

Ageing of Nuclear Fuel Cladding in Advanced Gas-Cooled reactors

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Abstract

Within the United Kingdom a significant contributor to electricity generation for the national grid is nuclear power. Due to improvements in technology many current nuclear reactors have received lifetime extensions, or are applying for them in the future. In order to ensure the safe running of these reactors and to ensure that all waste produced is processed and stored safely, it is important that all aspects of the process are understood.

In the reactor the uranium dioxide fuel is held inside stainless steel fuel rods. The behavior of this steel must be well understood, especially on removal from the reactor, as the fuel is air cooled, transferred to containers, transported and submerged in a pond to cool, and shield radiation. It is important that the physical properties of the steel can withstand this transportation and that it will not corrode and rupture in the cooling ponds.

The following body of work considers the effects of time in reactor of the 20% chromium, 25% nickel, niobium-stabilised stainless steel used to clad the uranium dioxide pellets and form fuel rods. Samples of the steel were held at 350°C, 550°C, 750°C and 850°C for 1000 hours and subsequently examined using scanning electron microscopy, scanning transmission electron microscopy and energy-dispersive x-ray spectroscopy to determine changes in the microstructure and precipitates present. Thermodynamic equilibrium software Thermo-Calc was also used to predict phases present and predict the effects of increasing carbon content on its microstructure.

This work observed development of G-phase in the sample held at 750°C for 1000 hours and coarser niobium carbide particles than the as-received steel in all treatments. This contrasts with observations in literature which saw more dramatic transformations, either in the form of greater variety of precipitate phases, or a much higher rate of transformation of niobium carbide to G-phase.

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1 Introduction

Nuclear power plants are used to generate approximately 20% of the electricity used in the United Kingdom. Currently, 14 of these are in operation, all of which are Advanced Gas-Cooled Reactors. The uranium dioxide fuel pellets, used to generate heat by way of fission, are packaged inside an austenitic, 20% chromium, 25% nickel, niobium-stabilised stainless steel tube. The steel cladding is approximately a metre long and has 12 small fins machined into its outer surface to improve heat exchange with, and flow of, the carbon dioxide gas coolant that flows upwards through the reactor.

The composition and initial annealing treatment of the steel are such that there is a dispersion of niobium carbide throughout it. This prevents the chromium in the steel from forming chromium carbides, ensuring that it forms the passivation layer on the surface that is characteristic of stainless steels, preventing corrosion. However, the environment within an AGR is extreme, with a range of temperatures between 350°C and 800°C possible in addition to the complex radiation field generated by nuclear fission and the highly radioactive fission products. This environment can cause transformation of the niobium carbide phase into G-phase and potentially allow for the formation of chromium carbides, which can deplete chromium from the passivation layer and cause sensitisation, that is, open the steel to corrosion. Microstructural changes can also affect the physical properties of the steel, with the formation of different secondary phases with different properties and morphologies affecting the strength of the steel overall. Similarly, radiation can cause to embrittlement of the steel through introduction of helium (α -particles) and the creation of voids within the steel matrix.

The many different outcomes for the steel based on its location in the reactor, composition, and reactor conditions need to be understood as they affect the safety of the steel when in reactor and when the fuel rods are removed at the end of their lifetime (approximately 5 years). Once out of the reactor, the fuel rods must be transported, packaged, cooled and stored. A fuel rod fracturing during handling, or corroding while in a cooling pond, would cause a release of nuclear waste into the environment.

As the current operating AGRs in the UK approach the end of their lifetimes, some have reduced their output, while others are looking to extending their lifetimes due to improvements in technology. With these changes, it is important to revaluate the behaviour of the steel to ensure safety at every stage in the nuclear fuel cycle.

Thermodynamic calculations were used to determine what secondary phases might precipitate during heat treatments and suggest that the carbon-rich environment within a reactor could lead to favourable conditions for chromium carbides. The experimental work demonstrated that the samples observed appear to have a more stable niobium carbide phase than those seen in literature [1], [2]. The only transformation observed was a coarsening in the niobium carbide particles and the occurrence of G-phase after heating at 750°C for 1000 hours.

2 Literature Review

2.1 Advanced Gas-Cooled Reactors

The United Kingdom produces approximately 20% of its electricity using nuclear power plants [3]. Of the nine plants, seven are Advanced Gas-Cooled Reactors (AGRs). With two reactors at each plant, there are 14 operational AGRs in the UK [4]. Most of these reactors are due to go offline and start their decommissioning by 2030; however, there may be lifetime extensions for some of these reactors.

AGRs power plants produce electricity in the same way that conventional power stations, by producing steam to spin a turbine. However, rather than using combustion to heat the water, an AGR uses a gas-cooled nuclear reactor to generate heat. The reactors operate using uranium oxide fuel which has had its uranium-235 isotope content enriched from natural levels. Uranium-235 is the most fissile isotope of uranium and its fissile cross-section is greatest with thermal neutrons. When a thermal neutron is absorbed by a U-235 nucleus it undergoes fission, that is: splitting into two smaller nuclei while ejecting free neutrons and releasing energy. The neutrons are moderated by graphite in the AGR; their energy is reduced so that they can cause the fission of another nucleus. The energy heats the inside of the reactor and is extracted using a coolant, in the case of AGRs this is carbon dioxide gas. The heat is then transferred to a second cooling circuit to prevent any contamination, which drives a turbine to generate electricity.

This process creates a harsh environment within the reactor, with very high temperatures and high levels of radiation, not only from the fission of uranium, but also the fission fragment nuclei. After it has reached the end of its time in reactor the fuel is stored in ponds, which cool and shield the radiation the spent fuel generates.

2.1.1 Fuel Arrays

AGRs use cylindrical, enriched uranium dioxide, ceramic pellets with a hole along the centre, as fuel. The pellets are stacked inside cladding which is an austenitic stainless steel tube with an inner diameter of 15 mm, a thickness of 0.38 mm and a length of around 900 mm. They have 12 ridges machined into the outside surface in order to increase heat transfer and improve gas flow over the surface. 36 of the resulting fuel pins are held in an array by steel bracers within a graphite sheath. This acts as a moderator and protection for the fuel rods. Figure 2.1 is taken from Barrable et al. [4] and shows the components of a fuel element. Fuel elements are stacked eight high and held together by a steel tie bar threaded through their centres to form a stringer. Stringers are placed in fuel channels within the moderator, in the core. For AGRs, graphite bricks act as the moderator, carbon dioxide is the primary coolant and high-boron steel control rods are used to control the neutron flux [5].



Figure 2.1: A schematic of a fuel element, taken from Barrable et al. [4].

2.1.2 In-Situ

Within a reactor the conditions are extreme. The coolant circulating through the core has a mean inlet temperature of approximately 340°C and a mean outlet temperature of around 640°C [5]. The circulation of the coolant from inlet to outlet can be seen in Figure 2.2. As this is the coolant temperature, the fuel and its cladding can be expected to be at a higher temperature than this. The cladding can, in places, reach temperatures up to 800°C [6]. Adding to the extreme environment is the complex radiation field within the reactor core. This is due to the neutron flux of a spectrum of energies from the fission process and moderation, and the radiation emitted by the fission products.



Figure 2.2: A simple diagram of the gas flow and some components within an AGR, taken from Nonbøl [5].

2.1.3 Post-Reactor

After the fuel has achieved its required burn up (refuelling happens after approximately five years [7]) it is removed from the reactor and placed in on-site storage. Initially the removed fuel assemblies are placed in a dry decay (or buffer) storage where the short-lived fission products can decay, reducing the activity of the fuel elements over about 30 days. After this the fuel elements are dismantled and the rods from fuel elements are placed in steel cans, with one can holding three elements' worth of rods (108 rods). The cans are then placed into on-site cooling ponds, where they remain for around 80 days. After this they are either held in on-site dry storage or transported to other facilities for storage or reprocessing [5]. There will often be a series of storage ponds involved in the spent fuel route [8].

A report from Kyffin [8] looks in particular at the different storage ponds used at Sellafield. The THORP (Thermal Oxide Reprocessing Plant) Receipt and Storage pond has water dosed to pH 11.4 in order to prevent corrosion of steels and to help delay the dissolution of radionuclides in the fuel, should the containment fail.

2.2 Stainless Steel

The steel cladding which contains the uranium was chosen over the previous Magnox (magnesium non-oxidising) cladding, a magnesium-aluminium alloy, to withstand the higher temperature in the AGR core. As a result of the higher neutron capture cross-section of the stainless steel, the uranium fuel had to be enriched in order to achieve criticality [6].

The steel composition currently used in reactors is nominally 20% Cr, 25% Ni, Nb stabilised (20Cr-25Ni-Nb) stainless steel [1]. The chromium forms a passivation layer of chromium oxide on the

surface, preventing corrosion [9]. The nickel is included in the alloy as a y-stabiliser: it increases the austenite phase within the steel. Without a phase stabiliser austenite is only present in carbonsteel above the eutectoid temperature of 723°C. Chromium further restricts austenite formation, while carbon promotes it [10]. These effects are illustrated in Figure 2.3, where carbon is shown affecting the austenite region (γ -loop). Figure 3a) shows the Fe-Cr phase diagram with no carbon, while Figure 3b) shows a close-up of the γ -loop with 0.4% added carbon. There is a more complex variety of phases and phase mixtures, the shape of the loop has been altered, and the austenite region now extends to concentrations with nearly 20% chromium. Competing effects must be balanced to achieve the desired properties in the steel, which leads to the composition used. Austenite is desirable as it is easy to work during manufacturing and it does not undergo a ductile/brittle transition as ferrite does. The niobium is in the steel to act as a stabiliser and prevent sensitisation. The steel contains a small amount of carbon, which readily forms metal carbides at certain temperatures. The niobium bonds preferentially with the carbon, preventing it from forming chromium carbides which would cause chromium depletion, weakening the passivation layer and sensitising the steel [11]. This helps prevent intergranular corrosion during the service life of the steel [10].

While in the reactor, the cladding's ductility is reduced due to neutron irradiation and helium embrittlement. The stainless steel cladding is vulnerable to oxidation, leading to the formation of different oxides at its surface. The inner surface, in contact with the fuel pellets, is also at risk of damage from corrosive fission products [8].



Figure 2.3: 3a) shows the iron-chromium phase equilibrium diagram and figure 3b) shows the ironchromium phase diagram with 0.4 wt.% carbon included. The α -phase is ferrite, γ represents austenite, σ shows the σ -phase and L is the liquid phase. K₀ is M₃C, K₁ is M₂₃C₆ and K₂ is M₇C [12].

2.2.1 Effects of Temperature

At temperatures above around 500°C, niobium can form other phases such as G-phase ($Ni_{16}Nb_6Si_7$) and $NiNb_3$. If, at elevated temperatures, these phases are formed it can deplete niobium in the bulk, allowing for free carbon to form other metal carbides, including chromium carbide. This is problematic as the steel can reach temperatures between 400 and 800°C in the reactor.

Earlier work looking at thermally ageing steels with the same nominal composition (20Cr-25Ni-Nb) observed that niobium carbide exists at grain boundaries and is transformed to M_6C during a heat treatment at 650°C [13]. There are also observations of σ -phase formation and $M_{23}C_6$ after long ageing periods at 700°C [14]. However, the latter phase was not stable over long heat

treatments. In the matrix, NbC was seen to nucleate at dislocations and transform into M_6C . The precipitate M_6C is also discussed by Sourmail[10]. It is described as generally only forming after long ageing periods and having its presence linked to other precipitates. It can contain various metal ions: iron, chromium, niobium and molybdenum being most common. It is also possible for silicon to be incorporated into this phase, forming M_5SiC .

Powell, Pilkington and Miller [1] investigated the effects of heating steel of the same nominal composition as used in this work to temperatures between 500 and 800°C. The full composition can be seen in Table 2.1. The study used one annealed sample and one thermo-mechanically treated steel with a residual dislocation network.

The precipitates found in the heat treated samples from [1] are displayed in Figure 2.4 in a timetemperature-precipitation diagram (TTP). The steel initially contains niobium carbonitride (Nb(C,N)), which can be seen to transform into various other precipitates over time and with elevated temperature.

Initial micrography [1] of the unheated material showed some Nb(C,N) along the grain boundaries, which increased with ageing. Within the grains, Nb(C,N) was found to precipitate on dislocations. Nb(C,N) did not appear within the matrix until after other precipitates were present at the grain boundaries, despite Nb(C,N) being quick to form at the grain boundaries. Most of the Nb(C,N) precipitates were fine, coarsening at large ageing times. No formation was observed above 750°C. G-phase nucleated on grain boundary Nb(C,N), growing quickly due to the ease of transport of silicon and nickel along the grain boundaries. G-phase was also found in the matrix where Nb(C,N)

Element	Al	В	С	Со	Cr			
Mass Percent	0.006	0.0003	0.037	0.003	19.36			
Element	Mn	N_2	Nb	Ni	Р			
Mass Percent	0.74	0.01	0.68	24.38	0.007			
Element	S	Si	Та	Ti	Fe			
Mass Percent	0.007	0.61	0.003	0.055	54.102			

Table 2.1: The composition, in weight percent, given for the steel cladding examined by Powell, Pilkington and Miller [1].



Figure 2.4: A time-temperature-precipitation graph reproduced from Powell et al. Each curve represents the point at which a particular precipitate was first observed, either at the grain boundaries or in the matrix [1].

had nucleated, although these areas took much longer to transform due to the reduced mobility away from the grain boundaries. $M_{23}C_6$ was not expected due to the amount of niobium in the steel; however, it was observed. The formation of $M_{23}C_6$ seems to be linked to the existence of Gphase, although after formation its particles did not coarsen over long ageing periods. It is likely linked to the G-phase as the niobium is taken into the silicide G-phase, increasing the carbon and nitrogen concentrations in those areas until metal carbides are favoured. σ -phase, an intermetallic phase of varied composition, was found mainly at grain boundaries. The temperature range it exists in agrees with the Fe-Cr-Ni phase diagram [15] in that the σ -phase occurs over a temperature range of 575-700°C. Other precipitates discussed here may exist outside the temperature seen in Figure 2.4, but σ -phase is expected to be confined to the temperatures shown here due to its thermodynamic stability. The formation of σ -phase also seems to be associated with G-phase. This is possibly because G-phase contains nickel, an austenite former, and the removal of nickel makes the formation of σ -phase possible [1]. Previously G-phase had only been observed in irradiated samples, but this study showed it forming in non-irradiated samples, suggesting that G-phase is not irradiation induced.

Building on this work, Ecob, Lobb and Kohler [2] looked at the formation of G-phase in a steel with a similar composition, shown in Table 2.2. The steel was received having already undergone a 1 h annealing treatment at 930°C in a hydrogen atmosphere. This steel was found to have an equiaxed austenite grain structure. A niobium carbide dispersion was seen at grain boundaries, similar to the niobium carbonitride dispersion seen by Powell et al. Unlike the previous study, niobium carbide was also seen throughout the matrix and G-phase was observed at grain boundaries.

Table 2121 The composition, in weight percent, given for the steer enduling examined by 2005 et an [2].									
Element	С	Cr	Mn	Nb	Ni	S	Si	Ti	Fe
Mass Percent	0.02	20.4	0.70	0.60	25.1	0.007	0.56	<130 p.p.m.	52.613

Table 2.2: The composition, in weight percent, given for the steel cladding examined by Ecob et al. [2].

In addition to looking at steel having undergone this annealing treatment; samples were treated at 750°C and 850°C in an argon atmosphere for 1000 h. Examination of these samples found no NbC either at grain boundaries or in the matrix, but did find growth of G-phase, both at grain boundaries and within the matrix. Using a shorter treatment (278 h) at 750°C, it was concluded that the G-phase formed via the transformation of NbC. The shorter treatment observed reprecipitated NbC, distinguished by its orientation to the matrix. As no NbC was seen after 1000 h, it was assumed that it all transformed into G-phase which leads to Ecob et al. inferring that the G-phase nucleated on the NbC. The only other phase observed was σ -phase, seen at grain boundaries in the 750°C treatment. At no point was $M_{23}C_6$ seen.

Sourmail [10] discussed other possible phases. For example, σ -phase is discussed further and, as well as being seen in association with M₂₃C₆, it is noted that it can also develop independently [16]. The Z-phase (Cr₂Nb₂N₂) has been known to form in high niobium stabilised austenitic steels. It also requires relatively high nitrogen content, which is not the case for this steel according to Powell, Pilkington and Miller [1]. However, Z-phase is seen to form at grain boundaries, usually as a dispersion of particles, at high temperatures and for long ageing times. For example, in a heat treatment by Raghavan et al. lasting 8000h at 593°C on an 18Cr-12Ni steel containing 0.09 wt.% nitrogen, it was seen to be the main precipitate [17]. In work done on a 20Cr-25Ni-Nb steel, the Z-phase was found to evolve from Nb(C,N) in heat treatments of 640h at 850°C [18]. The composition of this steel was different from that in the Powell et al. study, but this, along with the poor understanding of the phase, suggests Z-phase may have a role to play in the evolution on the steel.

Powell et al. believed that, due to their similar structures, G-phase has previously been misidentified as M_6C [1], this claim was reinforced by Ecob et al [2]. and discussed by Sourmail [10]. However it should be possible to distinguish the two by analysing their composition rather than relying on diffraction data only. M_6C has been seen to occur at long ageing times in an 18Cr-8Ni steel: approximately 50000h at 600°C and 2000h at 800°C [19]. There are mixed reports on the occurrence of M_6C , especially when comparing it to the stability of G-phase. It seems that in 20Cr-25Ni steel (as seen previously) G-phase is formation preferable, likely due to the high nickel content.

A known result of heating stainless steels is sensitisation to intergranular attack. This effect is seen in material heated to temperatures between 350 and 520°C due to chromium depletion and nickel enrichment at the grain boundaries [8]. This is also significantly affected by radiation, as discussed in section 2.2.2. Intergranular attack is a concern in the storage ponds used at various points after the fuel is removed from the core. It is also possibly a longer term concern as there are no plans for an ultimate disposal route of spent fuel, so there is no limit on how long waste may be stored. Testing has shown that it is possible to retard, or even completely arrest corrosion using appropriately dosed pond water, but in tests on samples from dosed pond water, a small number of cracks larger than 40 μ m were found on the surface of the cladding [8].

2.2.2 Effects of Radiation

As discussed, sensitisation can occur in stainless steels due to heat treatments altering the microstructure and precipitates. This can lead to a susceptibility to intergranular attack in the post-reactor storage. Sensitisation due to the depletion of the chromium oxide layer by the formation of chromium carbides can also be induced by radiation. Radiation can exacerbate sensitisation by causing more defects in the matrix, providing more nucleation sites for precipitation [20]. In order to investigate the effect of this, various steels have been irradiated using different methods in other studies.

Electron irradiated austenitic steels have been examined previously, noting segregation of metal species due to irradiation around grain boundaries [22, 23]. Ashworth, Norris and Jones [20] performed similar experiments on 20Cr-25Ni-Nb based steels. The irradiation was performed using 1 MeV electrons across high-energy grain boundaries. Samples were irradiated at 7.2 dpa over a range of temperatures. No segregation was seen at 200°C, but at 350 and 450°C the segregation increased with temperature, giving a steep gradient in concentrations of metal ions going from the grain boundary into the bulk as shown in Figure 2.5. In particular there is noticeable chromium depletion and nickel enrichment at the grain boundaries. At 500°C the segregation was also observed. Other samples were heat treated to 450°C and then irradiated over a range time periods giving nominal doses between 0.6 and 7.2 dpa. Below irradiation of 1.8 dpa segregation increased slowly, whereas above that, it increased much more sharply. This is thought to be due to grain boundary migration.



Figure 2.5: Metal ion concentration across a grain boundary in a 20Cr-25Ni-Nb steel after irradiation at 450°C to 7.2 dpa. Adapted from Ashworth et al. [20].

K. Farrell et al. examined an 8Cr-25Ni and 10Cr-30Ni steel irradiated to around 15 dpa using the EBR-II at 575 and 625°C [23]. This was found to cause precipitation at the grain boundaries, identified as G-phase and a Laves phase, which in niobium stabilised steels gives rise to formation of M_6C [10]. Also, in these samples, small gas bubbles were seen at the grain boundaries and on the surfaces of the phases as well as throughout the grains in small quantities. There was noticeable segregation at the intergranular fracture facets and grain boundaries. Silicon, titanium and nickel are enriched at the feature, while iron and chromium are depleted; this effect persists for around 250 nm at the fractures. It can be seen that these segregated elements form the G and Laves phases, both of which are situated at the grain boundaries.

Studies of in-reactor materials are scarce. In 1971, some characterisation of AGR cladding was done by Sumerling and Rhodes [24]. The cladding was taken from a reactor, irradiated to a thermal neutron dose between 1 and 1×10^{21} neutrons/cm² at 650-700°C. M₆C and σ -phase particles were found at the grain boundaries, and finer particles of NbC and Laves phase were found within the bulk.

As well as precipitation, a significant effect of irradiation is the introduction of defects into the microstructure [25]. Above approximately 700°C, this has no significant effect on the microstructure as the defects are not thermally stable; defects anneal out of the steel, leaving it similar to heat treated steel of the same temperature. The only observed defect is gas bubbles, such as helium. Below around 300°C defect clusters, dislocation loops, and network dislocations are typically seen and their presence is largely unaffected by the temperature of the sample during irradiation [26]. Between 300 and 700°C the behaviour is more complex and, as well as the previous defects, leads to precipitation of various species, voids, and gas bubbles [27]. As temperatures increase through this regime, so does the tendency of the defects to anneal out.

Cavity formation, such as void or helium bubble formation, can be a significant defect in irradiated samples, clustering at grain boundaries [28] or, in lower concentrations, dispersing through grains. Cavities tend to occur in the 300 to 700°C temperature range [25]. The densities decrease with increasing temperature due to thermal stability. Void formation is coupled to radiation-induced sensitisation. The formation of cavities is driven by voids in the material, which can be created by radiation damage and grow over time, often by combining with other defects. Helium enters the steel due to alpha radiation, potentially damaging the structure as it does. The helium can either come from alpha decay of fission products in the fuel or activation of boron in the alloy and its

decay into lithium [24], as well as other transmutation reactions [29]. The helium, being a noble gas, does not bind to the lattice and has a low solubility in the structure, so instead tends to nucleate on vacancies in the material and voids. In this way, cavities can form as many helium atoms nucleate on the same vacancy, thereby expanding it, or similarly, helium migrating into a void can cause it to swell [30].

For a type 316 stainless steel, network and dislocation loop density increases gradually up to 300°C, then drops off above this temperature. In the higher temperature region between 300 and 700°C, loops are formed at a relatively low radiation dose, and then reach a density limit at about 5 dpa as seen in Figure 2.6. Once this maximum loop density is reached, it will either remain fairly constant or, at higher temperatures, decrease. The loop and network dislocation density behave similarly, but the network dislocation requires a higher irradiation to achieve peak density. This behaviour can be seen in Figure 2.6, with dislocations increasing to a maximum, then decreasing by orders of magnitude from around 400°C to 800°C [25].



Figure 2.6: The left graph shows the dislocation loop density increasing with dose from fission neutron irradiation between 375 and 400°C. The right hand graph shows temperature dependence of the total dislocation density in 316 stainless steel, irradiated in fast reactors over a range of temperatures. Taken from Zinkle et al. [25].

When it comes to the effect of radiation on precipitates, there are three possible outcomes:

- 1) The phase developing more quickly at a lower temperature and/or in greater amounts (or vice versa), but otherwise being unaffected by radiation. These phases include M_6C , Laves, $M_{23}C_6$, MC and σ -phase.
- The phase could be radiation modified: still occurring in both thermal ageing and during irradiation, but the composition is altered when irradiated. Radiation-modified phases include M₆C, Laves and M₂P.
- Formation of a radiation-induced phase; a phase which is only produced when the steel is irradiated, often under other specific conditions.

The main driving force behind the difference in phases is radiation-induced segregation. Phases formed include γ' (Ni₃Si), MP, M₂P, and M₃P [27]. G-phase is also listed as a radiation-induced phase by Maziasz [27], which is contrary to the findings of Powell et al. [1]. Powell et al. suggest that G-phase has been wrongly put in this category before. However, Maziasz refers to 316 and related austenitic steels, which are significantly different in terms of composition from the 20Cr-25Ni-Nb used in the other study, which could account for the difference [31].

The γ' , G, and some phosphide phases are often induced in type 316 stainless steel by neutron irradiation between 400 and 650°C. This is also the case for similar steels modified with niobium. Without irradiation, these steels (around 600°C) form MC, M₆C and M₂₃C₆ carbides, as well as Laves and σ -phase [31]. The γ' -phase has been seen in fast-neutron irradiated type 316 steels mostly from 400 to 550°C, but also above 600°C for steels with greater than 2 wt.% silicon.

Generally, increased silicon, titanium or niobium concentration increases the amount of G-phase evolution during irradiation in a Fast Breeder Reactor from 400-650°C [27]. The formation of G-phase is often linked with the formation of voids in steels and it generally forms as particles coarser than those of γ' -phase [31]. If there is a greater amount of carbon and less silicon, MC tends to dominate the microstructure for steels containing titanium or niobium for temperatures greater than 500°C [27].

The metal phosphide phases tend to form in a needle-like morphology, generally directly associated with large voids in the structure. They have been seen to form up to around 600°C, but are unstable with large doses (over 30dpa) [31].

Due to these effects of radiation, prediction of which phases will be present may be challenging. Stable phases will depend not only on the composition of the steel, but also the operating temperature of the reactor and the radiation field. Both of these are highly dependent on the position of the fuel rod within the reactor [27].

2.2.3 Corrosion Resistance

One of the possible effects of high temperature and/or irradiation is the development or degradation of oxide layers on the surface of the steel. Due to this, the outer surface of the steel cladding within the reactor is vulnerable to oxidation, leading to changes in the chromium (III) oxide layer, especially on the upper, hotter elements. As well as being affected by the heat and radiation, the inner surface of the cladding can also be damaged by its contact with the fission products and oxidising fuel pellets [8].

The surface of austenitic, 18 wt.% Cr steel forms a M_2O_3 oxide scale, typically a corundum phase, $(Cr,Fe)_2O_3$, that is close to pure chromium oxide. If this is damaged a duplex spinel oxide forms; spinels have the form AB_2O_4 , where A is iron(II) or nickel(II) and B is iron(III) or chromium(III) [32]. This layer grows much more quickly than the M_2O_3 layer, but in the long term it becomes comparable due to a chromium rich layer forming at its base. Peak CO_2 oxidation rates are generally seen to occur between 550-600°C. In 20Cr-25Ni steels, chromium depletion can make the spinel phase the more stable oxide, rather than the corundum phase. This is also why the spinel phase can form when the scale is damaged, the cracking of the scale can cause chromium rich oxide layer found on 18 wt.% Cr steels forms almost immediately on exposure to CO_2 atmospheres [34]. If the oxidation layer covers the surface and remains unbroken, it provides excellent corrosion resistance.

Chromium depletion has been shown to occur due to radiation induced segregation in section 2.2.2 and discussed in section 2.2.1 as happening due to the thermodynamics of various phases. It can also be caused by the precipitation of phases such as $(Fe,Cr)_{23}C_6$ and result in sensitisation of the steel, which can lead to corrosion, especially in the form of intergranular attack. Temperature dependence of sensitisation has been demonstrated by Pande et al. [35] where a 19Cr-8Ni stainless steel was heated to 600°C for 25h, creating a sensitised sample, and 800°C for 48h to generate a stabilised sample. The sensitised sample was found to have significantly more chromium depletion at its boundaries than the stabilised one.

Sensitisation was seen in samples taken from reactors and examined by Kyffin in 2014, but chromium depletion in their samples was not significantly changed compared to samples from the 1980s [8]. This suggests that the changing burn-up and dwell time in the intervening years may not have had a significant effect on the evolution of the steel.

One result of chromium depletion is the possibility of intergranular stress corrosion cracking (IGSCC). This has been seen to occur below a grain boundary chromium concentration of around 13.5% [36]. Cracks in the microstructure can lead to increased corrosion as they increase the surface area and can allow penetration of the passivation layer [8]. In cases where there is sufficient IGSCC (sufficient being approximately 23% of grain boundaries depleted below 13.5 wt.% chromium) there can be macroscopic brittle failure. It is estimated that in an 18Cr-8Ni stainless steel, these conditions could be met after a heat treatment at 600°C for 54h [36]. This is one of the most serious possible effects of corrosion: a failure of the cladding leading to a failure in containment.

If the chromium depletion is significant enough, it could be that the passivation layer on the surface starts to break down, allowing for uniform corrosion. However, this would require a high degree of sensitisation and is made less likely by the high chromium component in this steel. If corrosion is to occur, it will more likely be localised: pitting, crevice corrosion, or stress corrosion cracking. These can occur where there are defects in the passivation layer. There are also environments which increase the chance of corrosion, including the composition of solution and high temperatures [37]. Due to this, the cooling ponds are maintained at a particular pH [8]. This helps retard any corrosion that may be made possible due to the chromium depletion caused by high temperatures and irradiation.

2.2.4 Effects on Physical Properties

The evolution of the steel clad due to temperature and irradiation has been discussed in the previous sections. The steel composition is carefully selected to give the desired properties: thermal and corrosion resistance, strength, fracture toughness, etc. However, as mentioned, the composition and microstructure of the steel after some time is different from its original state, which may significantly alter its physical properties. This effect has been used intentionally, for example, heat treatments are used to alter the hardness of some steels by causing the precipitation of the γ' -phase [23].

An example of changes in physical properties due to ageing and phase transformation is demonstrated by Ecob, Lobb and Kohler [2]. As discussed earlier, samples were annealed, then treated at 750°C and 850°C for 1000 h. It was found that NbC had a greater strengthening effect than G-phase per volume fraction, as the transformation from NbC to G-phase caused an approximate increase in the volume fraction by a factor of ten, so even though there is a decrease in minimum creep rates of around a factor of two, it is still an overall decrease in strength per

volume fraction. The transformation to G-phase also leads to an increase in creep rate at 750°C as it is more deformable than NbC. However, in terms of creep ductility there were no negative effects observed on strains to failure [38]. It was stressed that the findings reported would not apply at lower temperatures as G-phase at lower temperatures deforms much less easily.

Hunn et al. irradiated type 316LN steel using iron ions and helium [39]. Iron was used so that the composition would be unchanged and the effect of damage could be observed without secondary effects. Samples were irradiated at 200°C with 3.5 MeV ions. From doses between 0 and 1 dpa, there was a percentage hardness increase from 0 to 40%. For doses (up to 50dpa) above this, the hardness saturated, levelling off at just below a 50% hardness increase. TEM analysis found that the hardness increase was due to an increase in defects (vacancies and interstitial clusters) that prevented dislocation motion through the material. The explanation is in good agreement with observation as the defects saturate at around 1 dpa, the same level that the hardness increase begins to level off. When helium was used the effects were different due to the helium affecting the microstructure and causing bubbles as well as defects. Initially, the iron implantation causes the hardness to increase more quickly, but as it begins to level off around 1dpa, the helium implantation continues increasing the hardness, not levelling off until around 10 dpa, as seen in Figure 2.7. In this particular case, 360 keV helium ions have increased the hardness of the steel by 90%. It can also be seen from Figure 2.7 that this effect was only measured at 150 nm. This is due to the nanoindentation measurement, but serves to illustrate that the effect will only be over the penetration depth of the radiation particles.



Figure 2.7: A graph showing a comparison between the effect of helium ion implantation and iron ion implantation on hardness in 316LN steel [39].

In a study of 15Cr-25Ni steels by Yamamoto et al. helium implantation caused samples to fracture prematurely when compared to non-implanted samples [29]. The fracture mode was also altered. The non-implanted samples failed in a transgranular, ductile manner, while the implanted steel failed in a brittle, intergranular fashion. This was believed to be due to cavities formed at the grain boundaries, identified using SEM and TEM. The same study also examined the effect of precipitates on the helium implantation. It was found that the helium nucleated on precipitate boundaries, meaning that dispersed precipitates, such as MC let to more dispersed helium bubbles, which reduced the detrimental effect of the helium.

Tests were done on the 20Cr-25Ni-Nb stabilised steel, on samples with the tubular geometry of the fuel cladding [24], differentiating them from those previously which had used plates or strips of metal. However, it was found that the tensile properties of a section of tube taken from a

reactor and a similarly irradiated steel strip did not differ significantly. This could suggest that any changes to the surfaces of the tube due to high-temperature exposure to CO_2 and the fuel have a negligible effect on the tensile properties of the steel, although the surface in contact with the fuel has a higher gas bubble formation to a depth of 7 μ m due to the ejection of gaseous fission products. In the unirradiated samples examined, there were no micro-cracks or cavity chains observed; because of this, larger cracks were not initiated. It is thought that the small grain size and precipitates also contributed to the lack of propagation of fractures. However, in the irradiated samples, cracks were thought to propagate using networks of gas bubbles found at the grain boundaries, or nucleated on precipitates. However, the gas bubbles observed were not sufficiently large to explain the extent of crack propagation. It is suggested that the strain put on the material increases mobility of the helium, allowing more to gather in the bubbles or grain boundaries and increase the crack size.

It is generally observed that helium implantation causes embrittlement of steel [28], altering its hardness and ductility from its original state. This helium implantation is due to alpha irradiation from fission products and from transmutation of elements which make up the alloy. Helium bubble formation is affected by precipitates present as they can provide nucleation sites. Therefore understanding the precipitation sequence may help the understanding of long term mechanical properties.

2.3 Summary

The effects of heating and irradiating steels have been examined many times and are varied and complex, with some specifics not being well agreed on. Complicating comparisons and predictions are the significant effects that even slightly different alloy compositions have.

In the literature examining the effects of temperature on different alloys of steel, generally speaking the initial precipitate dispersion develops with time; coarsening, nucleating other phases and in some cases disappearing. In the case of 20%Cr-25%Ni-Nb steel, an initial dispersion of spherical niobium carbide particles is seen. On ageing, older papers report the formation of M_6C carbides, but more recently it is believed that plate-like G-phase (Ni₁₆Nb₆Si₇) precipitates on the niobium carbide particles, transforming it. There are reported observations of $M_{23}C_6$ appearing next, its appearance assumed to be related to the dissolution of NbC by the formation of G-phase, freeing the carbon to form other carbides. Others, however, report only seeing the intermetallic σ -phase. It appears that this is dependent on the exact composition of the steel being examined, beyond its nominal composition. As heat treating steel is the main focus of the research presented below, these precipitates will be used to guide the microscopy and other investigations of the treated samples.

The effects of the radiation experienced by steel in a reactor have been examined to a lesser degree, especially using in-reactor samples. However, the literature shows there are many effects that radiation can have on the steel and that these effects are dependent on temperature. Literature has shown radiation to lead to grain boundary segregation, which in turn can lead to intergranular corrosion. There are phases which are altered, enhanced or completely induced into the steel by radiation, such as metal phosphides present, the Laves phase and the γ' -phase. In addition to affecting the precipitate behaviour of the steel directly, irradiation can also introduce voids, dislocations and other defects into the steel structure. These, again, are affected by the temperature, effectively being annealed out of the steel at higher temperatures, and migrating through it at lower temperatures. These give additional sites for precipitate nucleation and affect the properties of the steel.

The practical outcome of these changes is that the behaviour of the steel changes. Depending on the composition of the steel and the combination of irradiation and temperature that the steel is subject to, it can be transformed from stabilised stainless steel to sensitised, become susceptible to intergranular corrosion, and change in strength. All of these effects are potential hazards when it comes to the cooling and long-term storage of spent fuel and demonstrate the importance of understanding exactly how the steel will behave when planning for any changes in reactor behaviour, such as life-time extensions.

3 Methodology

3.1 Sectioning

The initial tubing was received in its manufactured form, containing no fuel. The tube was sectioned before any heat treatment. The steel tubing was initially sectioned into 15 and 30 mm lengths and then these sections cut into sixths. Figure 3.1 illustrates this.



Figure 3.1: A sketch showing how a length of the tubing is sectioned, with dashed lines indicating the cuts and dotted indicating the location of the thermal exchange fins.

The steel tubing was sectioned using a Struers Secatom-50 and a Buehler AcuThin abrasive blade¹ The cutting disc was cooled with tapwater.

3.2 Heat treatment

3.2.1 Thermal Gradient Test

In order to determine if there would be a thermal gradient across the samples during the treatment, a piece approximately 15mm long was sectioned, then cut in half axially. The sample then had a K-type thermocouple spot welded to the inside and outside surface of the tube to measure the temperature of each surface and show any temperature variations across the sample (Figure 3.2).



Figure 3.2: Sample prepared for annealing treatment, spot welded to two thermocouples.

The heat treatment was performed in a tube furnace² under an atmosphere of argon gas³ (99.998% purity) at positive pressure.

¹ Part number 11-4207-010

² Elite Thermal Systems Limited, single zone tube furnace, TSH18 model

³ BOC Pureshield argon (99.998%) EC No. 231-147-0

In order to simulate the annealing process, a tube furnace was heated to 918°C. The tube furnace was kept at a positive pressure, with an atmosphere of argon flowing through it. The sample was placed into the furnace at temperature as seen in Figure 3.3 and then held at temperature for 40 minutes. When the heat treatment was complete, the sample was removed at temperature and air cooled. The readings were downloaded from the thermocouple data logger and analysed.



Figure 3.3: Experimental set up for annealing treatment simulation. 1) The tube furnace is heated to 918°C. 2) Argon gas flows in to the tube through the inlet hole in the end cap. 3) The sample is placed into the furnace, with thermocouples attached and feeding out of the other end cap. 4) The end cap is screwed on, argon flowing out of the same hole the thermocouples feed out of and into the data logger. 5) This is connected to a computer. 6) The computer which tabulates and records the readings.

3.2.2 Annealing

All the sections thermally aged were initially annealed using a method intended to replicate the industrial annealing process, 40 minutes at 918°C [40]. This was done in an alumina boat in a Lenton tube furnace with 95% argon, 5% hydrogen gas⁴ continually pumped through the tube at positive pressure to maintain atmosphere.

3.2.3 Ageing

Ageing was carried out for up to 1008 hours (42 days). It was not possible to supply gas to the tube furnace consistently for 1008 hours. In order to remove this need and to ensure a known atmosphere for the duration of the heat treatment, samples were sealed in quartz tubing⁵ (inner diameter 10 mm, outer diameter 12mm) under the required atmosphere. The set-up is shown in Figure 3.4. The tube was initially sealed at one end using an oxy-acetylene torch. The sample was placed in the tube and the tube was necked, leaving a small aperture to change the atmosphere. A pump⁶ was used to remove air from the tube. This was backfilled with either argon or carbon dioxide. The process was repeated twice to ensure any contamination from the pump and tube was removed. Finally, the tube was filled to a pressure of 0.9 bar (at room temperature) with the desired atmosphere and sealed using an oxy-acetylene torch. The seal was tested by immersing the sealed tube in water.

⁴ BOC Welding mixture ISO 14175-R1-ArH-5

⁵ Multilab, Quartz Tube Open Both Ends, outer diameter 12mm, inner diameter 10 mm. Part No. ML13615

⁶ Oerlikon Leybold Vacuum Turbolab 80



Figure 3.4: A labelled photograph of the set-up used to fill quartz tubing with the desired atmosphere.

- (1) Quartz tubing, open end connected to set-up
- (2) 'Necked' region narrowed to ease tube sealing
- (3) Section of tube containing samples
- (4) Sealed tube end
- (5) Screw-in air-tight connector

- (6) Pressure gauge
- (7) Gas inlet valve
- (8) PenningVac PTR90 gauge
- (9) Pump isolation valve
- (10) Pump system: Oerlikon Leybold Vacuum Turbolab 80

Sealed tubes were heated to temperature in a Lenton box furnace, held in place on a refractory brick with grooves cut into it. On removal from the furnace, the quartz tubes are held in water and broken using a pair of tongs, quench cooling the samples. The full matrix of 1008 hour treatments can be seen below in Table 3.1.

Table 3.1: A table showing all sample treatment conditions used.

Temperature Atmosphere	350°C	550°C	750°C	850°C
Carbon Dioxide				
Argon				

3.3 Sample preparation for analysis

3.3.1 Scanning Electron Microscopy (SEM)

In order to prepare samples for scanning electron microscopy (SEM) they were first mounted end on in epoxy-resin, supported by a plastic clip, as illustrated in Figure 3.5 then ground using a series of

grinding papers⁷, before being polished using diamond suspensions⁸ and colloidal silica suspension⁹. The series is described in Table 3.2.



Figure 3.5: A diagram of a steel section mounted in epoxy resin and supported by a clip.

10010 3.2	Tuble 5.2. The grinning and polising stages used to prepare steer sumples for SEW.							
Stage	1	2	3	4	5	6	7	
Material	SiC paper	SiC paper	SiC paper	SiC paper	Diamond suspension	Diamond suspension	Colloidal silica	
Grade	P400	P800	P1200	P2500	6 µm	1 µm	0.06 µm	

Table 3.2: The grinding and polishing stages used to prepare steel samples for SEM.



Figure 3.6: A diagram showing the electro-etching set-up. (1) Beaker. (2) Etchant: 10 wt.% oxalic acid solution. (3) Sample (anode). (4) Steel tubing (cathode). (5) Basetech BT305 Variable Power Supply Unit.

In order to highlight the precipitates and grain structure, the polished samples were then electro polished in 10 wt.% oxalic acid¹⁰ at approximately 6 V.cm⁻² using a set up as detailed in Figure 3.6.

As the steel was set in non-conductive epoxy-resin, it was necessary to carbon-coat the samples¹¹ and use silver conductive paint¹² to prevent charge build-up during analysis using SEM.

3.3.2 Transmission Electron Microscopy (TEM)

In order to prepare the steel for TEM, the curved sections were ground flat using a stainless steel holder while secured to it with crystal bond (Figure 3.7a). As the material was curved and had ribs on the outer surface (as in Figure 3.7b), it was necessary to add a few steps to ensure the sample was

⁷ Buehler CarbiMet silicon carbide paper

⁸ Buehler MetaDi diamond suspension

⁹ MetPrep Silco colloidal silica suspension

¹⁰ Oxalic Acid: Sigma-Aldrich catalogue number 75688, ≥99.0% purity

¹¹ Edwards Vacuum Carbon Coater

¹² Silver Conductive Paint from RS Pro. RS Stock No. 186-3600

prepared to a high standard. Initially, the outer surface had to be ground flat without adhering the sample to the holder. When the ribs were removed and a flat surface exposed, the sample could be inverted and attached to the holder, grinding the inside flat before inverting the sample again and grinding the outside until the sample was ground to the desired thickness. The steel was made flat on both sides using the same series of grinding papers as the SEM samples, up to P2500 paper, but not polished. The samples were ground to a thickness of approximately 50 µm before being punched into 3mm discs. These were electropolished¹³ at -35°C, approximately 30 V (varying between samples) and flow speed of 18 with a solution of 5% perchloric acid, 35% butoxyethanol and 60% methanol.



Figure 3.7: a) A photograph of the upside down, stainless steel holder used to prepare TEM samples, with a partially prepared sample affixed to the top. The inner part applies pressure while the ring prevents it tilting, keeping the sample an even thickness. b) A diagram showing the inner and outer radii of the tube, with ribs on the outer surface. The dashed lines show a 3 mm wide region, 0.3 mm deep, that TEM foils can come from.

3.4 Analytical Methods

3.4.1 Scanning Electron Microscopy (SEM)

3.4.1.1 Function and Parameters

The microscope used for SEM work analysing these steel samples was an FEI Inspect F50 Field Emission Gun (FEG) SEM. As with all FEG-SEMs, the microscope generates electrons using a high voltage electron gun. The electrons are pulled away from it towards the first anode due to a potential difference, then accelerated through the gun column using the potential difference between the first and second anodes. The electrons then pass through apertures and magnetic lenses to focus and orientate the beam onto the sample. The beam is rastered using deflector coils to scan an area of the sample surface. (Figure 3.8)

¹³ Streuers Twin-jet electropolisher



Figure 3.8: A schematic of the internal workings of a Scanning Electron Microscope.

There are two main ways in which the beam interacts with the sample to produce electrons for detection and so to form a grey-scale image. Secondary electrons (SE) are produced by inelastic scattering interactions between the beam/primary electrons and valence electrons (Figure 3.9a). A primary electron imparts enough energy to a valence electron to eject it from the sample. As these interactions produce low energy electrons, secondary electrons are generated from close to the sample surface and give an image with topographical information. Backscattered electrons (BSE) are generated by elastic scattering, or reflection, of primary electrons from the incident beam back out of the sample by the positively charged nuclei (Figure 3.9b). As the charge of the protons in the nucleus causes the scattering, heavier nuclei (greater *Z* number) scatter electrons more strongly and so appear brighter in the resulting grey-scale image. As these interactions are elastic, BSE are of higher energy than SE.





More information can be taken from the sample using energy dispersive x-ray spectroscopy (EDX). This technique allows for elemental analysis. When an electron is ejected from a lower energy level within an atom (as with SE production) an electron from a higher energy often drops down to fill the orbital, emitting a characteristic x-ray in the process (Figure 3.9c).

For this work, BSE detection was used to highlight the location of precipitates in the sample, with a beam energy of 15 kV, spot size of 3.5 and at most images were taken at 8000 times magnification.

3.4.1.2 Image Analysis

In order to determine average precipitate size and number density, two columns of images were taken across the sample at 8000 times magnification and analysed using the FIJI [42] software package of ImageJ [43][44].



Figure 3.10: An SEM image illustrating the distribution of micrographs taken across the sample for measurements. This micrograph shows a cross-section of the sample, with a heat exchange fin to the right of the image.

The images were imported to ImageJ, cropped to remove the information bar and any of the resin sample mounting. The threshold of the greyscale image was adjusted to select areas that were above a limit in the grey-scale histogram. This limit was determined by taking the threshold to the top 2% of the histogram (with black being the background) and then adjusting it by eye and masking areas of the sample that were obvious false positives. This was needed as, due to the topology of the sample and the contrast of the image, ridges in the etched crystal structure were often light enough to be mistaken for the edges of precipitates, as seen in Figure 3.11.



Figure 3.11: (a) Part of a micrograph of the steel surface, white areas are precipitates. (b) The same micrograph in ImageJ, threshold highlighting all areas above a certain brightness.

This was corrected by masking large areas of false positives (as seen in Figure 3.11) with black, taking care not to mask any precipitates within that area, and then adjusting the threshold by eye to get a compromise between false positives and precipitate coverage. False positives are further limited by putting limits on the particle measurement, adding a minimum precipitate size of 8 pixels and, as the

niobium carbide precipitates are largely round, a circularity limit of 0.5. The software then counts and measures the remaining highlighted areas, giving number, number density, and area fraction.

In order to quantify error in these values, the standard deviation between micrographs of the same sample was used. Note that this does not directly account for any error in not identifying or misidentifying precipitates based on grey-scale thresholds, as described above. It also assumes that the samples are relatively homogenous in terms of precipitate distribution.

3.4.1.3 Energy Dispersive X-ray Spectroscopy (EDX) Analysis

In order to determine the composition of precipitates and the bulk of the steel, EDX spectroscopy was performed. EDX maps were taken of areas of the samples, selected due to containing precipitates characteristic of the sample, or being an area of interest, showing a precipitate composition not seen elsewhere, for example. To investigate the compositions semi-quantitatively, point scans were used, scanning the bulk and precipitates across the sample. The semi-quantitative values were averaged across measurements for precipitates of similar composition in a sample to give a more reliable idea of a species' composition for each steel treatment. Any error in these measurements could be considered dependent, that is from the same source: the SEM-EDX system, errors provided by the system for each measurement were also averaged [45]. It is not believed that the errors provided by the system account for its semi-quantitative nature.

3.4.2 Scanning Transmission Electron Microscopy (STEM)

3.4.2.1 Function and Parameters

6 out of the 8 conditions examined using SEM were also examined using STEM. The two samples treated at 550°C were excluded as they were deemed to be less significant than the two temperature extremes and the samples treated at 750°C, the temperature that literature suggests G-phase will form most quickly at. The samples were imaged using a 200 kV, 14.4 μ A beam and spot size 6, with a condenser aperture of 40 μ m on a JEOL JEM-F200 TEM.

Within a TEM, the electron beam passes through an electromagnetic condenser lens system, the sample, then the objective lens system and onto a screen or CCD camera.

Unlike SEM, TEM scatters electrons through a sample rather than back up, away from the sample. While there are many possible outcomes of electron interaction, TEM imaging utilises elastically and inelastically scattered electrons, while the EDX spectroscopy uses inelastic scattering, largely as described previously in Section 3.4.1.1.

STEM is different from conventional TEM as the especially fine electron beam is rastered across the sample, allowing for EDX spectroscopy mapping to take place.

3.5 Thermo-Calc Software

Thermo-Calc Software was a company founded in 1997, after almost 30 years of developing software and databases for thermodynamic calculations [46].

Generally speaking, the lower the Gibbs free energy of a system, the more stable it is; if the Gibbs free energy of a system is minimised, i.e. any change in the system results in a positive change in the Gibbs free energy, then the system is considered to be in equilibrium [47].

The basis of the software is the CALPHAD method, standing for Calculation of Phase Diagrams or Computer Coupling of Phase Diagrams and Thermochemistry [48]. This method utilises all possible

thermodynamic information available for phase equilibria and thermochemical data of a system. This information is used to describe the phases of the system in terms of Gibbs free energy. Then, a mathematical model is applied to this description of the system, optimising the fit of the data available to the model and accounting for the existence of multiple phases simultaneously. By doing this, it is possible to calculate the stable phases present and so produce a phase diagram, as well as other thermodynamic properties for each phase and the system [49].

3.5.1 Thermo-Calc Equilibrium Calculations

Thermo-Calc minimises the Gibbs Free energy of a given system in order to calculate the state of that system [50]. The composition was analysed from a section of steel using ICP-OES¹⁴ and this measured composition, listed in Table 3.3 was used as the basis for calculations discussed here.

Element	Fe	Ni	Cr	Nb	Mn	Si
Weight Percent	53.67	24.6	19.74	0.68	0.68	0.55
Element	С	Р	Ti	Мо	S	Ν
Weight Percent	0.047	0.012	0.01	<0.01	<0.003	0.0071

Table 3.3: The composition of a steel sample measured using ICP-OES.

The calculations are run using the Thermo-Calc Software TCFE Steels/Fe-alloys database version 8.1, to provide thermodynamic information and software version Thermo-Calc 2018b.

This composition was entered into the equilibrium calculator and processed, outputting a property diagram indicating the equilibrium fraction of each phase present over the temperature range defined (300°C to 900°C). The composition of these equilibrium phases can be output at the heat treatment temperatures described in Table 3.1.

3.5.2 DICTRA Diffusion Calculations

3.5.2.1 Function

One of the modules of the software is called 'DICTRA', the diffusion module of Thermo-Calc [51]. It uses computation kinetics to simulate various compositional changes due to diffusion.

DICTRA [48] performs calculations for a pre-defined system at points along a grid extending into the matrix phase perpendicular to the interface surface. Other phases can be defined as spherical phases embedded within the matrix; no diffusion occurs within these additional phases. These phases have a composition that is either set by the user or defined as the equilibrium composition, as calculated by Thermo-Calc. Non-matrix phases can grow or shrink, including to the point of disappearing. DICTRA calculates iteratively, with each iteration having two steps. The first step is to calculate the diffusion of a species (in this case carbon) into the matrix from an interface using mobility data. It then calculates the new equilibrium compositions of the matrix and precipitates (in this case, niobium carbide, G-phase, $M_{23}C_6$ and σ -phase). The calculations are performed at a user-defined timestep at each grid point through the diffusion process.

¹⁴ Inductively Coupled Plasma – Optical Emission Spectrometry. Performed by Element Materials Technology, info.sheffield@element.com

3.5.2.2 Set-Up and Parameters

Initially, the environment must be defined. Here, the simulation is looking at carbon diffusion across a boundary and into the steel. An illustration of the set up can be seen in Figure 3.12.



Figure 3.12: A diagram illustrating the initial conditions of the DICTRA calculations.

The diffusion calculations are run using the Thermo-Calc Software TCFE Steels/Fe-alloys database version 8.1, which provides thermodynamic data, and the Thermo-Calc Software Steels/Fe-Alloys Mobility Database version 3.0 to provide diffusion information. After selecting an appropriate database, the components and required phases must be selected. In this case, the elements listed in Table 3.3. and the austenite phase as the bulk matrix (designated FCC_A1) and the precipitates listed by Powel, Pilkington and Miller [1], namely niobium carbide (DICTRA_FCC_A1), G-phase (G_PHASE), $M_{23}C_6$ (M23C6), σ -phase (SIGMA). A graphite phase is also included as there is no carbon dioxide gaseous phase available in the database to replicate the heat treatments described in section 3.2.3.

The global conditions are set with atmospheric pressure (101325 Pa), each of the four temperatures listed previously, a sample of width 300 μ m. The concentrations of various precipitates and components are calculated at discrete points across the width of the sample to find how the sample changes with time. This one-dimensional grid is distributed with the space between each point determined by a geometric sequence. The first point is set at a distance of 10⁻⁷ m from the boundary. There are 50 points in the sequence, with the geometric ration, r, equal to 1.125. These values were chosen to give a higher resolution near the diffusion interface while ensuring the calculation can still complete in a reasonable time with the resources available.

The composition entered for the austenite matrix phase was calculated using the Thermo-Calc equilibrium software with one change made. The result of the calculation can be seen in see Table 3.4 . The equilibrium was calculated at 750°C as at this temperature, the equilibrium composition was over 99% austenite. As the only precipitate present at the start point of the calculation, niobium carbide was assumed to have absorbed all of the carbon and a corresponding amount of niobium, with the remaining niobium present in solution in the matrix.

Element	Ni	Cr	Mn	Si	Nb		
Weight Percent	24.5	19.9	0.681	0.555	0.2688		
Element	Р	Мо	С	Ν	Ti	Fe	
Weight Percent	0.0121	0.0101	5.88E-04	1.73E-04	7.34E-05	Bal.	

Table 3.4: The equilibrium austenite composition calculated by Thermo-Calc, with niobium amended.

However, the initial fraction of niobium carbide must be input as a volume fraction. The weight fraction of carbon measured (Table 3.3) is 0.00047. Assuming that approximately all of the carbon is

bound to niobium as the steel is stabilised, there is a molar ratio of 1:1 for niobium and carbon. Using approximate atomic mass (Nb = 93, C = 12), this leads to:

Mole fraction of carbon = mass fraction C/atomic mass C = 0.00047/12

Mole fraction of C = Mole fraction of NbC = 3.916x10⁻⁵

Mass frac. of NbC = Mole frac. of NbC x atomic mass NbC = $3.916 \times 10^{-5} \times (93+12) = 0.0041125$

This gives a niobium carbide weight fraction of 0.0041125. Assuming a density of 7.8 g/cm³ for NbC and 7.96 g/cm³ for the steel [52]:

	Steel	NbC	NbC as a Percentage of the Steel
Mass (g)	1000	4.1125	0.41125
Density (g/cm ³)	7.96	7.8	-
Volume (cm ³)	125.682	0.527244	0.419506

Table 3.5: A table showing values needed to calculate the volume fraction of niobium carbide.

Table 3.5 shows a calculated niobium carbide volume fraction of 0.00419506.

As the measured weight percent of niobium is 0.68% (Table 3.3) and 0.41125 - 0.047 = 0.3642% is bound up in niobium carbide, there must be 0.3158 wt.% niobium remaining in the austenite.

The niobium carbide phase was approximated to a 1:1 molar ratio in the simulation and given an initial volume fraction as discussed above. All other precipitation phases had no initial presence but were set to an equilibrium composition.

The interface, or boundary, is set so that so that carbon can diffuse across it, but no other elements. The activity of carbon at the boundary is set at 0.1. This value is largely arbitrary and can be altered to better fit observation.

The calculation simulated a heat treatment of up to 1000 hours for each temperature with a maximum timestep of 1000 s. This low value was necessary to prevent the model altering with the geometric ratio value, *r*, due to the inherent time-step dependence of the result when using the so called disperse-system model, rather than the homogenisation model. This model is the oldest take on diffusion in multi-phase systems in DICTRA, and it is known that unlike other calculation types the result can be time step dependent as well as resolution dependent.

Once the system is established, the set-up is saved and the calculation run, outputting data for weight fraction of carbon to show its ingress and each of the phases to show the effect of increased carbon concentration.

4 Results

4.1 Possible Thermal Gradient

Figure 4.1 and Figure 4.2 show the temperature variation between the outer and inner surface during heat treatment and air cooling. In the Figure 4.1 inset there is a difference of about 4°C between the inside and outside surfaces of the sample. This can also be seen on the heating section of the curve in Figure 4.2, but not the cooling curve. This seems unusual as the sample is around 0.3mm thick and the difference seems to be constant. The thermocouples used have a quoted error of ±3°C.



Figure 4.1: A graph showing the temperature of the outside and inside surfaces of the cladding as it is placed in the furnace, held at temperature, and then removed from the furnace and air cooled. The inset shows the temperature differences between the two surfaces while held at temperature in the furnace. The red line shows the furnace temperature.



Figure 4.2: A graph showing the heating and cooling sections of the data, seen in Figure 4.1, with an expanded *x*-axis.

The small temperature difference in the two surfaces of the sample suggests that there will not be a significant temperature gradient through the bulk of the steel and in turn, no precipitation concentration gradient.

4.2 Scanning Electron Microscopy & Energy Dispersive X-Ray Spectroscopy Analysis

4.2.1 Introduction

In this sub-chapter, a series of images taken using FEI Inspect F50 FEG- SEM of longitudinally mounted cladding sections are presented, followed by EDX images and data demonstrating the composition of the steel and precipitates.

4.2.2 As-Received Sample

Figure 4.3 shows a lower magnification image of the untreated steel sample. The red grid in the figure illustrates the distribution of micrographs taken and analysed to calculate the information in Table 4.1. These data describe the distribution of the precipitates through the imaged area. In Figure 4.4, examples of the micrographs captured can be seen, illustrating the distribution of precipitates. There does not appear to be a preferential location for the precipitates; they occur throughout the bulk and at grain boundaries. Throughout the micrographs, the precipitates seem largely spherical with an average diameter of $0.033\pm0.007 \,\mu$ m. This leads to a precipitate to bulk area fraction of 0.0043 ± 0.009 and there is a precipitate number density of $0.13\pm0.02 \,\mu$ m⁻².



Figure 4.3: A micrograph of a longitudinal sample of steel, taken at 100 times magnification, with a 15 kV beam energy and a spot size of 3.5. There are higher magnification micrographs tiled in the area in the centre of the image. The heat transfer rib can be seen to the bottom of the image. The areas highlighted with red illustrate the approximate area that 8000 times magnification images were taken from, providing an area for analysis from the centre of the tube wall.


Figure 4.4: Images taken at 8000 times magnification of a sample of the steel as-received from the supplier using an Inspect F SEM, beam energy 15kV and a spot size of 3.5. (a) Shows the image from the top left of the grid shown in Figure 4.3. (b) Shows the image from the bottom right of the same grid.

Table 4.1: The numbers in the table are calculated by analysing the images taken from the sample in Figure 4.3 and measuring the precipitates highlighted by being a lighter colour in the backscattered electron emission scan.

Average Diameter (μm)	Diameter Standard Deviation (µm)	Total Area Imaged (μm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (µm ⁻²)	Number Density Standard Deviation (µm ⁻²)
0.033	0.007	13129.34	0.0043	0.0009	0.13	0.02

The samples were examined using EDX-SEM, and all precipitates in the as-received sample were niobium rich. There was no other component of the steel seen to be enriched. Knowing that the precipitates cannot be pure niobium metal, and that the EDX-SEM cannot reliably measure carbon, this suggests that the precipitates are all niobium carbide.

4.2.3 350°C Heat Treated Samples

4.2.3.1 Argon Atmosphere

Figure 4.5 shows an image of the steel sample treated at 350°C for 1008 hours at low magnification. The red rectangles outline the area that images have been taken from, giving coverage of two crosssections of the cladding wall. From this area, the images have been analysed to give information about the precipitates. The heat transfer rib can be seen to the right of the image and the dark spot in the centre of the image is carbon contamination from sample preparation.



Figure 4.5: A micrograph of a longitudinal sample of steel, taken at 250 times magnification. The areas highlighted with red illustrate the approximate area that the 8000 times magnification images were taken.

Figure 4.6 shows two of the images taken from the area described in Figure 4.5. The outer surface of the cladding tube can be seen in Figure 4.6a and an image from close to the centre of the tube wall (approximately 145 μ m from the surface) in Figure 4.6b. The grain structure of the steel can be seen, although the quality of the etch and the size of the grains prevent any meaningful analysis from these images. However, etching and use of backscattered electron imaging has highlighted the precipitates present, showing as the light, round inclusions. The inclusions in these and the other images collected for this sample were processed using ImageJ software [43], [44]. The results of this analysis can be seen in **Error! Reference source not found.**. The precipitates appear to be largely spherical and are calculated to have an average diameter of 0.039±0.009 μ m. This leads to a precipitate to bulk area fraction of 0.015±0.005 and there is a precipitate number density of 0.4±0.1 μ m⁻².

The precipitates seen in Figure 4.6, and throughout the sample, are mostly circular/spherical, aside from a few larger and elongated, but still rounded, precipitates as seen in Figure 4.6a. The precipitates clearly have a different composition to the bulk, seen by lighter colour in the backscattered electron images, indicating a lighter element. In order to determine the composition of the particles, EDX mapping was performed on the area in Figure 4.6a, producing Figure 4.7. From Figure 4.7 it is clear that the precipitates are niobium rich. Dark spots in the iron, nickel and chromium maps indicate that the precipitates are deficient in these three bulk components. The samples are carbon coated to prevent charge build up with the epoxy resin mounting, however the AZtec image capturing software can adjust concentrations if notified of a coated sample. The carbon map, although only qualitative, indicates there is higher carbon concentration in locations with enriched niobium. This can be seen even more clearly in Figure 4.8, where the niobium and carbon maps are overlaid and the areas with higher concentrations of both niobium and carbon are ringed in red. This can be seen in maps from across the sample, with no other compositions appearing. This suggests that all the precipitates in this sample are niobium carbide. The only other enrichment of an element in Figure 4.7 is seen in chromium and oxygen at the surface of the tube. This indicates an intact passivation layer, which is to be expected in a stabilised stainless steel.



Figure 4.6: Images taken of the sample, treated for 1008 hours at 350° C in an argon atmosphere, at 8000 times magnification. a) The top of this image shows the upper surface of the sample, with some edge rounding visible from sample preparation. b) An image from close to the centre of the tube wall. The centre of the image approximately 145 μ m from the surface shown in image (a).

Table 4.2: The numbers in the table are calculated by analysing the images taken from the sample in Figure4.5 and measuring the precipitates highlighted by being a lighter colour in the backscattered electron emission

scan.						
Average	Diameter	Total Area Area Area Fraction Number		Number Density		
Diameter	Standard	Imaged (um ²)	Fraction of	Standard	Density (um ⁻²)	Standard Deviation
(μm)	Deviation (µm)		Precipitates	Deviation	2 chorey (phili)	(µm ⁻²)
0.039	0.009	26131.17	0.015	0.005	0.4	0.1







Figure 4.8: An overlay of the niobium and carbon maps shown in Figure 4.7. The coinciding areas of enriched niobium and enriched carbon are highlighted with red rings.

Table 4.3 shows semi-quantitative results of EDX point scans from the bulk of the steel across the width of the sample. The average weight percent of the three majority components is similar to that measured in the as-received steel Table 3.3, with slightly higher chromium content and slightly lower iron content. The EDX spectroscopy system was unable to detect all the minor components observed in the steel using ICP-OES, and carbon is not included as the sample was carbon coated. In comparison Table 4.4 shows point scans of the niobium rich precipitates. As the scan is only semi-quantitative and the precipitates are embedded in the bulk, it is difficult to know if the weight percent of the three

main bulk constituents is an accurate reflection of the precipitate composition, or simply picked up from the bulk due to the interaction volume of the electron beam, or the spot size. Comparing with the ratios of weight percent of the three most common metals in the bulk, it appears there has been enrichment of chromium and depletion of nickel in the immediate area of the precipitate. The precipitates are undoubtedly niobium rich and it is notable that there is a detectable titanium component in the precipitate, when it was not seen in the bulk. There is also a change (around 4%) in the detected oxygen. The numbers suggest a niobium-rich precipitate, with no other significant metal components. Comparing this to thermodynamic calculations performed in Section 4.4.1 suggests that the phase is niobium carbide with some titanium and possible nitrogen content.

Je: =====	,											
	1	L	2	2	3	3	4	4	5	5		
Bulk Component	wt.%	wt.% error	Average wt.%	Average wt.% error								
0	0.88	0.07	0.77	0.08	0.83	0.08	0.85	0.08	0.91	0.09	0.85	0.08
Si	0.61	0.04	0.64	0.04	0.62	0.04	0.67	0.04	0.59	0.04	0.63	0.04
Cr	20.7	0.2	21.0	0.2	20.6	0.2	20.6	0.2	20.8	0.2	20.7	0.2
Fe	53.0	0.2	53.0	0.2	51.6	0.2	52.6	0.2	52.8	0.3	52.6	0.2
Ni	24.6	0.2	24.2	0.2	24.0	0.2	24.3	0.2	24.5	0.3	24.3	0.2
Nb	0.3	0.1	0.4	0.1	2.4	0.1	1.0	0.1	0.4	0.1	0.9	0.1

Table 4.3: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 350°C in an argon atmosphere

Table 4.4: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 350°C in an argon atmosphere

NbC		1		2		3	Average	Average
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error
0	5.1	0.2	5.0	0.2	4.4	0.2	4.8	0.2
Si	0.26	0.04	0.34	0.04	0.21	0.03	0.27	0.04
Ti	0.42	0.07	0.28	0.07	0.42	0.06	0.37	0.07
Cr	5.3	0.1	4.2	0.1	3.9	0.1	4.5	0.1
Fe	9.9	0.2	7.6	0.2	8.2	0.2	8.6	0.2
Ni	3.8	0.2	3.0	0.2	3.0	0.2	3.3	0.2
Nb	75.4	0.3	79.6	0.3	79.9	0.3	78.3	0.3

4.2.3.2 Carbon Dioxide Atmosphere

Figure 4.9 shows micrographs taken of the sample treated for 1008 hours at 350°C in a carbon dioxide atmosphere. These images were selected as illustrative of all those taken of the sample. The distribution of images was the same as that illustrated in Figure 4.5, with Figure 4.10a taken from the tube surface, while Figure 4.10b is taken from approximately the centre of the tube wall.

Measuring these using ImageJ software gives the results seen in Table 4.5. The precipitates' average diameter of $0.039\pm0.009 \ \mu\text{m}$. This leads to a precipitate to bulk area fraction of 0.015 ± 0.005 and there is a precipitate number density of $0.4\pm0.1 \ \mu\text{m}^{-2}$.

The precipitates seem to be all be similar, but some appear significantly larger, as seen in Figure 4.9b. In order to determine a qualitative composition of the precipitates, an EDX map of the area shown in Figure 4.9a was taken, seen in Figure 4.10. Once again, the precipitates are niobium rich with the

carbon map showing some enrichment coinciding with the niobium rich spots. As the steel cannot contain pure niobium metal, it seems likely that the precipitates are niobium carbide.



Figure 4.9: The sample treated for 1008 hours at 350° C in a carbon dioxide atmosphere, at 8000 times magnification. a) The top of this image shows the upper surface of the sample, with some edge rounding visible from sample preparation. b) An image from close to the centre of the tube wall, approximately 145 μ m from the surface shown in image (a).

Table 4.5: Physical characteristics of precipitates observed in the sample, calculated by analysing micrographs of the steel sample in Figure 4.9 and measuring the precipitates present, seen as a white/lighter grey.

Average Diameter	Diameter Standard	Total Area	Area Fraction of	Area Fraction Standard	Number	Number Density Standard Deviation
(µm)	Deviation (µm)	iniageu (µiii)	Precipitates	Deviation	Density (µm)	(µm⁻²)
0.044	0.007	27250.52	0.018	0.006	0.41	0.098



Figure 4.10: Qualitative EDX maps of the sample treated for 1008 hours at 350°C in a carbon dioxide atmosphere. The same area is covered as in Figure 4.9a. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

In order to determine that the larger precipitates are also niobium carbide, point EDX analysis was performed. The results of this can be seen in Table 4.6, indicating that the precipitate is almost entirely niobium. As the detector unreliably measures carbon, it wasn't included in the scan. This measurement was repeated on other precipitates which stood out, each giving similar results. This suggests that all of the precipitates visible in the sample are niobium carbide.

Element	wt.%	wt.% Error
Nb	89.6	0.2
Fe	1.98	0.07
Cr	1.16	0.05
Ni	0.96	0.09
Ti	0.19	0.04

Table 4.6: Semi-quantitative EDX analysis performed on the large precipitate in the top centre of Figure 4.9b.

Semi-quantitative point EDX analysis was also performed on the bulk of the steel across the width of the sample, the results of which can be seen in Table 4.7. The average weight percent of the three majority components is like that measured in the as-received steel (Table 3.3), with slightly higher chromium content and slightly lower iron content. The EDX spectroscopy system was unable to detect all the minor components observed in the steel using ICP-OES, and carbon is not included as the sample was carbon coated. In comparison, Table 4.8 shows point scans of the niobium rich precipitates. As the scan is only semi-quantitative and the precipitates are embedded in the bulk, it is difficult to know if the weight percent of the three main bulk constituents is an accurate reflection of the precipitate content, or picked up from the bulk due to the electron beam interaction volume and spot size. For scan 3, it seems more likely that the relatively high quantities of iron, nickel and chromium content have been picked up from the bulk, although comparing with the ratios of weight percent of these metals in the bulk, it appears there has been enrichment of chromium and depletion of nickel in the immediate area of the precipitate. The precipitates themselves are undoubtedly niobium rich and there is a small titanium component, which was not seen in the bulk. There is also a change (around 4%) in oxygen content. The numbers suggest a niobium-rich precipitate, with no other major metal components. This suggests that the phase is niobium carbide, containing some titanium and possible nitrogen, Nb,Ti(C,N).

	-	L	2	2	3	3	4	4	5			Average
Bulk Component	wt.%	wt.% error	Average wt.%	wt.% error								
0	1.01	0.06	0.83	0.08	0.85	0.08	1.03	0.07	0.95	0.09	0.93	0.08
Si	0.81	0.03	0.62	0.04	0.67	0.04	0.64	0.04	0.62	0.04	0.67	0.04
Cr	20.6	0.1	20.6	0.2	20.6	0.2	20.8	0.2	20.9	0.2	20.7	0.1
Fe	52.5	0.2	51.6	0.2	52.6	0.2	52.7	0.2	52.8	0.3	52.4	0.2
Ni	24.7	0.2	24.0	0.2	24.3	0.2	24.4	0.2	24.5	0.2	24.4	0.2
Nb	0.31	0.07	2.4	0.1	1.0	0.1	0.4	0.1	0.3	0.1	0.9	0.1

Table 4.7: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 350° C in a carbon dioxide atmosphere

NbC		1		2		3	Average	Average wt.%
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	error
0	8.1	0.1	4.7	0.1	4.4	0.1	5.7	0.1
Si	0.30	0.02	0.20	0.02	0.40	0.03	0.30	0.02
Ti	0.27	0.04	0.26	0.04	0.29	0.05	0.27	0.04
Cr	2.73	0.06	1.70	0.06	8.7	0.1	4.39	0.07
Fe	3.31	0.08	2.60	0.08	17.9	0.1	7.9	0.1
Ni	1.3	0.1	1.12	0.09	6.6	0.2	3.0	0.1
Nb	84.0	0.2	89.4	0.2	61.8	0.2	78.4	0.2

Table 4.8: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 350°C in a carbon dioxide atmosphere

4.2.4 550°C Heat Treated Samples

4.2.4.1 Argon Atmosphere

The sample treated for 1008 hours at 550°C in an argon atmosphere can be seen in Figure 4.11. In Figure 4.11a the edge of the sample is suffering from a combination of edge rounding and overetching. However, although the grain structure is unclear, there is still a distinction between the bulk and the bright precipitates, allowing them to be analysed using ImageJ software. Table 4.9 describes precipitates from Figure 4.11. From analysis of micrographs, the average diameter of the largely spherical precipitates is $0.04\pm0.01 \,\mu\text{m}$. This leads to a precipitate to bulk area fraction of 0.013 ± 0.005 and there is a precipitate number density of $0.31\pm0.06 \,\mu\text{m}^{-2}$. In order to determine the composition of the precipitates, EDX was used to create a map of Figure 4.11a with point EDX analysis on other precipitates.



Figure 4.11: Images taken of the sample, treated for 1008 hours at 550°C in an argon atmosphere, at 8000 times magnification. It appears from these images that the sample is over-etched. a) The top of this image shows the upper surface of the sample. b) An image from close to the centre of the tube wall. The centre of the image approximately 145 μ m from the surface shown in image (a).

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Average Diameter (μm)	Diameter Standard Deviation (µm)	Total Area Imaged (µm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (µm ⁻²)	Number Density Standard Deviation (µm ⁻²)
0.04	0.01	26783.08	0.013	0.005	0.31	0.06

Table 4.9: Physical characteristics of precipitates observed in the sample, calculated by analysing micrographs of the steel sample seen in Figure 4.11 and measuring the precipitates using ImageJ software.

In Figure 4.12, the maps show a distribution of niobium-rich particles with no enrichment of any of the bulk metals that might indicate other phases such as G-phase ($Ni_{16}Nb_6Si_7$) [2] or chromium carbide. The carbon map shows some impurities, but no carbon enrichment coinciding with the niobium enrichment. This is likely due to the carbon coating on the sample and resin mounting, and the difficulty the EDX system has detecting carbon. This, along with other maps and point analysis of other precipitates, suggests that all the precipitates in this sample are niobium carbide.

Table 4.10 shows semi-quantitative results of EDX point scans from the bulk of the steel across the width of the sample. The average weight percent of the three majority components is similar to that in the as-received steel with slightly higher chromium content and slightly lower iron content. In comparison, Table 4.11 shows point scans of the niobium rich precipitates. It is difficult to know if the measured concentrations of the three main matrix constituents is an accurate reflection of the precipitate content. However, comparing the point EDX with the ratios of weight percent of the bulk, there is enrichment of chromium and depletion of nickel in the immediate vicinity of the precipitate, which was not seen in the bulk. There is also a change (approximately 4%) in the detected oxygen. The EDX readings show a niobium-rich precipitate. This suggests that the phase is niobium carbide with some titanium and possible nitrogen content.



Figure 4.12: Qualitative EDX maps of the sample treated for 1008 hours at 550°C in an argon atmosphere. The same area is scanned as in Figure 4.11a. Each colour corresponds to the element its image is labelled with.

······································												
	1	1	ź	2	3	3	2	1	5	5		Average
Bulk Component	wt.%	wt.% error	Average wt.%	wt.% error								
0	0.86	0.08	1.07	0.08	1.03	0.08	0.84	0.08	0.91	0.08	0.94	0.08
Si	0.76	0.04	0.75	0.04	0.81	0.04	0.66	0.04	0.71	0.04	0.74	0.04
Cr	20.9	0.2	20.7	0.2	20.7	0.2	20.6	0.2	20.7	0.2	20.7	0.2
Fe	52.2	0.2	52.2	0.2	53.0	0.2	53.4	0.2	53.4	0.2	52.8	0.2
Ni	24.7	0.2	24.7	0.2	24.0	0.2	24.2	0.2	24.0	0.2	24.3	0.2
Nb	0.6	0.1	0.6	0.1	0.4	0.1	0.3	0.1	0.3	0.1	0.5	0.1

Table 4.10: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 550°C in an argon atmosphere.

Table 4.11: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 550°C in an argon atmosphere.

NbC		1		2		3	Average	Average wt.%
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	error
0	4.0	0.2	7.0	0.2	3.1	0.2	4.7	0.2
Si	0.18	0.03	0.3	0.04	0.15	0.03	0.21	0.03
Ti	0.2	0.07	0.53	0.07	0.17	0.06	0.30	0.07
Cr	1.39	0.09	2.46	0.09	0.95	0.08	1.60	0.09
Fe	2.5	0.1	4.3	0.1	1.6	0.1	2.8	0.1
Ni	1.06	0.15	1.64	0.15	0.69	0.14	1.1	0.1
Nb	90.8	0.3	83.8	0.3	93.3	0.3	89.3	0.3

4.2.4.2 Carbon Dioxide Atmosphere

Another sample was treated for the same time and at the same temperature, but in a carbon dioxide atmosphere. Two of the images taken from it can be seen in Figure 4.13, with Figure 4.13a being from the edge of the sample and Figure 4.13b being approximately from the centre of the tube wall. Overetching and edge rounding are noticeable in the sample, but the precipitates are still distinguishable from the bulk. The results of analysing micrographs of the sample, distributed in a pattern as seen in Figure 4.5, can be seen in Table 4.12. It states that the average precipitate diameter is 0.032 ± 0.008 µm. This leads to a precipitate to bulk area fraction of 0.012 ± 0.005 and there is a precipitate number density of 0.40 ± 0.09 µm⁻².

EDX was performed on the sample, obtaining maps and performing point analysis on the bulk and precipitates. Figure 4.14 shows an example of this, with an EDX map of area Figure 4.13a. The image highlighting niobium shows that there are areas of high niobium concentration, with the most obvious being in the bottom left corner of the image. This corresponds with an area of enriched carbon concentration and an area of the three depleted bulk metals. This suggests that the precipitates are niobium carbide.



Figure 4.13: Images taken of the sample, treated for 1008 hours at 550°C in a carbon dioxide atmosphere, at 8000 times magnification. a) The top of this image shows the upper surface of the sample, with dramatic edge rounding visible from a difficult sample preparation. b) An image from close to the centre of the tube wall. The centre of the image approximately 145 µm from the surface shown in image (a).

Table 4.12: Physical characteristics of precipitates observed in the sample, calculated by analysing micrographs of the steel sample seen in Figure 4.13 and measuring the precipitates using ImageJ software.

Average Diameter (μm)	Diameter Standard Deviation (µm)	Total Area Imaged (μm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (µm ⁻²)	Number Density Standard Deviation (µm ⁻²)
0.032	0.008	25953.45	0.012	0.005	0.40	0.09



Figure 4.14: Qualitative EDX maps of the sample treated for 1008 hours at 550°C in a carbon dioxide atmosphere. The same area is scanned as in Figure 4.13a. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

Table 4.13 shows the results of semi-quantitative EDX point scans of the bulk, taken from across the width of the sample. The average weight percent of the three majority components is like that seen in the with slightly higher chromium content and slightly lower iron content. The EDX system is unable to accurately detect many minor components and lighter elements. Table 4.14 shows point scans of the precipitates. Comparing the ratio of the 3 major bulk metals in the precipitates and in the bulk, enrichment of chromium and depletion of nickel immediately adjacent to the precipitate is seen. However, the precipitates are undoubtedly niobium rich and it is notable that there is a detectable titanium component in the precipitate, which was not seen in the bulk. There is also a change (around 7%) in the detected oxygen. This indicates a niobium-rich precipitate containing no other significant metal components. Comparing this to thermodynamic information from literature, and calculations performed using Thermo-Calc, suggests that the phase is niobium carbide with some titanium and nitrogen content.

	-	1	2		3	3	4	4	ļ	5		
Bulk Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	Average wt.%	Average wt.% error
0	0.84	0.05	1.27	0.05	1.16	0.05	1.00	0.05	0.83	0.05	1.02	0.05
Si	0.76	0.03	1.17	0.03	1.10	0.03	0.77	0.03	0.77	0.03	0.91	0.03
Cr	20.4	0.1	20.12	0.09	20.2	0.1	20.0	0.1	20.6	0.1	20.3	0.1
Fe	53.6	0.2	53.3	0.1	53.2	0.2	53.5	0.2	52.9	0.2	53.3	0.2
Ni	24.1	0.2	23.9	0.1	24.1	0.2	23.7	0.2	24.5	0.2	24.1	0.1
Nb	0.30	0.07	0.34	0.07	0.26	0.07	1.03	0.07	0.33	0.07	0.45	0.07

Table 4.13: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 550°C in a carbon dioxide atmosphere.

Table 4.14: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 550°C in a carbon dioxide atmosphere.

NbC		1		2		3	Average	Average
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error
0	8.5	0.1	7.4	0.1	8.6	0.1	8.2	0.1
Si	0.84	0.02	0.48	0.02	1.03	0.03	0.78	0.02
Ti	0.43	0.03	0	0	0	0	0.14	0.01
Cr	5.36	0.06	2.23	0.06	2.37	0.06	3.32	0.06
Fe	8.43	0.08	4.49	0.08	3.36	0.08	5.4	0.1
Ni	3.17	0.09	1.69	0.09	1.3	0.1	2.0	0.1
Nb	73.2	0.2	83.7	0.2	83.4	0.2	80.1	0.2

4.2.5 750°C Heat Treated Samples

4.2.5.1 Argon Atmosphere

Shown in Figure 4.15 is a sample treated at 750°C for 1008 hours in an argon atmosphere. Edge rounding can be seen in Figure 4.15a, which is of the tube's outer surface, while Figure 4.15b is from the centre of the tube wall. In this sample, not all the precipitates appear to be spherical, but, the same precipitate measurements were applied for comparison, giving the results shown in Table 4.15. The average precipitate diameter is $0.04\pm0.02 \ \mu m$, leading to a precipitate area fraction of 0.015 ± 0.005 . There is a precipitate number density of $0.4\pm0.1 \ \mu m^{-2}$.



Figure 4.15: Images taken of the sample treated for 1008 hours at 750°C in an argon atmosphere. a) The top of this image shows the upper surface of the sample, with some edge rounding visible from sample preparation. b) An image from close to the centre of the tube wall. The centre of the image approximately 145 μ m from the surface shown in image (a).

Table 4.15: Physical measurements of precipitates observed in the sample, calculated by analysing micrographs of the steel sample seen in Figure 4.15 using ImageJ software.

Average Diameter (μm)	Diameter Standard Deviation (µm)	Total Area Imaged (μm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (µm ⁻²)	Number Density Standard Deviation (µm ⁻²)
0.04	0.02	25450.97	0.015	0.005	0.4	0.1

In Figure 4.15b, taken from approximately the centre of the tube wall, the precipitate morphology seems as with previous samples; spherical precipitates distributed through the sample, with some variance in size. Similarly, Figure 4.15a contains many familiar spherical precipitates, but for the first time there are some that seem irregular. The most obvious is on the right of the image, just over 10 μ m from the top of the image, which is also the surface of the tube. It should be noted that the majority of the irregular precipitates are located at the tubes inner and outer surfaces, with very few anywhere approaching the centre of the tube. In Figure 4.16, the irregular precipitates can be seen as an enriched region in the nickel, niobium and silicon maps. These regions are further highlighted in Figure 4.17. Those which are circled in white show areas enriched in those three elements, suggesting the presence of G-phase (Ni₁₆Nb₆Si₇). The areas highlighted with green circles show only niobium enrichment. As the carbon map in Figure 4.16 shows no significant areas in enrichment, but as it is known that carbon detection is unreliable, precipitates with only niobium enrichment shown are likely to be niobium carbide. Niobium carbide appears throughout the sample, while the G-phase appears preferentially at the surfaces of the sample. In the micrographs examined from this sample, the furthest instance of G-phase from the surface is around 90 μ m into the sample.



Figure 4.16: Qualitative EDX maps of the sample treated for 1008 hours at 750°C in an argon atmosphere. The same area is scanned as in Figure 4.15a. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.



Figure 4.17: EDX maps of nickel, niobium and silicon taken from Figure 4.16. The areas circled in white highlight areas enriched in all three elements. The areas circled in green indicate areas enriched in niobium, depleted nickel and little change in silicon.

Point EDX scans were performed on the areas highlighted with white rings in Figure 4.17. The results of these scans can be seen in Table 4.16. The data for nickel, niobium and silicon are taken and normalised in Table 4.17 to give the composition of just the elements highlighted in the map. It is likely that the iron picked up in the point scan is from the bulk, and the oxygen is likely from the oxide surface layer found on the steel. These data suggest that the precipitate seen in this sample is G-phase.

G-phase C	omponent	0	Si	Cr	Fe	Ni	Nb
Sample	wt.%	6.95	11.22	6.04	10.7	39.8	25.3
1	wt.% error	0.09	0.06	0.07	0.1	0.2	0.2
Sample	wt.%	3.62	8.86	6.74	18.1	41.1	21.5
2	wt.% error	0.08	0.06	0.07	0.1	0.2	0.2
Sample	wt.%	2.19	6.63	9.5	23.6	32.4	25.6
3	wt.% error	0.06	0.05	0.1	0.2	0.2	0.2
Sample	wt.%	0.51	8.76	6.84	11.6	46.5	25.9
4	wt.% error	0.03	0.06	0.08	0.1	0.2	0.2
Sample	wt.%	0.36	2.96	15.9	23.9	48.9	8
5	wt.% error	0.02	0.04	0.1	0.2	0.2	0.1
Sample	wt.%	0.27	4.55	5.55	11.5	59.8	18.3
6	wt.% error	0.02	0.05	0.09	0.1	0.2	0.2
Sample	wt.%	8.3	12.82	17.3	10.8	31.9	18.8
7	wt.% error	0.1	0.08	0.1	0.1	0.2	0.2
Sample	wt.%	0.39	4.1	11.5	16	52.7	15.2
8	wt.% error	0.03	0.05	0.1	0.2	0.2	0.2
Sample	wt.%	0.31	4.15	9.2	19.7	53.3	13.3
9	wt.% error	0.02	0.05	0.1	0.2	0.2	0.2
Average w	/t.%	2.5	7.12	9.8	16.2	45.1	19.1
Average w	t.% error	0.1	0.06	0.1	0.1	0.2	0.2

Table 4.16: The results of semi-quantitative EDX point scans of nickel-niobium-silicon rich areas seen in Figure 4.16. Some minor constituents have been omitted.

Table 4.17: The results from Table 4.16 with normalised precipitate composition to only include nickel, niobium and silicon, the elements highlighted in the EDX maps in Figure 4.16.

No	rmalised G-phase	Si	Ni	Nb
1	wt.%	14.71	52.11	33.2
1	wt.% error	0.08	0.09	0.1
2	wt.%	12.4	57.52	30.1
2	wt.% error	0.08	0.1	0.2
2	wt.%	10.26	50.1	39.6
5	wt.% error	0.08	0.2	0.2
4	wt.%	10.8	57.31	31.9
4	wt.% error	0.07	0.1	0.1
	wt.%	4.94	81.7	13.4
5	wt.% error	0.07	0.2	0.3
6	wt.%	5.51	72.4	22.1
0	wt.% error	0.06	0.1	0.2
7	wt.%	20.2	50.3	29.5
	wt.% error	0.1	0.2	0.2
0	wt.%	5.7	73.2	21.1
0	wt.% error	0.07	0.2	0.2
0	wt.%	5.87	75.3	18.8
9	wt.% error	0.07	0.2	0.2
	Average wt.%	10.04	63.3	26.6
A	verage wt.% error	0.08	0.1	0.2

In order to attempt to compare the composition of the phase to G-phase in literature, the average normalised weight-percent was converted into a mole ratio of the constituents, as seen in Table 4.18. G-phase exists as Ni₁₆Nb₆Si₇. According to the EDX measurements and calculations, the ratio of elements is approximately Ni_{3.76}Nb₁Si_{1.25} or Ni_{22.57}Nb₆Si_{7.48}.

Normalised G- phase components	Average wt.%	Average wt.% error	Relative atomic mass	Mole ratio	Normalised Mole Ratio	(Normalised Mole Ratio)x6
Si	10.04	0.08	28.09	0.36	1.25	7.48
Ni	63.3	0.1	58.69	1.08	3.76	22.57
Nb	26.6	0.2	92.91	0.29	1.00	6.00

Table 4.18: Using the average of the normalised values shown in Table 4.17 and the relative atomic masses of the components, the weight percent is converted into a mole ratio.

As the two precipitates are clearly of different composition and morphology, with each type relatively consistent within itself, a count of each type of precipitate can be made. The measurements from each of these counts can be seen in Table 4.19, developing on Table 4.15. Niobium carbide precipitates are found to have an average diameter of $0.033\pm0.006 \,\mu$ m, an area fraction of 0.012 ± 0.003 and a number density of $0.4\pm0.1 \,\mu$ m⁻². For the G-phase precipitates, there is an average precipitate diameter of $0.5\pm0.45 \,\mu$ m, an area fraction of 0.005 ± 0.008 and a number density of $0.006\pm0.008 \,\mu$ m⁻². These extremely large error values are due to the small number of G-phase particles observed: only 147 compared to the over 9000 niobium carbide particles.

Table 4.19: Physical measurements of precipitates observed in the sample, calculated by analysing micrographs of the steel sample seen in Figure 4.15 using ImageJ software. The two precipitates are differentiated using SEM-EDX information and precipitate morphology.

Phase	Average Diameter (μm)	Diameter Standard Deviation (μm)	Total Area Imaged (μm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (µm ⁻²)	Number Density Standard Deviation (μm ⁻²)
Niobium Carbide	0.033	0.006	25450.97	0.012	0.003	0.4	0.1
G-phase	0.50	0.45	25450.97	0.005	0.008	0.006	0.008

In addition to identifying this new phase, Table 4.20 shows the results of EDX point scans from the steel bulk across the width of the sample. The three major constituents each have a similar weight percent to those seen in the as-received steel, with slightly higher chromium content and slightly lower iron content. Table 4.21 shows point scans of the niobium rich precipitates. It is difficult to know if the weight percent of the three main bulk components within the precipitate is accurate, or simply detected in the bulk, due to the electron beam interaction volume. Comparing the ratios of the three most common metals in the bulk to their presence in the precipitate, it appears there has been enrichment of chromium and depletion of nickel in the immediate area of the precipitate. The precipitate is niobium rich and contains a small amount of titanium, which was not seen in the bulk. There is also a change (around 6%) in the detected oxygen. The measurements show a niobium-rich precipitate. This suggests that the phase is niobium carbide with some titanium content.

NbC		1		2		3	Average	Average
Component	wt.%	wt.% error	wt.%	wt.% error	wt.% wt.% error		wt.%	wt.% error
0	6.7	0.2	11.0	0.2	4.3	0.1	7.3	0.2
Si	0.98	0.04	1.50	0.04	0.47	0.03	0.98	0.04
Ti	0.35	0.06	0.46	0.06	0.44	0.05	0.42	0.06
Cr	1.12	0.08	2.78	0.09	0.93	0.06	1.61	0.08
Fe	2.0	0.1	4.3	0.1	1.68	0.08	2.7	0.1
Ni	0.8	0.1	1.9	0.1	0.7	0.1	1.2	0.1
Nb	87.9	0.3	78.1	0.3	91.4	0.2	85.8	0.2

Table 4.20: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 750°C in an argon atmosphere.

Table 4.21: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 750°C in an argon atmosphere.

	1 2 3 4		4	Ľ,	5							
Bulk	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	Average	Average
component		enor		enoi		enoi		enoi		enoi	VV C. 70	Wt.70 CITOI
0	1.63	0.07	1.09	0.08	1.14	0.08	1.34	0.08	1.30	0.06	1.30	0.07
Si	1.30	0.03	0.91	0.04	1.01	0.04	1.11	0.04	0.78	0.03	1.02	0.04
Cr	20.2	0.1	20.2	0.1	20.1	0.1	20.3	0.1	20.5	0.1	20.3	0.1
Fe	52.3	0.2	53.4	0.2	53.2	0.2	52.8	0.2	53.6	0.2	53.1	0.2
Ni	24.2	0.2	24.2	0.2	24.2	0.2	24.2	0.2	23.6	0.2	24.1	0.2
Nb	0.36	0.08	0.2	0.1	0.3	0.1	0.2	0.1	0.18	0.07	0.26	0.09

4.2.5.2 Carbon Dioxide Atmosphere

Figure 4.18 contains two micrographs of a sample treated at 750°C for 1008 hours in a carbon dioxide atmosphere. In both images there are precipitates visible. The precipitates as measured using ImageJ software and found to have an average diameter of $0.04\pm0.03 \ \mu$ m, an area fraction of 0.014 ± 0.006 and a number density of $0.3\pm0.1 \ \mu$ m⁻², shown in Table 4.22.



Figure 4.18: Images taken of the sample, treated for 1008 hours at 750°C in a carbon dioxide atmosphere, at 8000 times magnification. a) The top of this image shows the upper surface of the sample, with some edge rounding visible from sample preparation. b) An image from close to the centre of the tube wall. The centre of the image approximately 145 μ m from the surface shown in image (a).

Average Diameter (μm)	Diameter Standard Deviation (µm)	Total Area Imaged (µm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (µm ⁻²)	Number Density Standard Deviation (µm ⁻²)
0.04	0.03	26156.86	0.014	0.006	0.3	0.1

Table 4.22: Physical measurements of precipitates observed in the sample, calculated by analysing micrographs of the steel sample seen in Figure 4.18 with ImageJ software.

As with the precipitates seen in Section 4.2.5.1, there appear to be two different precipitate morphologies in Figure 4.18. Both of these morphologies are present in Figure 4.18a: the circular/spherical precipitates as well as elongated, irregular precipitates. However, Figure 4.18b, taken near the centre of the tube wall, appears to show only spherical precipitates. This reflects the general trend that most of the irregular precipitates were seen near the tube surfaces, with fewer observed the further into the tube wall was examined. In order to determine if these are the same differences as in the previous sample, EDX analysis was performed. A map of Figure 4.18a can be seen in Figure 4.19. From this it can be seen that the non-spherical precipitates are nickel, niobium and silicon rich and depleted in iron and chromium, while the spherical precipitates are enriched in niobium and depleted in the three bulk metals. This again suggests that both niobium carbide and G-phase are present.

Point EDX scans were performed on the areas highlighted with white rings in Figure 4.20. The results of these scans can be seen in Table 4.23. The data for nickel, niobium and silicon are taken and normalised in Table 4.24 to give the composition of just these elements in the precipitate, as they are the ones highlighted in the map. It is likely that the iron picked up in the point scan is from the bulk, and the oxygen is likely from the oxide surface layer found on the steel. These data suggest that the precipitate seen in this sample is G-phase.



Figure 4.19: Qualitative EDX maps of the sample treated for 1008 hours at 750°C in a carbon dioxide atmosphere. The same area is scanned as in Figure 4.18a. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.



Figure 4.20: EDX maps of nickel, niobium and silicon taken from Figure 4.19. The areas circled in white highlight areas enriched in all three elements. The areas circled in green indicate areas enriched in niobium, depleted nickel and no change in silicon.

4 5 1 2 З Average G-phase wt.% wt.% wt.% wt.% wt.% Average wt.% Component wt.% wt.% wt.% wt.% wt.% error error error error error wt.% error 0 0.76 0.05 1.16 0.06 2.1 0.09 2.8 0.1 2.4 0.1 1.85 0.08 10.04 Si 3.99 0.06 7.01 0.07 0.07 9.93 0.07 6.49 0.06 7.49 0.07 Cr 5.5 0.1 4.2 0.1 4.11 0.08 5.34 0.08 7.6 0.1 5.34 0.10 Fe 9.9 0.2 9.7 0.1 10.3 0.1 12.7 0.1 19.9 0.2 12.5 0.1

61.2

18.6

Ni

Nb

0.3

0.2

54.8

23.2

0.2

0.2

44.5

28.9

Table 4.23: A table listing the results of semi-quantitative EDX point scans of nickel-niobium-silicon rich areas seen in Figure 4.19. A few minor constituents have been omitted.

Table 4.24: A table taking the results from Table 4.23 and normalising the precipitate composition to only include nickel, niobium and silicon, the elements highlighted in the EDX maps in Figure 4.20.

0.2

0.2

41.5

27.7

0.2

0.2

45.0

18.6

0.2

0.2

49.4

23.4

0.2

0.2

G-phase	1	L	2	2	3	3	2	1	ŗ	5		Average
Component	wt %	wt.% error	wt %	wt.% error	wt %	wt.% error	wt %	wt.% error	wt %	wt.% error	Average	wt.% error
C:	4.70	0.07	0.25	0.00	12.02	0.00	42.54	0.00	0.20	0.00	0.07	0.00
SI	4.76	0.07	8.25	0.08	12.03	0.08	12.54	0.09	9.26	0.09	9.37	0.08
Ni	73.1	0.2	64.5	0.1	53.3	0.1	52.46	0.10	64.1	0.1	61.5	0.1
Nb	22.2	0.2	27.2	0.2	34.6	0.2	35.0	0.2	26.6	0.2	29.1	0.2

To compare the EDX measurements to the composition of G-phase in literature, the average normalised weight-percent was converted into a mole ratio of the chemical components, as seen in Table 4.25. G-phase usually exists as $Ni_{16}Nb_6Si_7$ [2]. According to the EDX measurements and calculations, the ratio of elements is approximately $Ni_{3.34}Nb_1Si_{1.06}$ or $Ni_{20.05}Nb_6Si_{6.38}$.

Table 4.25:Using the average of the normalised values shown in Table 4.24 and the relative atomic masses of the components, the weight percent is converted into a mole ratio.

Normalised G- phase components	Average wt.%	Average wt.% error	Relative atomic mass	Mole ratio	Normalised Mole Ratio	(Normalised Mole Ratio)x6
Si	9.37	0.08	28.09	0.33	1.06	6.38
Ni	61.5	0.1	58.69	1.05	3.34	20.05
Nb	29.1	0.2	92.91	0.31	1.00	6.00

As the two precipitates are of two different compositions, each with a distinct morphology, a count of each species of precipitate can be made. The measurements from each of these counts can be seen in Table 4.26. The niobium carbide precipitates have an average diameter of $0.04\pm0.01 \,\mu$ m, an area fraction of 0.010 ± 0.004 and a number density of $0.3\pm0.1 \,\mu$ m⁻². The precipitates classified as G-phase an average diameter of $0.6\pm1.2 \,\mu$ m, an area fraction of 0.004 ± 0.009 and a number density of $0.002\pm0.006 \,\mu$ m⁻². These extremely large errors are due to the small number of G-phase particles present, only 45 compared to the 8054 niobium-rich precipitates. There is also much greater variation in particle size, with the range in G-phase particle size being 3.631 μ m, but the range in niobium carbide only 0.05 μ m.

Table 4.26: Physical measurements of precipitates observed in the sample, calculated by analysing micrographs of the steel sample in Figure 4.18 using ImageJ software. The two precipitates are differentiated using SEM-EDX information and precipitate morphology.

Phase	Average Diameter (μm)	Diameter Standard Deviation (μm)	Total Area Imaged (μm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (μm ⁻²)	Number Density Standard Deviation (µm ⁻²)
Niobium Carbide	0.04	0.01	26593.89	0.010	0.004	0.3	0.1
G-phase	0.6	1.2	26525.16	0.004	0.009	0.002	0.006

In addition to identifying G-phase, Table 4.27 shows results of semi-quantitative EDX point scans from the bulk matrix, taken at points across the width of the sample. The average weight percent of the three majority components is akin to the as-received steel, with slightly higher chromium content and slightly lower iron content. The EDX system is unable to detect the minor components of the steel. In contrast to the bulk, Table 4.28 shows point scans of the niobium rich precipitates. As the precipitates are embedded in the bulk, it is difficult to know if the weight percent is an accurate reflection of the precipitate content, or if the interaction volume of the electron beam and spot size lead to detection of the bulk. Comparing with the weight percent ratio of the bulk metals in both the bulk and precipitates, it appears there has been enrichment of chromium and depletion of nickel immediately adjacent to the precipitate. The major component of the precipitates is clearly niobium. There is also a titanium component in the precipitate, when titanium was not detected in the bulk. There is also a change (around 5%) in the detected oxygen. The EDX results show a predominantly niobium precipitate. Comparing this to thermodynamic calculations suggests that the phase is niobium carbide with some titanium and possible nitrogen content.

	í.	1		2	3		4		5			
Bulk Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	Average wt.%	Average wt.% error
0	1.21	0.08	0.87	0.08	0.75	0.04	0.58	0.05	0.81	0.04	0.84	0.06
Si	0.93	0.04	0.74	0.04	0.66	0.02	0.68	0.03	0.65	0.02	0.73	0.03
Cr	20.6	0.1	20.2	0.1	20.32	0.07	20.34	0.09	20.38	0.09	20.4	0.1
Fe	52.9	0.2	53.6	0.2	53.4	0.1	53.4	0.1	53.9	0.2	53.4	0.2
Ni	24.2	0.2	24.4	0.2	24.3	0.1	24.5	0.1	24.1	0.2	24.3	0.2
Nb	0.2	0.1	0.3	0.1	0.61	0.05	0.51	0.07	0.09	0.06	0.34	0.08

Table 4.27: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 750°C in a carbon dioxide atmosphere.

NbC		1		2		3	Average	Average
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error
0	7.7	0.2	8.7	0.2	5.7	0.2	7.4	0.2
Si	0.81	0.04	0.95	0.04	0.49	0.03	0.75	0.04
Ti	0.35	0.06	0.38	0.06	0.11	0.06	0.28	0.06
Cr	1.24	0.08	3.7	0.1	1.21	0.08	2.05	0.09
Fe	2.5	0.1	7.5	0.2	1.9	0.1	4.0	0.1
Ni	1.0	0.1	2.7	0.2	0.8	0.1	1.5	0.1
Nb	86.5	0.2	76.1	0.3	89.7	0.2	84.1	0.3

Table 4.28: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 750°C in a carbon dioxide atmosphere.

4.2.6 850°C Heat Treated Samples

4.2.6.1 Argon Atmosphere

Figure 4.21 shows two micrographs taken of a sample treated at 850°C in an argon atmosphere for 1008 hours. Figure 4.21a shows the edge of the sample, the surface of the tubing, at the top edge of the image and Figure 4.21b shows an image from the centre of the sample. In micrographs of the sample, the precipitates all appear roughly spherical.

The results of analysing a series of micrographs, distributed over the sample as in Figure 4.5, are that the precipitates have an average diameter of $0.05\pm0.02 \ \mu$ m, an area fraction of 0.014 ± 0.004 and a number density of $0.28\pm0.07 \ \mu$ m⁻², as in Table 4.29. These precipitates seem to all have a similar, spherical morphology. Their composition was determined using EDX scans. A map of one of these scans can be seen in Figure 4.22.



Figure 4.21: Images taken of the sample, treated for 1008 hours at 850°C in an argon atmosphere, at 8000 times magnification. a) The top of this image shows the upper surface of the sample. b) An image from close to the centre of the tube wall. The centre of the image approximately 145 μ m from the surface shown in image (a).

microgr	microgruphs of the steel sumple in Figure 4.21 using intager software.								
Average	Diameter	Total Area	Area Eraction	Area Fraction	Number	Number Density			
Diameter	Standard	Includ Area	of Procipitatos	Standard	Density	Standard			
(µm)	Deviation (µm)	iiiiageu (µiii-)	of Precipitates	Deviation	(µm⁻²)	Deviation (µm ⁻²)			
0.05	0.02	26144.48	0.014	0.004	0.28	0.07			

Table 4.29: Physical measurements of precipitates observed in the sample, calculated by analysing micrographs of the steel sample in Figure 4.21 using ImageJ software.



Figure 4.22: Qualitative EDX maps of the sample treated for 1008 hours at 850°C in an argon atmosphere. The same area is scanned as in Figure 4.21a. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element. In the niobium map, it is clear that there is drift in the scan. There appears to be carbon and silicon enrichment in the top left of the image.

The top left of Figure 4.22 shows enrichment of carbon and silicon. On the BSE micrograph, Figure 4.21a, there is a dark rectangular area that coincides with this enrichment. It seems likely that this is contamination from carbon coating the sample over a more deeply etched section of the sample.

From Figure 4.22 it can be seen, especially in the niobium map, that there is drift in the scan. This is due to charge build up caused by the epoxy sample mount. However, it is still possible to see areas of enrichment and depletion and the scan is already qualitative. Point EDX scans that take less time, and so are less affected by drift, can be done to determine a semi-quantitative composition. From EDX mapping it appears that all of the precipitates are niobium-rich.

Table 4.30 shows semi-quantitative results of EDX point scans from the bulk of the steel across the width of the sample. The weight percent of the three main elements is similar to that in the as-received steel, with slightly higher chromium and slightly lower iron content. In Table 4.31 are the results of point scans of niobium rich precipitates. Comparing the relative amounts of chromium and nickel in the bulk and precipitates, or rather the immediate area of the precipitate, included in the measurement due to the electron beam interaction volume, it appears there has been enrichment of chromium and depletion of nickel. The precipitates are niobium rich with a small titanium component,

which was not seen in the bulk. There is also a change (around 6%) in the detected oxygen. Comparing this to thermodynamic calculations suggests that the phase is niobium carbide with some titanium and possible nitrogen content.

		1		2	3		4		5			
Bulk Component	wt.%	wt.% error	Average wt.%	Average wt.% error								
0	1.14	0.05	1.08	0.07	1.15	0.09	1.94	0.08	1.36	0.08	1.33	0.07
Si	1.12	0.03	1.04	0.04	1.10	0.04	1.30	0.04	1.29	0.04	1.17	0.04
Cr	20.4	0.1	20.9	0.2	20.6	0.2	20.7	0.2	20.6	0.2	20.7	0.1
Fe	52.9	0.2	53.2	0.2	52.5	0.2	51.0	0.2	52.3	0.2	52.4	0.2
Ni	24.3	0.2	23.6	0.2	24.1	0.2	23.0	0.2	23.8	0.2	23.8	0.2
Nb	0.19	0.07	0.2	0.1	0.5	0.1	2.1	0.1	0.6	0.1	0.7	0.1

Table 4.30: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 850°C in an argon atmosphere.

Table 4.31: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 850°C in an argon atmosphere.

NbC		1		2		3	Average	Average
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error
0	7.7	0.2	8.7	0.2	5.7	0.2	7.4	0.2
Si	0.81	0.04	0.95	0.04	0.49	0.03	0.75	0.04
Ti	0.35	0.06	0.38	0.06	0.11	0.06	0.28	0.06
Cr	1.24	0.08	3.7	0.1	1.21	0.08	2.05	0.09
Fe	2.5	0.1	7.5	0.2	1.9	0.1	4.0	0.1
Ni	1.0	0.1	2.7	0.2	0.8	0.1	1.5	0.1
Nb	86.5	0.2	76.1	0.3	89.7	0.2	84.1	0.3

4.2.6.2 Carbon Dioxide Atmosphere

Two of many micrographs taken of a sample treated at 850°C in a carbon dioxide atmosphere for 1008 hours can be seen in Figure 4.23. Figure 4.23a shows the edge of the sample, the surface of the tubing, at the top edge of the image and Figure 4.23b shows an image from the centre of the sample. The precipitates visible in the micrographs appear to be spherical. Analysing the precipitate size and distribution within the micrographs shows that the precipitates have an average diameter of 0.050±0.006 μ m, an area fraction of 0.020±0.004 and a number density of 0.32±0.08 μ m⁻², displayed in Table 4.32. In order to determine whether these results are covering only one composition of precipitate, EDX analysis was performed on the sample, producing element maps and point scans. An example of the EDX analysis in the form of an EDX map can be seen in Figure 4.24.



Figure 4.23: Images taken of the sample, treated for 1008 hours at 850°C in a carbon dioxide atmosphere, at 8000 times magnification. a) The top of this image shows the upper surface of the sample, at an angle. The black area is the epoxy sample mounting. b) An image from close to the centre of the tube wall. The centre of the image approximately 175 μ m from the surface shown in image (a).



Figure 4.24: Qualitative EDX maps of the sample treated for 1008 hours at 850°C in a carbon dioxide atmosphere. The same area is scanned as in Figure 4.23b. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

Table 4.32: Data calculated by analysing images taken of the steel sample shown in Figure 4.23 and measuring the precipitates using ImageJ software.

Average Diameter (μm)	Diameter Standard Deviation (µm)	Total Area Imaged (μm²)	Area Fraction of Precipitates	Area Fraction Standard Deviation	Number Density (μm ⁻²)	Number Density Standard Deviation (µm ⁻²)
0.050	0.006	26195.60	0.020	0.004	0.32	0.08

Table 4.33 shows semi-quantitative results of EDX point scans from the bulk of the steel, taken from points across the width of the sample. The average weight percent of the three majority components is similar to the as-received sample, with slightly higher chromium content and slightly lower iron content. The EDX system was unable to detect all the minor components in the steel and carbon is not included as the sample was carbon coated. In comparison, Table 4.34 shows point scans of the niobium-rich precipitates. As the scan is only semi-quantitative and the precipitates are embedded in the bulk, it is difficult to know if the weight percent of the three main bulk constituents is an accurate reflection of the precipitate content, or simply picked up due to the electron beam interaction volume, or the spot size. The ratio of weight percent of the three most common metals in the bulk, appears to have undergone enrichment of chromium and depletion of nickel in the immediate area of the precipitate. The precipitates are undoubtedly niobium rich with a small titanium component in the precipitate. The precipitates are undoubtedly niobium rich with a small titanium component in the precipitate. There is also a change (around 6%) in the detected oxygen. Comparing this to thermodynamic information suggests that the phase is niobium carbide with some titanium content and possible nitrogen content.

		1		2	3		4		5			
Bulk Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	Average wt.%	Average wt.% error
0	0.76	0.05	1.12	0.04	1.05	0.04	1.23	0.04	1.25	0.04	1.08	0.04
Si	1.36	0.03	1.06	0.02	0.92	0.02	1.09	0.02	1.16	0.02	1.12	0.02
Cr	20.0	0.1	20.1 5	0.08	20.79	0.08	18.75	0.08	20.51	0.08	20.0	0.1
Fe	51.9	0.2	53.3	0.2	52.4	0.2	54.0	0.2	52.4	0.2	52.8	0.2
Ni	23.9	0.2	24.4	0.2	24.6	0.2	24.6	0.2	24.5	0.2	24.4	0.2
Nb	2.07	0.08	0.02	0.05	0.24	0.05	0.31	0.05	0.19	0.05	0.56	0.06

Table 4.33: The results of EDX point scans, from across the sample, of the bulk composition of the sample treated for 1008 hours at 850°C in a carbon dioxide atmosphere.

Table 4.34: The results of EDX point scans, from across the sample, of the niobium carbide precipitate composition of the sample treated for 1008 hours at 850°C in a carbon dioxide atmosphere.

NbC		1		2		3	Average	Average
Component	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error	wt.%	wt.% error
0	6.7	0.1	7.9	0.1	6.6	0.1	7.1	0.1
Si	0.62	0.02	0.99	0.02	0.67	0.02	0.76	0.02
Ti	0.19	0.03	0.38	0.03	0	0	0.19	0.02
Cr	1.69	0.04	2.68	0.05	1.26	0.04	1.88	0.04
Fe	2.35	0.06	5.20	0.06	2.10	0.06	3.2	0.1
Ni	1.05	0.07	1.90	0.07	0.88	0.07	1.3	0.1
Nb	87.4	0.2	81.0	0.2	88.5	0.2	85.6	0.2

4.3 Scanning Transmission Electron Microscopy (STEM)

4.3.1 Introduction

6 out of the 8 conditions examined using SEM were also examined using STEM. Selected were both atmosphere treatments for 1008 hours at 350°C, 750°C and 850°C. The samples were imaged using a

200 kV, 14.4 μ A beam and spot size 6, with a condenser aperture of 40 μ m on a JEOL JEM-F200 TEM. Use of STEM allows observation of smaller precipitates that could not be resolved using SEM.

4.3.2 350°C Heat Treated Samples

4.3.2.1 Argon Atmosphere

In Figure 4.25 an area containing various precipitates is shown. It is taken from a sample treated at 350°C for 1008 hours in an argon atmosphere. In order to determine the composition of the precipitates, EDX was used. A map of the area is seen in Figure 4.26. The large precipitate in the bottom left of the image can be seen to be niobium rich and the area is depleted of the three bulk elements. There is also some carbon enrichment visible, although as with the SEM-EDX, detection of lighter elements is unreliable. However, this can be taken as an indication that the particle is niobium carbide. Looking across the map of the area, all the precipitates appear to be niobium rich. There is no obvious enrichment in the other maps, suggesting that all of the precipitates are niobium carbide. This was seen for EDX scans across the sample.



Figure 4.25: A bright field STEM image, taken at 150000 times magnification, of a thin film made from a steel sample treated at 350°C in an argon atmosphere for 1008 hours.



Figure 4.26: An STEM-EDS map of the area shown in Figure 4.25. Qualitative EDX maps of the sample treated for 1008 hours at 350°C in an argon atmosphere. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

4.3.2.2 Carbon Dioxide Atmosphere

Figure 4.27 shows an area of a sample treated at 350°C for 1008 hours in a carbon dioxide atmosphere. Within the imaged area there is a distribution of precipitates, as well as dislocations in the bulk structure. An EDX map of the area is seen in Figure 4.28. The large precipitate in the bottom left of the image can be seen to be niobium rich and the area is depleted of the three bulk elements. There is also some carbon enrichment visible, although as with the SEM-EDX, detection of lighter elements is unreliable. However, this can be taken as an indication that the particle is niobium carbide. Looking across the map of the area, all the precipitates appear to be niobium rich. There is no obvious enrichment in the other maps, suggesting that all of the precipitates are niobium carbide. This was seen for EDX scans across the sample.



Figure 4.27: A bright field STEM image, taken at 100000 times magnification, of a thin film made from a steel sample treated at 350°C in an carbon dioxide atmosphere for 1008 hours.



Figure 4.28: An STEM-EDS map of the area shown in Figure 4.27. Qualitative EDX maps of the sample treated for 1008 hours at 350°C in a carbon dioxide atmosphere. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

4.3.3 750°C Heat Treated Samples

4.3.3.1 Argon Atmosphere

Figure 4.29 shows an area of a sample treated at 750°C for 1008 hours in an argon atmosphere. Within the imaged area there is a distribution of precipitates, as well as dislocations in the bulk structure. There is one large precipitate, a line of smaller precipitates above that and a scattering of smaller precipitates below that. An EDX map of the area is seen in Figure 4.30. The large precipitate and the line of precipitates above it are niobium rich and the area of the large precipitate is depleted of the three bulk elements. There is also some carbon enrichment visible, although as with the SEM-EDX, detection of lighter elements is unreliable. However, this can be taken as an indication that the particle is niobium carbide. Looking across the map of the area, all the precipitates detected by the EDX appear to be niobium rich. There is no obvious enrichment in the other maps, suggesting that all of the precipitates are niobium carbide. This was seen for EDX scans across the sample.

In comparison to the SEM analysis of this treatment condition, Section 4.2.5.1, only niobium carbide precipitates were observed, no other compositions. This is likely due to the G-phase precipitates being seen close to the surface of the tubing, while the TEM samples were created from material away from the inside and outside walls of the tubing, see Figure 3.7.



Figure 4.29: A bright field STEM image, taken at 100000 times magnification, of a thin film made from a steel sample treated at 750°C in an argon atmosphere for 1008 hours.



Figure 4.30: An STEM-EDS map of the area shown in Figure 4.29. Qualitative EDX maps of the sample treated for 1008 hours at 750°C in an argon atmosphere. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

Carbon Dioxide Atmosphere

Figure 4.31 shows an area of a sample treated at 750°C for 1008 hours in a carbon dioxide atmosphere. Within the imaged area there is a distribution of precipitates. The scan shows two large precipitates, one smaller one to the left of the image and other possible small precipitates or dislocations around the image. An EDX map of the area is seen in Figure 4.32. The large precipitates and the smaller precipitate to the left of it are niobium rich and the area of these precipitates is depleted of the three bulk elements. There also seems to be a small niobium enriched area to the right of the image. There is clear carbon enrichment visible, although as with the SEM-EDX, detection of lighter elements is unreliable. However, this can be taken as an indication that the particle is niobium carbide. Looking

across the map of the area, all the precipitates detected by the EDX appear to be niobium rich. There is no obvious enrichment in the other maps, suggesting that all of the precipitates are niobium carbide. This was seen for EDX scans across the sample. No other precipitate compositions were seen during examination of the sample.



Figure 4.31: A dark field STEM image, taken at 120000 times magnification, of a thin film made from a steel sample treated at 750°C in a carbon dioxide atmosphere for 1008 hours.



Figure 4.32: An STEM-EDS map of the area shown in Figure 4.31. Qualitative EDX maps of the sample treated for 1008 hours at 750°C in a carbon dioxide atmosphere. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

4.3.4 850°C Heat Treated Samples

4.3.4.1 Argon Atmosphere

Figure 4.33 shows an area of a sample treated at 850°C for 1008 hours in an argon atmosphere. Within the imaged area there is one large precipitate, as well as twin boundaries and dislocations in the bulk structure. An EDX map of the area is seen in Figure 4.34. The precipitate is niobium rich and the area of the large precipitate is depleted of the three bulk elements. There is also some carbon enrichment visible, although as with the SEM-EDX, detection of lighter elements is unreliable. However, this can be taken as an indication that the particle is niobium carbide. There is no obvious enrichment in the

other elemental maps, suggesting that the precipitates are niobium carbide. This was seen for EDX scans across the sample.



Figure 4.33: A bright field STEM image, taken at 120000 times magnification, of a thin film made from a steel sample treated at 850°C in an argon atmosphere for 1008 hours.



Figure 4.34: An STEM-EDS map of the area shown in Figure 4.33. Qualitative EDX maps of the sample treated for 1008 hours at 850°C in an argon atmosphere. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element.

4.3.4.2 Carbon Dioxide Atmosphere

Figure 4.35 shows an area of a sample treated at 850°C for 1008 hours in an argon atmosphere. Within the imaged area there is one large precipitate, as well as twin boundaries and dislocations in the bulk structure. An EDX map of the area is seen in Figure 4.36. The precipitate is niobium rich and the area of the large precipitate is depleted of the three bulk elements. There is also some carbon enrichment visible, although as with the SEM-EDX, detection of lighter elements is unreliable. However, this can be taken as an indication that the particle is niobium carbide. There is no obvious enrichment in the other elemental maps, suggesting that the precipitates are niobium carbide. This was seen for EDX scans across the sample.



Figure 4.35: A bright field STEM image, taken at 120000 times magnification, of a thin film made from a steel sample treated at 850°C in a carbon dioxide atmosphere for 1008 hours.



Figure 4.36: An STEM-EDS map of the area shown in Figure 4.35. Qualitative EDX maps of the sample treated for 1008 hours at 850°C in a carbon dioxide atmosphere. Each colour corresponds to the element its image is labelled with, with denser/bolder colour indicating greater concentration of that element

4.4 Thermo-Calc Calculations

4.4.1 Equilibrium Calculations

Using Thermo-Calc software [53], an equilibrium property diagram was producing using the measured composition of the provided steel. This can be seen in Table 4.35.

Table 4.35: The composition of the steel cladding provided, measured using ICP-OES and given in mass percent. As in Table 3.3.

Element	S	Ν	Ti	Мо	Р	С
Mass Percent	0.003	0.0071	0.01	0.01	0.012	0.047
Element	Si	Nb	Mn	Cr	Ni	Fe
Mass Percent	0.55	0.68	0.68	19.74	24.6	53.66

The resulting property diagram, in Figure 4.37 shows the mass fraction of all phases present at equilibrium, as calculated by Thermo-Calc.



Figure 4.37: An equilibrium property diagram produced using the composition in Table 4.35. It shows all the phases present at equilibrium and their mass fraction.



Figure 4.38: The minor phases seen in Figure 4.37. The same calculation and output, but (a) with the y-axis limited to 0.02 and (b) with the y axis set to 0.001.

As is expected, the major phase is austenite. At lower temperatures, there is a significant proportion of ferrite and other bulk phases. However, the bulk phase in the steel examined is always austenite due to pre-treatment and the relatively short length of the heat treatments described previously. Its calculated equilibrium composition is given in Table 4.36.

Component		Mass Fraction a	at Temperature	
component	350°C	550°C	750°C	850°C
Fe	0.46628	0.56667	0.5418	0.53932
Ni	0.44559	0.27609	0.24537	0.24724
Cr	0.06409	0.14339	0.1993	0.19839
Mn	0.01446	0.00787	0.00681	0.00678
Si	0.00958	0.00587	0.00555	0.00553
Nb	6.35E-06	0.00007	0.00093	0.00249
Р	6.32E-07	0.00002	0.00012	0.00012
Мо	4.94E-07	0.00001	0.0001	0.0001
С	4.15E-10	7.81E-07	5.88E-06	0.00001
Ті	5.23E-11	2.05E-07	1.73E-06	4.47E-06
Ν	1.56E-11	3.99E-09	7.34E-07	2.66E-06
S	5.70E-13	5.76E-13	9.72E-12	1.30E-10

Table 4.36: A table showing the equilibrium composition of the austenite phase, as calculated by Thermo-Calc, for each of the four heat treatment temperatures.

The data from Table 4.36 shows the equilibrium austenite composition for each of the four heat treatment temperatures described above, while Figure 4.39 shows the equilibrium composition of the austenite phase across the full temperature range simulated.



Figure 4.39: A graph showing the calculated equilibrium composition of the austenite phase shown in Figure 4.37, across the same temperature range.

As well as the bulk matrix composition, the composition at equilibrium was calculated each of the four major phases of interest. The graphs showing the mass fraction of each of the chemical components as a fraction of the mass of the precipitate can be seen in Figure 4.40: niobium carbide, G-phase, chromium carbide, and sigma-phase.



Figure 4.40: A graph showing the calculated equilibrium composition of phases shown in Figure 4.37, across the same temperature range. The quantity of each component is displayed as its mass as a fraction of the total mass of the precipitate. Top left: NbC, Top right: G-phase, Bottom left: $Cr_{23}C_6$, Bottom right: sigma-phase.

Figure 4.40 shows the mass fraction of precipitate components. To illustrate the calculated compositions differently and allow calculation of the chemical formulae, the mole ratios of the components within the precipitates were calculated. The distribution of elements within each precipitate, changing with temperature, is shown in Figure 4.41.

In order to calculate an approximate chemical formula for each precipitate, the mole fraction of each component is averaged across the temperature range for which the precipitate is present, as shown in Figure 4.41. These average phase compositions can be seen in Table 4.37.

Table 4.37: A list of average phase compositions across the temperature range, as calculated using Thermo-Calc.

Phase	Chemical formula (average composition)
Niobium Carbide	Nb ₁₂ (C ₁₀ , N _{1.1})
G-phase	Ni ₁₆ Nb ₇ Si ₆
Metal carbide (M ₂₃ C ₆)	(Cr ₂₂ ,Fe ₁)C ₆
Sigma-phase	Cr ₁₀ Fe ₉ Ni ₁



Figure 4.41: A graph showing the calculated equilibrium composition of phases shown in Figure 4.37, across the same temperature range. The quantity of each component is displayed as the number of moles of the element as a fraction of the precipitate. Top left: NbC, Top right: G-phase, Bottom left: Cr₂₃C₆, Bottom right: sigma-phase.

As described in Section 3.5, Thermo-Calc operates by calculating the Gibbs free energy of possible phases, minimising the Gibbs free energy of the system, and using this to determine the composition and amount of each phase. Figure 4.42 shows the Gibbs free energy calculated for each of the phases shown in Figure 4.37. As the Gibbs free energy relates to the stability of a phase, the position each phase appears on Figure 4.42. Generally speaking, the lower, or more negative, the Gibbs free energy of a phase is at a particular temperature, the earlier it will form in a precipitation sequence. This is not a definite rule as the Gibbs free energy must be minimised across the system, not simply for each phase, so the interactions between phases and chemicals within the material and the relationship with the Gibbs energy of each phase mean that the predicted precipitation sequence from calculating the Gibbs free energy is only an approximation. For the four phases considered in the DICTRA calculations the sequence is as expected. NbC first, then G-phase, $Cr_{23}C_6$ and σ -phase. TiN and MnS have significantly lower Gibbs free energy than the other phases.



Figure 4.42: A graph showing the calculated Gibbs free energy of phases present using the steel composition listed in Table 4.35.

4.4.2 DICTRA Calculations

4.4.2.1 Introduction

The DICTRA module in Thermo-Calc calculates diffusion of a chemical or chemicals across a boundary. The configuration set up in the calculation is illustrated in Figure 3.12.

This setup was run at each of the four temperatures used in heat treating samples for 1000 hours, or 3600000 seconds. The composition of the bulk is the austenite equilibrium composition as calculated and shown in Figure 4.37 and listed in Table 3.4.

4.4.2.2 350°C Carbon Ingress Calculation

Figure 4.43 shows the results of the DICTRA calculation of carbon ingress into the steel at 350°C. There is so little carbon ingress at this temperature that the different plots indicating each time completely overlap, apart from very close to the steel-carbon interface.


Figure 4.43: A graph showing the calculated carbon content diffusing across the steel at 350°C, measured in weight percent, against depth into the steel. The carbon distribution is plotted for various times, illustrated in the key.

Figure 4.44 shows the phase distribution of the phases discussed in Powell et al. within the steel. Figure 4.44(a) shows the initial setup: mostly austenite phase with a small amount (0.41125 wt.%) of niobium carbide. Figure 4.44(b) shows the same diffusion at 1 second. It keeps the same, set amount of niobium carbide, but the austenite phase has reduced to accommodate a calculated equilibrium amount of σ -phase.



Figure 4.44: The phase distribution (by mass fraction) of the phases listed in the key across the depth of the sample at (a) T=0 seconds and (b) T=1 second, at 350 °C.

As there is negligible carbon ingress at this temperature, up to 1000 hours, there is negligible change in composition, such as the chromium content in Figure 4.46 and so no change in the phases. This can be seen by comparing Figure 4.44b to Figure 4.45. The only change over 1000 hours is at the very surface of the steel.



Figure 4.45: The phase distribution (by mass fraction) of the phases listed in the key across the depth of the sample at T=1000 hours.



Figure 4.46: Two graphs showing the calculated chromium distribution across the sample at different times in 350°C. b shows the same data as graph a, but with an expanded y-axis.

4.4.2.3 550°C Carbon Ingress Calculation

Figure 4.47 shows the results of the DICTRA calculation of carbon ingress into the steel at 550°C. There is noticeable carbon ingress at this temperature, increasing slightly with time, however the depth of penetration is still under a tenth of the total sample width.



Figure 4.47: A graph showing the calculated carbon content diffusing across the steel at 550°C, measured in weight percent, against depth into the steel. The carbon distribution is plotted for various times, illustrated in the key.

Figure 4.48a shows an initial state similar to Figure 4.44b, although with different mass fractions of sigma-phase. However, as carbon diffuses into the steel, it gives rise to the formation of $M_{23}C_6$, in this case, predominantly chromium carbide. In Figure 4.48c, 1000 hours at 550°C in contact with carbon, the metal carbide has replaced sigma-phase in the area of carbon ingress. This can be seen most clearly in Figure 4.49, where the carbon content correlates well with $Cr_{23}C_6$.



Figure 4.48: : The phase distribution (by mass fraction) of the phases listed in the key across the depth of the steel sample at a) T=1 s, b) T=360000 s, c) T=360000 s, when heated to $550^{\circ}C$ with carbon ingress at the boundary, as detailed in Figure 4.47.

Figure 4.50 shows the chromium distribution across the sample. There is some depletion immediately at the surface, but otherwise the distribution is constant, decreasing very slightly with time



Figure 4.49: A side-by-side comparison of the change in weight percent carbon in the steel, as shown in Figure 4.47, with the mass fraction of metal carbides in the steel at increasing times.



Figure 4.50: Two graphs showing the calculated chromium distribution across the sample at different times in 550°C. b shows the same data as the one on the left, but with an expanded y-axis.

4.4.2.4 750°C Carbon Ingress Calculation

The carbon ingress into the steel at 750°C, as calculated by DICTRA, is shown in Figure 4.51. With the increased temperature there is significantly greater carbon ingress, after 1000 hours there is increased carbon content across the entire steel sample. The carbon content also appears to reach a maximum at around 1.75 wt.%. This can be seen more clearly in Figure 4.52, the same data as in Figure 4.51, but focused on the longer times and closer to the surface of the steel. Between 500 and 1000 hours more carbon diffuses into the steel, but the weight percent at the surface changes by a very small amount.



Figure 4.51: A graph showing the calculated carbon content diffusing across the steel at 750°C, measured in weight percent, against depth into the steel. The carbon distribution is plotted for various times, illustrated in the key.



Figure 4.52: A graph showing the calculated carbon content diffusing across the steel at 750°C, as in Figure 4.51. This graph shows the same data with expanded y- and x-axes.

Looking at the phase distribution in this calculation, it can be seen that the presence of sigma-phase is no longer energetically preferable. Compare Figure 4.53 to Figure 4.44, at 750°C there is no introduction of sigma-phase at T=1 second. However, there is still an increase in $Cr_{23}C_6$ with carbon. This increase can be seen in Figure 4.54 and once again, the increased in chromium carbide correlates with the carbon increase.

The chromium distribution, seen in Figure 4.55, mirrors the carbon distribution seen in Figure 4.51. This gives some depletion of chromium, but depletion that starts to converge at a threshold less than one weight percent lower than the start point.



Figure 4.53: The phase distribution (by mass fraction) of the phases listed in the key across the depth of the sample at (a) T=0 seconds and (b) T=1 second, at 750°C.



Figure 4.54: The phase distribution (by mass fraction) calculated across the depth of the steel sample at a) T=360000 seconds, b): T=1800000 seconds, c) T=3600000 seconds in a 750°C atmosphere is carbon ingress.



Figure 4.55: Two graphs showing the calculated chromium distribution across the sample at different times in 750°C. b shows the same data as the one on the left, but with an expanded y-axis.

4.4.2.5 850°C Carbon Ingress Calculation

The carbon ingress into the steel at 850°C, as calculated by DICTRA, is shown in Figure 4.56. With the increased temperature there is significantly greater carbon ingress again, up to the same 1.75 wt.% threshold. At 850°C the carbon ingress is much faster again, with the 1.75 wt.% threshold being reached by 500 hours in the calculation.

Once again, 850°C seems to be above the formation temperature range for sigma-phase as it does not appear in Figure 4.57. Again, the $Cr_{23}C_6$ content increases with the carbon content increase. The carbide formation reaches a threshold in line with the carbon ingress doing the same.



Figure 4.56:A graph showing the calculated carbon content diffusing across the steel at 850°C, measured in weight percent, against depth into the steel. The carbon distribution is plotted for various times, illustrated in the key.



Figure 4.57: The above graphs show the phase distribution within the steel during the calculation of the 850°C. Each graph shows the distribution at different times through the calculation, a) at 36000 seconds, b) at 360000 seconds, c) at 1800000 seconds, d) at 360000 seconds.

The chromium distribution, seen in Figure 4.58, mirrors the carbon distribution seen in Figure 4.56. This gives some depletion of chromium, but depletion that reaches a threshold less than one weight percent lower than the start point.



Figure 4.58: Two graphs showing the calculated chromium distribution across the sample at different times in 850°C. b shows the same data as the one on the left, but with an expanded y-axis.

5 Discussion of Results

5.1 Thermal Gradients

In Section 4.1 the issue of a potential thermal gradient was addressed. This was examined due to observed segregation in previous studies of the cladding. The only difference in temperature between the two faces of the cladding in the furnace is a small one during heating and while maintaining temperature. There is no difference in the cooling curves, which was in air rather than in furnace. While it is possible that the difference in temperature is due to a systematic error with the thermocouples, the difference disappearing when the sample is removed from the furnace. The argon gas flowing in is not pre-heated, and the sample was resting with the outside of the tubing sample against the wall of the furnace and the inside facing into the furnace. The flow of relatively cold argon into the furnace could have caused a temperature difference. This would also explain why there is no difference in cooling, as the sample is air cooled outside of the furnace. Due to this result, there will not be any expectation of a temperature gradient through the samples.

In samples taken from reactors there is precipitate banding seen. This effect is partly due to the penetration depth of radiation in the steel [39], but there is also a difference in temperature from the ceramic fuel pellets inside the steel cladding undergoing fission to the carbon dioxide coolant flowing through the reactor. As the precipitate formation is dependent on temperature, it is possible that this could lead to banding or segregation of precipitates. However, it is not known how severe any thermal gradient would be through a piece of steel as thin as the cladding. For the purposes of this study, replicating or examining any thermal gradient is not considered.

5.2 Microscopy and Spectroscopy

The analysis of BSE micrographs described in Section 4.2 is drawn together in Table 5.1. It shows the average diameter of precipitates observed, their area fraction and number density for every treatment condition analysed.

	Steel Treatment		Average Diameter (μm)	Area Fraction	Number Density (µm ⁻²)	
	As received	Argon	0.033±0.007	0.0043±0.0009	0.13±0.02	
	1008 h, 350°C (NbC	CO ₂	0.044±0.007	0.018±0.006	0.4±0.1	
	precipitates)	Argon	0.039±0.009	0.015±0.005	0.4±0.1	
	1008 h, 550°C (NbC	CO ₂	0.032±0.008	0.013±0.005	0.40±0.09	
	precipitates)	Argon	0.04±0.01	0.013±0.005	0.31±0.06	
	1008 h, 750°C (All	CO ₂	0.04±0.03	0.013±0.006	0.3±0.1	
	precipitates)	Argon	0.04±0.02	0.015±0.005	0.4±0.1	
	1008 h, 750°C (NbC precipitates)	CO ₂	0.04±0.01	0.010±0.004	0.3±0.1	
		Argon	0.033±0.006	0.012±0.003	0.4±0.1	
	1008 h, 750°C (G- phase precipitates)	CO ₂	0.6±1.2	0.004±0.009	0.002±0.006	
		Argon	0.5±0.5	0.005±0.008	0.006±0.008	
	1008 h, 850°C (NbC	CO ₂	0.050±0.006	0.015±0.004	0.32±0.08	
	precipitates)	Argon	0.05±0.02	0.014±0.004	0.28±0.07	

Table 5.1: The precipitate number and size analysis for each treatment condition, from section 4.2.

Looking only at the results for niobium carbide precipitates from Table 5.1, we can compare the effect of the conditions on that precipitate.

Figure 5.1 shows the average diameters of niobium carbide precipitates found in every heat treatment condition. Comparing the effect of heat treatment in carbon dioxide compared to argon, it doesn't seem to have made a great difference. The two conditions are very close, mostly within error of one another, when it comes to the precipitate diameter and swap which has the larger diameter. It does not appear that the carbon atmosphere had a significant effect on the size of the carbide particles over an inert argon atmosphere. There seems to be an increase in NbC diameter for both atmospheres at 850°C. It may be that the higher temperature increased mobility enough to lead to precipitate growth, but the overlap in error bars from the other temperatures with this point does not give confidence to that supposition.



Figure 5.1: This graph shows the average diameter of NbC precipitates observed in all steel treatment conditions. Data are taken from Table 5.1. The treatment of the As-Received sample is unknown, but it is presented for comparison.

In Figure 5.2, the area of niobium carbide precipitates observed in the sample, as a fraction of the total area observed, is plotted for the 8 different treatment conditions and the as-received sample. Once again, there is little difference between the average value for each condition, with the differences between atmospheres at the same temperature all within the calculated errors of one another. There is, as in Figure 5.1, an increase at 850°C. These results corroborate each other, suggesting there may be some niobium carbide precipitate growth at 850°C, leading to an increased particle diameter and an increased area fraction.

One clear change can be noted from Figure 5.2: the heat treatments all have significantly higher niobium carbide area fraction that the as-received steel. This does not have a corresponding increase in the niobium carbide precipitate diameter. However, a large increase can also be seen in the number density from the as-received steel to the heat treated samples, in Figure 5.3. Once again there is no clear trend across the different temperatures or between the two atmospheres.

It is difficult to draw any concrete conclusions here. It is possible that at 850°C there was niobium carbide particle growth, resulting in a larger area fraction and larger diameter particles. It also appears that for all heat treatments there is a greater number density and area fraction of niobium carbide particles than in the as-received steel. There are no strong correlations in the treated samples, so it may be that this increase is due to the initial annealing treatment, intended to replicate industrial process, which stabilises the steel.

The other clear observation that can be made from Table 5.1 is that G-phase was only observed in the samples treated at 750°C. There is no great variation in the G-phase measurements in the different atmospheres. This does not mean that none exists, but so little G-phase was observed that it is impossible to draw any quantitative conclusions. The G-phase observed different greatly from the small, evenly dispersed, spherical niobium carbide particles. It was only observed at the sample surfaces and the particles were an order of magnitude larger than the niobium-rich particles. The G-phase also had a different morphology, more plate-like and irregular in shape than the mostly spherical niobium carbide.



Figure 5.2: This shows the area fraction of NbC precipitates with respect to the steel bulk observed in all steel treatment conditions. Data are taken from Table 5.1. The treatment of the As-Received sample is unknown, it is included for comparison.



Figure 5.3: The average number density of NbC particles observed in all steel treatment conditions. Data are taken from Table 5.1. The treatment of the As-Received sample is unknown, but it is included for comparison.

In addition to the morphology of the precipitates, there were clear differences in composition. In Table 5.2 all averages of the scans of niobium-rich precipitates are presented. It was not possible to get a reliable reading for carbon composition and there is no obvious correlation with atmosphere or temperature and the weight percent of the components. It is also difficult to compare the averages of the scans due to small precipitates leading to readings from the bulk being detected, or the electron beam interaction volume measuring the bulk as well as the precipitate. It is, however, clear that the precipitates are niobium-rich. In comparison to the scans of the bulk composition, shown in Table 5.3, there is a detectable titanium presence, suggesting that it has been segregated from the bulk. In the bulk, the proportion of iron, nickel and chromium are all very similar and like the initial composition measurement. In the measurements for the niobium-rich precipitates, however, there is a higher percentage of chromium than nickel. This suggests that in the immediate vicinity of the niobium carbide there is depletion of nickel, or enrichment of chromium. It is possible that a depletion of nickel could be caused by the beginnings of G-phase formation, nucleating on the niobium rich phase as described by Powell et al. [1]. However, this should appear as an enrichment of nickel as G-phase has a much higher weight percent than the bulk here. It is unclear why this immediate surrounding should be different from the bulk if no other enrichment or depletion is seen.

Condition	350°C, CO₂ atmos	350°C, Ar atmos	550°C, CO₂atmos	550°C, Ar atmos	750°C, CO₂atmos	750°C, Ar atmos	850°C, CO₂atmos	850°C, Ar atmos
NbC	Average	Average	Average	Average	Average	Average	Average	Average
components	WL.70	WL.70	Wl.70	WL.70	Wl.70	WL.70	WL.70	WL.70
0	5.7±0.1	4.8±0.2	8.2±0.1	4.7±0.2	6.2±0.1	7.3±0.2	6.1±0.2	7.4±0.2
Si	0.30±0.02	0.27±0.04	0.78±0.02	0.21±0.03	0.35±0.02	0.98±0.04	0.51±0.03	0.75±0.04
Ti	0.27±0.04	0.4±0.1	0.14±0.01	0.3±0.1	0.40±0.04	0.4±0.1	0.37±0.05	0.3±0.1
Cr	4.39±0.07	4.5±0.1	3.32±0.06	1.60±0.09	3.36±0.06	1.61±0.08	2.19±0.08	2.05±0.09
Fe	7.9±0.1	8.6±0.2	5.43±0.08	2.8±0.1	6.2±0.1	2.7±0.1	3.9±0.1	4.0±0.1
Ni	3.0±0.1	3.3±0.2	2.05±0.09	1.1±0.1	2.4±0.1	1.2±0.1	1.6±0.1	1.5±0.1
Nb	78.4±0.2	78.3±0.3	80.1±0.2	89.3±0.3	81.5±0.2	85.8±0.2	85.5±0.2	84.1±0.3

Table 5.2: The average weight percent for each component of every point scan of niobium-rich precipitates in each treatment condition.

Table 5.3: The average weight percent for each component of every point scan of precipitate-free bulk in each treatment condition.

Condition	350°C,	350°C,	550°C,	550°C,	750°C,	750°C,	850°C,	850°C,
	CO_2 atmos.	Ar atmos.						
Bulk	Average	Average	Average	Average	Average	Average	Average	Average
Components	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
0	0.93±0.08	0.85±0.08	1.02±0.05	0.94±0.08	0.84±0.06	1.30±0.07	1.08±0.04	1.33±0.07
Si	0.67±0.04	0.63±0.04	0.91±0.03	0.74±0.04	0.73±0.03	1.02±0.04	1.12±0.02	1.17±0.04
Cr	20.7±0.1	20.7±0.2	20.3±0.1	20.7±0.2	20.4±0.1	20.3±0.1	20.0±0.1	20.7±0.1
Fe	52.4±0.2	52.6±0.2	53.3±0.2	52.8±0.2	53.4±0.2	53.1±0.2	52.8±0.2	52.4±0.2
Ni	24.4±0.2	24.3±0.2	24.1±0.1	24.3±0.2	24.3±0.2	24.1±0.2	24.4±0.2	23.8±0.2
Nb	0.9±0.1	0.9±0.1	0.45±0.07	0.5±0.1	0.34±0.08	0.26±0.09	0.56±0.06	0.7±0.1

While this alteration in the composition is unexplained, the plate-like precipitates, measured composition shown in Table 5.4(A), appear to be G-phase. The ratio of elements does not match the composition from literature. Both of the treatments at 750°C have more nickel than would be expected when converted to mole ratios. The mole ratio for carbon dioxide can be expressed as $Ni_{20.05}Nb_6Si_{6.38}$, while it can be expressed as $Ni_{22.57}Nb_6Si_{7.48}$ for the argon atmosphere. This excess nickel can be explained with a contribution from the bulk due to the interaction volume of the electron beam.

(A)	750°C,	750°C,		
(~)	CO ₂ atmos.	Ar atmos.		
G-phase component	Average wt.%	Average wt.%		
0	1.85±0.08	2.5±0.1		
Si	7.49±0.07	7.12±0.06		
Ti	5.34±0.10	9.84±0.10		
Cr	12.5±0.1	16.2±0.1		
Fe	49.4±0.2	45.1±0.2		
Ni	23.4±0.2	19.1±0.2		
Nb	1.85±0.08	2.5±0.1		

Table 5.4: (A) composition of the irregular precipitates in the 750°C heat treated samples, measured by point
EDX. (B) shows these data normalised to just the documented G-phase components.

(P)	750°C,	750°C,	
(D)	CO ₂ atmos.	Ar atmos.	
Normalised G-phase	Average wt.%	Average wt.%	
Si	9.37±0.08	10.04±0.08	
Ni	61.5±0.1	63.3±0.1	
Nb	29.1±0.2	26.6±0.2	

The silicon quantity for the G-phase measurements varies from lower than expected to higher. It is difficult to say how accurate this semi-quantitative data is, especially with the added difficulty of detecting a lighter element. However, it seems safe to assume that this is an approximation of G-phase due to the majority components.

The appearance of G-phase at 750°C correlates with the TTP diagram (Figure 2.4) produced by Powell et al [1] which suggests that G-phase will first form at this temperature. However, it was observed to form within hours at 750°C. After 1000 hours, G-phase and $M_{23}C_6$ were observed in 850°C treated samples and in samples treated at 575°C. It was also the case that the initial condition of the steel in that study was with niobium carbide only observed at grain boundaries, unlike this study, where it was observed dispersed throughout. This may compare more favourably with Ecob et al. [2] This study observed an initial distribution of niobium carbide which, after 1000 hours at 750 and 850°C, transformed into G-phase, leaving no NbC remaining. At 750°C, σ -phase was observed.

There are therefore, many differences between the results seen here and the literature. It seems that, despite similar annealing treatments, the initial conditions of the steel were quite different and the differences in the composition of the steel have a profound effect on the precipitation behaviour. The stability of the niobium carbide seems to vary, with it completely transforming for Ecob et al., precipitating in the matrix and disappearing from the boundaries for Powell et al. and changing very little across samples here. Here, G-phase was seen at 750°C, but at no other temperatures. It is possible that the samples examined here experienced the other extreme, with NbC so stable little change was seen and G-phase only formed at the optimum temperature.

STEM was employed to get a more precise reading on smaller particles, hopefully using the higher resolution to find evidence of developing phases on a smaller scale, such as G-phase. However, the only precipitates that were found in all samples examined were niobium carbide. The EDX spectroscopy performed using the STEM did little more than confirm the particles were niobium carbide. There was no more accurate compositional information due to the low atomic number of carbon.

5.3 Simulations and Calculations

The Thermo-Calc software that was used to simulate various conditions for this steel has one significant drawback when trying to apply it to the heat treatments described in this study. It minimises the Gibbs Free Energy of a system to find the equilibrium values for that system. However,

the treatments are not only dynamic, but also being performed on a pre-treated steel of unspecified history. This made trying to replicate the experimental work difficult.

A simple example of this exists in the initial property diagram in Section 4.4.1. Below 460°C, Thermo-Calc predicts the appearance of a ferritic phase, which is not seen in the 350°C treatment. This is not a contradiction, as the difference between a treated state and equilibrium can be tens of thousands of hours. It does however, highlight the problem with trying to compare microscopy of heat treated material with the calculations performed by this software.

As stated, the as-received steel contained a niobium carbide dispersion throughout the material. This is barely seen in the equilibrium property diagram, with the main non-bulk phase being σ -phase. However, taking the plot of phases' Gibbs Free Energy (Figure 4.42) as an approximate precipitation sequence, niobium carbide is one of the first phases expected to form, after titanium nitride (not observed due to low nitrogen content), manganese sulphide (not observed due to low sulphur content), and Z-phase (CrNbN, again not seen due to low nitrogen content [54]). However, niobium carbide is predicted to be stable for higher temperatures, while G-phase is predicted in a similar energy range, but at lower temperatures.

As this shows, not all phases calculated are present, either as they exist in quantities too small to detect, or due to the pre-treatment of the steel. It is also possible that phases might not be as distinct as they are in Thermo-Calc, for example, G-phase might not be distinct from NiNb₃ only using SEM and EDX, a phase that features prominently in the Gibbs Free Energy graph (Figure 4.42).

Accepting this, the approximate precipitation sequence in the form of Gibbs Free Energy, and the property diagram agree with the precipitation sequence found by Powell et al. [1]. This is especially clear with σ -phase as the precipitate with the highest calculated Gibbs Free Energy in Section 4.4.1 and the final precipitate in their experimental TTP diagram.

DICTRA, the Thermo-Calc diffusion module, was used to look at the effect of carbon ingress from an external source. The carbon ingress activity was arbitrary, but the results can still be taken as indicative of the change in carbon ingress into the steel with different timescales at different temperatures.

As might be expected, with increasing time, carbon ingresses further into the steel. With increasing temperature, carbon ingress occurs on a shorter timescale. This is up to a threshold of around 1.7 wt.%.

With the carbon ingress, the amount of niobium carbide does not change. This is because the system is still calculated at an equilibrium. The carbon ingress is calculated based on mobility data, then the system equilibrium is calculated based on the new composition with increased carbon. This is why at T=0 s the equilibrium phases are not yet present, as the first calculation hasn't completed yet. Due to this, for the lower temperatures there exists the equilibrium σ -phase. At 350°C there is not enough energy in the system for carbon ingress, so the system does not change. As carbon ingresses at 550°C, the σ -phase and, to some extent, the austenite are replaced with chromium carbide (Cr₂₃C₆). Scaling with time and temperature and omitting σ -phase above the temperature it is an equilibrium phase, this is repeated across the different conditions. The chromium carbide reaches a threshold as the carbon does, unable to form more carbide with the supply of carbon limited.

While this illustrates a potential problem with heat treatments in a carbon-rich environment, such as the carbon dioxide cooled, graphite moderated AGR (any carbon ingress risks sensitising the steel, leaving it prone to corrosion once removed from the reactor), it is not directly relatable to the heat

treatments seen here or the conditions within a reactor for two reasons. First of all, a more accurate carbon activity coefficient is needed for either situation to make a prediction on how much carbon will ingress into the steel, enabling the model to accurately calculate the amount of carbon entering the steel. Any calculations of the activity by the software gave an answer (for the steel in pure carbon dioxide) so low as to have no effect on the carbon ingress, much as seen for the 350°C case, but at all temperatures. The second problem with using DICTRA in this case is that it still calculates the phase composition of the system at equilibrium, which is too much of a simplification in this case. In the heat treatments performed, the steel starts with a niobium carbide dispersion throughout which then, depending on the temperature, develops throughout the treatment. It might be expected that excess carbon dissolving into the steel would be bound with niobium in solution in the austenite, or that in an inert atmosphere, the high temperatures would make other phases, such as the G-phase seen in the 750°C sample, more energetically favourable while providing the energy to allow phase transformations.

Thermo-Calc and the DICTRA module can be used to make predictions. It is clear that as more carbon ingresses into the steel it will lead to a more favourable environment for $M_{23}C_6$ carbides to form, but it moves straight to the equilibrium condition with no phase transformation process or diffusion beyond that bringing the carbon in to the steel. These are known limitations of the software which explain and account for the difference between the experimental results and the calculations seen here.

6 Conclusions

In conclusion, all heat treatments increased the number of niobium carbide precipitates present, but there was no reliable difference between the different temperatures or between the atmospheres at the same temperature.

At 750°C G-phase was detected near the surfaces of the sample despite Thermo-Calc predicting its existence below 550°C. This does agree with literature, however, with Powell et al. [1] and Ecob et al. [2] documenting its appearance . However, this was seen within 10 hours of treatment, while at 1000 hours they also observed $M_{23}C_6$ and σ -phase at the grain boundaries and a decrease in niobium carbide. This difference is possibly due to a difference in the pre-treatment of the steel, which was undisclosed for the samples presented here. Following a suggested explanation from Ecob et al. it appears that the stability of the niobium carbide varies. Ecob et al. believed that they saw full transformation of NbC to G-phase as the NbC was particularly unstable. It seems that in this steel, either due to an unknown pre-treatment or the differences in composition, the niobium carbide is more stable than either of those observed, only transforming to G-phase at long treatment times, still remaining at the grain boundaries and in the matrix and with no further transformations.

The equilibrium and DICTRA calculations are indicative of changes the steel can undergo, an increase of carbon leads to an increase in carbides, but without thermodynamic kinetic calculations are difficult to make any qualitative predictions on the evolution of the steel from.

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