. This stabilised for a period of ~50 hours, and started another increase, albeit slower, to a maximum R_{ct} of 22 MΩ at ~270 hours. This then decreased to as low as 2 MΩ at ~300 hours. Given that R_{ct} is inversely proportional to the corrosion rate, the results indicate that the pH 11.4 environment is most beneficial for preventing corrosion. This supports past industrial plant experience which has shown that NaOH dosing (pH 11.4) has a positive impact on inhibiting corrosion [19]. These pretreated specimens were then subjected to potentiodynamic polarisation in chloride electrolytes. Post corrosion observation of specimens immersed in 100 and 1000 ppm [Cl⁻] showed signs of crevice corrosion alongside IG pitting. In most of the experiments E_b was not distinct, likely due to crevice corrosion at the higher [Cl⁻]. The polarisation curves showed there is a trend of increasing current densities with [Cl⁻], but importantly the experiment did not show a benefit to using a high pH pretreatment. The 1 ppm [Cl⁻] experiments showed passive current densities with no discernible difference between the two types of specimens. Whilst the 1000 ppm [Cl⁻] experiment showed notably higher current densities, compared to the lower concentrations, there was no decrease in current density with pretreated specimens. It was only in the 100 ppm [Cl⁻] experiments where a difference was observed, where all high pH pretreated specimens showed a higher passive current density throughout. In regard to OCP, pretreated specimens were more negative by ~40 mV at 1 ppm, ~100 mV at 100 ppm [Cl⁻], and similar at 1000 ppm [Cl⁻]. IG pitting occurred in close vicinity to NbC precipitates (Figure 17(iii-viii)). It is proposed that these IG pit sites initiated at locations in which Nb-rich precipitates had been partially dissolved during the pretreatment phase, forming initiation sites for localised corrosion. These findings are in agreement with past work by Clark et al [5] who showed IG pitting initiation around NbC precipitates. Al-Shater et al [4] showed evidence of the pit-to-crack transition on thermally sensitised 20Cr-25Ni-Nb when polarised, with pits acting as nucleation sites for intergranular SCC initiation. These small pits observed here may not only serve as initiation sites for IGC, but initiation of intergranular SCC in the presence of residual or applied stresses.

6. Conclusions

A range of techniques including: immersion, TLM, AFM, d.c. and a.c. electrochemical experiments were utilised in this paper to ascertain the effect of NaOH on NbC precipitates. The results indicate that pH 11.4 / 11.5 NaOH has a beneficial effect on corrosion resistance by suppressing the transpassive current density when chloride is added to the system. Post-immersion characterisation indicates modification and dissolution of the NbC precipitates in NaOH, which is greatly accelerated at pH 13. Complete dissolution of precipitates was not observed but there is evidence in this paper that small pits form at these voids. A high pH 13 pretreatment was sufficient to cause modification and dissolution of Nb-rich precipitates in

20Cr-25Ni-Nb stainless steel, but the NaOH pretreatment did not increase short-term resistance to localised corrosion.

It is proposed that changes to NbC precipitates initiate at fine surface scratches and then proceeds either by: (a) more susceptible areas of the carbide or (b) a different phase present in the carbide. In this paper, the change in NbC from an intact precipitate to a lamellar structure is observed over a 4 day period. Over 28 days exposure further dissolution is observed.

7. Acknowledgements

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Tables:

	Fe	Cr	Ni	Nb	C	Si	Mn	S	P	N	Mo	Ti	B
Tube	Bal	19.7	24.6	0.65	0.049	0.57	0.75	<0.003	0.01	0.015	0.01	N/D	N/D
End cap	Bal	19.4	25.5	0.61	0.052	0.53	0.70	0.008	0.004	0.1	0.03	0.035	0.0007

Table 1 Composition of AGR fuel cladding tube and end cap obtained using inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (values in wt %, N/D = not detected).

pH	E_{corr}, mV	E_b, mV
2	-383	N/D
7	-138	N/D
9	-155	N/D
11.5	-339	710

Table 2 Summary of corrosion parameters following polarisation experiments at room temperature on NbC sputtering target specimens (N/D = not detected).

Electrolyte temperature, °C	pH	ΔE, mV
50	9	685.7 ± 5.2
50	11.5	784.5 ± 21.6
60	9	589.6 ± 32.4
60	11.5	775 ± 26.9

Table 3 Change in potential (Eb-Ecorr) taken from potentiodynamic experiments for sensitised 20Cr-25Ni-Nb stainless steel at elevated temperature in 50 ppm chloride.

	C K	O K	Al K	Si K	Cr K	Fe K	Ni K	Ga L	Nb L	Totals
Wt%	9.48	4.91	0.64	0.39	2.21	3.86	1.66	0.51	76.35	100
At%	37.54	14.59	1.13	0.66	2.02	3.28	1.35	0.35	39.08	

Table 4 EDS results corresponding from the EDS point analysis in Figure 20(i). C and Nb are highlighted in green.

Figure Captions:

Figure 1 Flow diagram showing the main experiments and characterisation performed at each of the main stages.

Figure 2 Backscatter electron image of NbC precipitates (i) 3 days in pH 11.5 NaOH, (ii) 7 days immersion in pH 11.4 NaOH.

Figure 3 (i) NbC precipitates (tilted view) following immersion in pH 13 NaOH for 4 days, (ii) FIB cross section, (iii) corresponding EDS false colour map for Nb following FIB milling.

Figure 4 (i, iii) Precipitates following immersion in pH 13 NaOH for 28 days, (ii, iv) and after FIB milling, (v) EDS overlay for Nb following FIB milling.

Figure 5 AFM topography maps of an NbC precipitate following immersion in pH 13 NaOH for 4 days. (i) AFM topography map, (ii) SKPFM map (brighter areas more noble).

Figure 6 NbC precipitates following electrolytic etching in pH 14.7 NaOH (20 wt%) and EDS mapping.

Figure 7 Open circuit potential recorded during the time lapse microscopy experiment in pH 11.4 (green line) and in pH 13 (red line) NaOH. Arrows show the time in which the electrolyte was changed to pH 13 and the time at which modification of the precipitates was observed.

Figure 8 (i) Still image from the TLM experiment in pH 11.4 NaOH, (ii) still image from the TLM experiment following the introduction of pH 13 NaOH, (iii) SEM micrograph of the set of precipitates following the experiment (iv-vi) EDS mapping of the precipitates following the experiment.

Figure 9 AFM topography map of precipitates observed in time lapse microscopy experiment (image rotated 90° clockwise to match optical and SEM images).

Figure 10 Polarisation curves for NbC in 500 ppm [Cl$^-$] at different pH.

Figure 11 Surface of the NbC specimen following polarisation in 500 ppm [Cl$^-$] at pH 11.5.

Figure 12 ZRA experiment of NbC coupled with 304 stainless steel in 500 ppm [Cl$^-$] at room temperature, pH 7. After 7.3 hours pH 11.5 NaOH was introduced. The left axis shows the coupled potential (red), and the right hand axis shows the galvanic current (purple).

Figure 13 Potentiodynamic experiments in chloride electrolytes: (i) without NaOH, (ii) with 2.5 mM dm^{-3} NaOH (pH 11.4).

Figure 14 Bode and Nyquist plots for EIS experiments in pH 11.4 and pH 13 NaOH environments over a 12 day period (0 ppm [Cl$^-$]).

Figure 15 Charge transfer resistance for specimens immersed in pH 11.4 (orange curve) and pH 13 (blue curve) NaOH environments derived from EIS data fitting. Error bars are shown for both sets of results.

Figure 16 Potentiodynamic experiments in 1, 100 and 1000 ppm [Cl$^-$] using 15 day pretreated specimens (blue curves), and control specimens (yellow curves).

Figure 17 Example intergranular pits imaged following polarisation in 100 ppm [Cl$^-$] for a control specimen (i, ii), and pretreated specimens (iii-viii). The red arrows highlight Nb-rich precipitates, confirmed by EDS analysis. These specimens were sputter coated with Au prior to imaging.

Figure 18 Elemental maps obtained by SIMS for the thermally sensitised alloy in cross section view (i) Nb, (ii) C. Bright areas denote locations of enrichment. Black arrows show some of the locations where there is Nb and C enrichment.

Figure 19 EDS mapping following polarisation in 1000 ppm [Cl$^-$]. (i) Secondary electron image of a precipitate within the thermally sensitised alloy, milled using a FIB-SEM. EDS analysis was undertaken within the purple box, (ii) Nb, (iii) C, (iv) Cl, (v) Na, (vi) O, (vii) Ni, (viii) Fe, (ix) Cr. White arrows in (i, ii, iii) show the location of the precipitate.

Figure 20: EDS spot analysis of an NbC precipitate on thermally sensitised 20Cr-25Ni-Nb stainless steel following milling with a FIB-SEM. (i) secondary electron image, (ii) corresponding EDS spectrum. Reproduced from [5][5].

[5] Reprinted from Corrosion Science 108365, R. N. Clark, J. R. Searle, T. M. Martin, W. S. Walters and G. Williams, The Role of Niobium Carbides in the Localised Corrosion Initiation of 20/25/Nb Advanced Gas-cooled Reactor Fuel Cladding, Copyright (2019), with permission from Elsevier