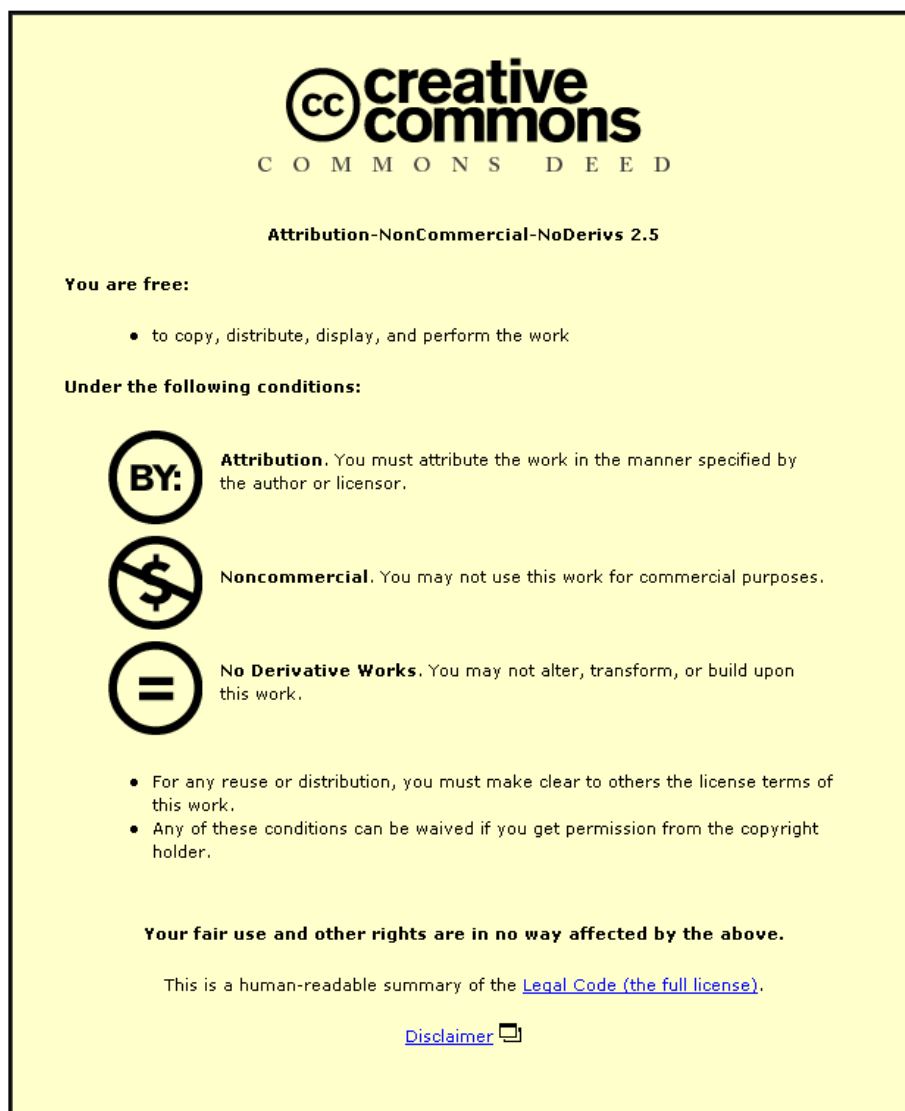


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Department of Materials

**Microstructural Evolution of Nimonic 263 for use in
Next Generation Power Plant**

Sean A Smith

Department of Materials

Loughborough University

A doctoral thesis submitted in partial fulfilment of the requirements for the
award of Doctor of Philosophy

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Abstract

Environmental and economical demands are driving the need for the UK and the rest of the world to develop higher efficiency, next generation coal-fired plant. Higher efficiency energy recovery will ultimately result in a combination of cheaper energy for the consumer and enabling industry to meet emission targets. The intention is to increase operating parameters from 550°C and 17.5 MPa to 700°C and 30 MPa resulting in more efficient energy generation. This increase in operating parameters will also increase the demand on power plant materials, resulting in the use of some existing materials to be no longer viable. It is for this reason that nickel based alloys have been considered for areas of the plant which will experience high temperatures, pressure and will also require enhanced creep resistance.

Nickel based alloys will be used in high temperature, high pressure components such as steam headers. This research focuses on one of the candidate materials for this area of plant, the alloy Nimonic 263. The ultimate aim of the research is to study the microstructural evolution with respect to time at a range of high temperatures to help assess the suitability of the alloy. To fully assess the alloy's candidacy it must be studied in each product form in which it is likely to be used, and for this reason this research has considered Nimonic 263 as a forged, welded and cast alloy.

The alloy's expected equilibrium microstructure was calculated using thermodynamic calculations, which predicted the phases present and how their fractions varied with temperature. The calculations were expanded to calculate the composition of the constituent phases of the alloy and their variation with temperatures, and also to consider possible segregation tendencies on solidification.

Through thermodynamic calculations and experimental observations, Nimonic 263 was confirmed to have a gamma (γ) matrix which was strengthened by approximately 10 % gamma prime (γ'). The alloy also contained $M_{23}C_6$ which was present as a grain boundary precipitate, and the MX phase which was present throughout the microstructure. Significant microstructural transformations were observed as a result of time and temperature. As a result of isothermal ageing, the γ' precipitates were found to coarsen in accordance with standard particle coarsening theory, and the coarsening rate was found to increase as a function of the ageing temperature. After long term thermal exposure at 700°C and after shorter ageing times at higher temperatures, the γ' precipitates were observed to transform into the elongated 'needle' like Eta precipitates (η).

Thermodynamic equilibrium calculations performed on the supplied compositions of material examined in the welded and cast state predicted a similar microstructure to that predicted in the case of the material examined under isothermal ageing conditions. Due to the nature of the solidification process in welded and cast alloys, non-equilibrium calculations were carried out to understand the elemental segregation likely to occur in the alloy. The calculations predicted the elemental increase of molybdenum and titanium in some of the last metal to solidify, alternately the amount of aluminium present in the last metal to solidify was significantly reduced. The aluminium content of the alloy was both predicted to, and experimentally found to, have a significant effect on the precipitate evolution of these segregated areas, specifically in the welded microstructure.

Ultimately, the research has answered the question regarding the materials candidacy for next generation power plant. Throughout the investigation of Nimonic 263, it has been shown to have a stable microstructure in all product forms at the intended operating temperature of 700°C. One problem with its candidacy could be that once next generation plant has been built there will be understandable pressure to again increase plant efficiency, as has previously been the case. At this point alloy Nimonic 263 may no longer be considered a candidate material by some engineers and designers. At isothermal exposures of 750°C and above, in addition to a decrease in the alloy's creep strength, the alloy was shown to contain significant amounts of the potentially deleterious Eta phase. The recent development of new, alternative, candidate alloys which are reported to be more stable at higher temperatures also raises further questions about its usage.

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Chapter 1

Introduction

1.1 Power generation industry past, present and future

Nimonic 263 is a candidate alloy for use in steam headers and other high temperature components in next generation coal fired power stations. A steam header is a thick section pipe which transports superheated steam from the boiler to a series of turbines. In a coal fired plant, electricity is generated through the following process: Pulverised coal, produced by grinding coal to a fine powder, is injected into a boiler and combusted in order to heat up a series of pipes carrying water. The water, which is usually supplied from a reservoir within the station, is then heated to temperatures well in excess of its boiling point and high pressure steam is produced. The steam undergoes further heating during transportation through a network of tubes and headers until it reaches a series of turbines. The steam turns up to three turbines (depending on the particular plant configuration); high, medium and low pressure, with the overall aim of getting as much energy out of the steam as possible.

The excessive heat and pressure of the steam can cause the header and pipe networks to suffer a phenomenon known as ‘creep’ over a period of many years, potentially resulting in failure. Due to the complexities of the positioning and design of the headers and their connecting pipework these components are difficult to replace. Another issue with replacement of these components is the suspension of plant activities, whilst maintenance or replacements can be made ^[1]. Therefore, it is important that alloys with long predicted lifetimes are used such that they rarely, if ever, need to be replaced.

It is important to understand the basic principles of power generation along with both current and future requirements that the power generation industry may have: including increases in energy demand and associated increase in operating parameters to help meet such demands. Special attention is paid to the UK energy market which this research is focused towards.

1.2 Global / UK power demand

In the modern world electricity is an important commodity with the majority of homes and businesses relying on an ‘on demand’ supply. Based on current predictions over the next 25 years the global energy demand will increase by 55%; this increase encompasses an increase

in electricity demand from 15,000 TWh in 2004 to a predicted 30,000 TWh in 2030 ^[2]. The UK is following this trend and since the 1980's electricity demand has increased from 110 TWh to 350 TWh, this increase is set to continue with predictions that electricity demand in the UK will be at 400 TWh by 2020 ^[3,4]. Since this prediction was made in 2007 the figure of the UK's consumption of 350 TWh has remained relatively constant, in 2012 actual consumption in the UK was recorded at 356.96, 367.45 and 363.84 TWh's in years 2010, 2011 and 2012 respectively ^[5,6].

The intention is that this increase will be met by 35 GW of new generation capacity which will also cover the deficit left due to older plant being decommissioned. Plant is decommissioned for a number of reasons: they are no longer economical to run; will be unable to meet emissions targets, and; finally to reduce the reliance on fossil fuels. Figures from 2006 state that 72% of the electricity currently generated in the UK is produced from fossil fuels of which coal accounts for 50% ^[3]. The number of plant being decommissioned has increased since the introduction of the large combustion plant directive (LCPD). The LCPD was introduced by the European Union in 2001 and, in summary, the directive limits the amount of sulphur dioxide, nitrogen oxides and dust emitted from large combustion plants with an operating capacity over 50 MW each year. In addition to power plant the directive also covers petroleum refineries, steel works and other industrial processes that run on solid, liquid or gaseous fuel.

The directive places emission limits on new plant (licenses after 1st July 1987). Existing plant i.e. licensed before 1987 have 3 options:

- Meet new emission limits which will require the retrofitting of flue gas treatment equipment
- Opt out life derogation (20,000 hours between 1st January 2008 – 31st December 2015)
- Close before 1st January 2008

It was expected on the 1st of January 2008 that 11550 MW of generation capacity would be cut due to the directive, however, due to demand some of these stations have remained open ^[4]. Similar directives are in place across the developed world with inefficient plant being

phased out in preference to new more efficient plant. Contrary to the introduction of the LCPD 41% of the UK's energy in 2012 was produced from coal based sources ^[6]. A report by the technology strategy board (TSB) states that there will be a £10 trillion investment in global energy infrastructure from 2005 to 2030 ^[7]. This investment is spread between developed countries bringing online more efficient plant and developing countries such as China and India extending their generation capacity as their economies grow. A BBC article from 2007 further outlines the part developing countries are playing on the global energy infrastructure, stating that China was building two power plants each week ^[8].

1.3 Increasing the efficiency of current and new build plant

In addition to building new power stations, increasing the efficiency of current power stations is another option. The second route is economically preferable, especially in the current economic climate. Large gains are to be had by improving the efficiency of power plant; in 1993 typical efficiency was at just 42% ^[9]. To improve the efficiency of power plant, operating parameters have to be increased i.e. steam temperatures and pressures. As the government and other regulatory bodies introduced in quotas for CO₂ emissions, the power generation industry had to react. Emission cleaning technologies such as dry and wet bag scrubber systems were introduced. Plans for carbon capture technology are currently being investigated, which although reducing the amount of CO₂ released into the atmosphere can also decrease the efficiency of plant because of the power needed to run the CO₂ capture part of the plant.

Plant has been continuously increasing in efficiency since the 1950's. The average fuel mass required to generate one kilowatt-hour of electricity has been reduced by approximately half since 1990. Increasing the efficiency of plant creates both environmental and economic benefits and globally, nations are moving towards greener industry and infrastructure. The economic benefits are currently even more sought after due to rising fuel prices and the drive to keep down the cost of domestic energy. There are a number of different ways to increase plant efficiency, such as more efficient turbine systems, but the simplest method of improving efficiency is by increasing the temperature and pressures of the steam used for generation. The phrase 'steam parameters' is often used and refers chiefly to the temperature and pressure of the steam. An increase in steam parameters from 538°C / 30 MPa to 650°C / 40 MPa is calculated to give an increase in steam turbine efficiency of approximately 8% ^[10].

The graph below in Figure 1.2 shows how both the temperatures and pressures of steam used for generation have changed in Germany since the 1900's, and similar trends are relevant to the UK. Materials suitable for operation in a power plant will be required to be safe and reliable during their life times which can be up to and in excess of 30 years. As the generation portfolio changes conventional plant need to be able to respond in a flexible manner and therefore cycle more often. The ability for a plant to thermally cycle will become more prominent due to the continued introduction of renewable energy, which will periodically reduce loading on the grid and in turn conventional plant.

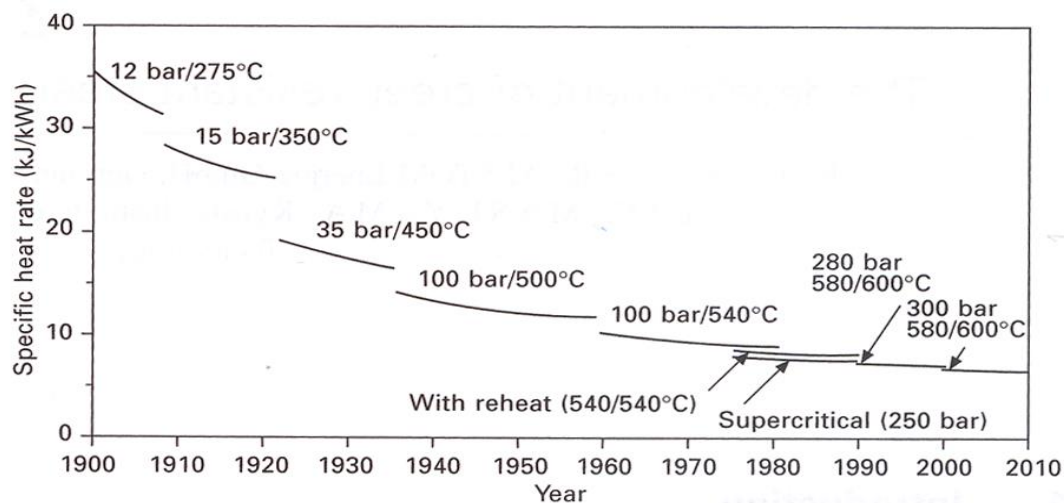


Fig 1.2: Graph showing operating parameters of power plant in Germany since 1900's ^[11]

Due to the aforementioned increase in demand on the grid and government legislation, new, more efficient plant is needed. The next generation of plant, termed Ultra Super Critical (USC), is likely to run at operating parameters approaching 700°C / 35 MPa, in order to achieve these parameters the materials used need to be re-evaluated. Nickel-based superalloys lend themselves to high temperature and pressure applications due to their significant creep strength and the ability to operate at temperatures up to 0.9 T_m . Operation at these elevated parameters would result in either instant or premature failure for the majority of existing power plant materials such as steels and austenitic stainless steel alloys. Steels and other materials, however, can still be used in some of the lower temperature applications present in plant.

1.4 Thermodynamics of power plant

The Rankine cycle forms the thermodynamic basis for the majority of steam power plants. Plant may use a number of different fuels such as coal, oil, gas or nuclear power to generate steam but the underlying principles remain the same. The Rankine cycle operates on the isentropic expansion of high-pressure gas, usually steam, to produce work^[12].

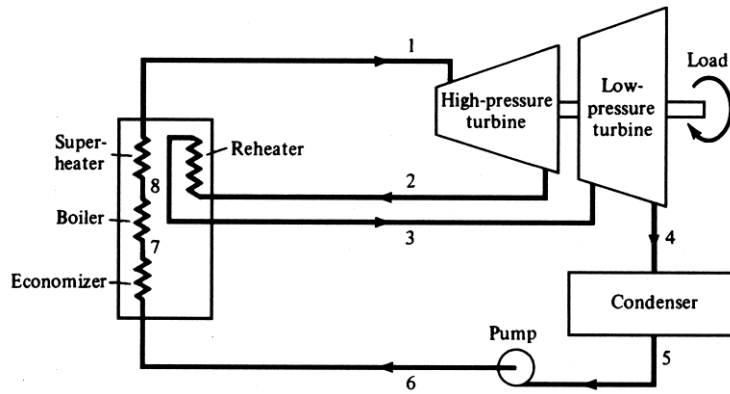


Figure 1.3: Schematic flow diagram of a Rankine cycle with superheater and reheat^[13]

The basic operation of a power plant producing energy using the Rankine model is shown in Figure 1.3. Firstly water is pumped, under pressure, into the steam generator. The water is then heated up through the economiser and boiler to produce high pressure steam (in USC plant steam is also passed through a superheater to provide a further increase in operating parameters). The high pressure steam is then passed through the high pressure turbine to generate electricity. Instead of venting the waste steam, it is taken back into the steam generator along line 2 where it is reheated and then fed back into the low pressure turbine. Some plant will have more than one re-heat cycle to improve efficiency, although often the improvement in efficiency from an additional reheat does little to justify the capital cost. Waste steam is then cooled by the condenser, forming water which is pumped back into the reservoir ready for re-circulating in the system.

1.5 Development of materials in power generation

New materials have continually been developed in order to function at the next set of operating parameters used in power plant. Until the 1920's unalloyed steels were used at a maximum temperature of 350°C and at pressure of about 15 bar (1.5 MPa)^[14]. After the 1920's the power generation industry started to increase operating parameters to around 450°C / 3.5 MPa. At this early stage industry developed materials on an individual basis as joint research programmes were uncommon. Due to this individual development a variety of

different low alloy steels were used depending on each plant and the country it was situated in. In the 1950's operating temperatures were further increased to $\sim 550^{\circ}\text{C}$, bringing about the development of 9-12 wt.% Cr steels. These materials have since been further developed, with T/P91 and 92 materials now operating at temperatures of $\sim 600^{\circ}\text{C}$ ^[11]. T/P91 and 92 are 9 Cr ferritic steels, which are strengthened by a fully martensitic microstructure which has a high dislocation density and is the fine dispersion of MX precipitates. These steels have a low coefficient thermal expansion and due to this lend themselves to piping applications.

1.6 Requirements of steam pipe materials and future materials development

Steam pipes and headers make up the focus of this research. The main function of these systems is to transport steam to and from the boiler and turbines. The amount of working fluid present in plant varies depending on its output and type; in a 660 MW $\sim 540^{\circ}\text{C}$ there is 1.26×10^4 kg/s circulating around the system. The pipes used must be large enough to pass the total quantity of steam, without a substantial pressure loss. The pipe walls must be thick enough to resist the high pressures generated from the containment of steam. Stresses are also introduced through the thermal expansion of the high temperature pipe work. This induced stress must be monitored and designed with flexibility in mind to prevent failure of the pipe or the deterioration of other components in contact with steam pipe. Designing a flexible solution can prove difficult when the typical dimensions for pipes can be up to 600 mm in diameter with wall thicknesses of up to 127 mm. One design solution involves using a number of pipes in parallel; in a 500 MW powerplant, four parallel pipes (355 mm outside diameter – 230 mm inside diameter) are used. This solution although alleviating the problem, complicates design and increase costs.

Nickel-based alloys lend themselves to high temperature and pressure applications due to their significant creep strength and the ability to operate at temperatures of up to $0.9 T_m$. Due to their chemistry nickel alloys also have a good resistance to oxidation and corrosion and in turn stress corrosion cracking (SCC). Although an important consideration in the intended environment and operating conditions, the effect of SCC is not studied in this thesis as it has been carried out by another project which is part of the same research programme. Header systems experience some of the highest temperatures and pressures in the power plant and it is therefore paramount that a suitable material is chosen and methodologies are put in place to predict their safe operating lifetimes. In particular Nimonic 263 has been chosen due to its improved welding characteristics when compared to other candidate allows. Its improved

weldability is as a result of its lower volume fraction of gamma prime. Nimonic 263 is one of the candidate alloys specifically being looked at for use as a header or piping material in a number of different programs, including THERMIE, Cooretec and AD700. The status of Nimonic 263 and other Nickel base materials as candidate alloys have resulted in a number of research projects focusing on their use for power generation. One of which is this project funded by phase II of the Supergen joint research program ^[15-18]. This research will study the effect of time and temperature on the microstructure of Nimonic 263 to assess the alloy's candidacy for next generation plant. The effect of increased pressure as a result of increased steam operating parameters is not considered as part of this research. This exclusion is due to the increased pressure having minimal effect on the alloys microstructure. The increase in pressure will, however, have an effect on the alloys oxidation properties which have been studied in a different project also part of the Supergen II joint research project, for which the subject of this thesis is a part of.

1.7 Organisation of Thesis

The literature review presented in Chapter 2 concentrates firstly on the historical developments in the research topic and materials development over the years. The chemistry of modern superalloys are discussed in terms of: each alloying element and their roles in the particular system. Literature regarding the phases present in Nimonic 263 is then presented in terms of their particular morphology, effect on the alloy and evolution. The different strengthening mechanisms in superalloys are reviewed. The effect that creep has on the alloy is discussed, with experimental values for Nimonic 263 presented.

The experimental procedures section, Chapter 3 gives an insight into the equipment and techniques used in this research to study Nimonic 263. The section presents the various techniques and parameters utilised when operating any experimental equipment; including the scientific principles relating to the operation of any analytical equipment.

In chapter 4 samples were taken from forged thick section experimental pipe and isothermally aged through a range of temperatures and exposure times with the aim to study the effect of ageing on the alloys microstructural evolution. Thermodynamic equilibrium calculations were carried out to predict the amount and chemical composition of the phases contained within the alloy as a function of temperature. These predictions were used in conjunction with microstructural observations to aid in identification. The alloy's

microstructure was observed, recorded and identified using both optical and electron microscopy in conjunction with the chemical analysis technique, energy dispersive X-ray analysis (EDX). The alloys microstructure was also linked to its mechanical properties using the hardness testing technique. Experimental observations were recorded and analysed with findings reporting important microstructural characteristics such as precipitate coarsening rate and the effect of ageing time and temperature on the alloys mechanical properties.

The welding of Nimonic 263 is explored in chapter 5, with special attention paid to the precipitation effects resulting from a segregated microstructure. The effect of this segregation on the microstructure is predicted using non-equilibrium calculations. Two welding consumables with different thermal histories were studied, one consumable with a composition similar to parent Nimonic 263 and the other with a modified composition. The weld microstructure from both sample sets were assessed in the as-welded condition and after their individual pre-service heat treatments. Similarly to the parent material studied in chapter 4 it is important to understand how the segregated weld microstructure evolved in plant conditions. The hardness of the welded samples were assessed with an aim to understand the effect of the welding process on both the parent and weld material and that of subsequent ageing.

The final results chapter, Chapter 6, studies the candidate alloy in the cast condition. The microstructure is again fully evaluated using a range of microscopy techniques.

Finally, the findings of the thesis are discussed and an assessment of the alloys status as a candidate alloy for next generation power plant is made. The thesis also makes recommendations as to any further work that could be carried out.

Chapter 2

Literature Review

2.1 History of Nickel-based Superalloys and the Nimonic Series

To meet industries high temperature demands in early 1900's, nickel-chromium alloys were one of the solutions considered. The first reference to these alloys was made by Marsh ^[19] in 1906 in connection to their high resistance to oxidation and ability to operate at elevated temperatures. In the 1920's and 30's stainless steels were the material of choice for high temperature applications; however, it soon became apparent that stainless steels were not up to specification: since they were limiting the functionality and service life of each application they were used in. To overcome the inherent limitations of existing materials a new type of material was needed, one that would eventually be termed the 'Superalloys'. Research into this group of alloys was also carried out by Tapsell and Bradley ^[20], who in 1925 conducted a study concluding that the creep resistance of 80-20 nickel-chromium was superior to that of any other available materials at that time; a patent was filed a year later in 1926 by Heraeus Vacuumschmelze A.G to protect their use ^[21]. As a result of that research the initial focus was placed on 80-20 nickel-chromium alloys for use at high temperatures. Many applications also demanded that the materials should also have a good creep resistance. Chevenard and later Bedford, Pilling and Mercia found that by adding small amounts of titanium and aluminium to 80-20 nickel-chromium alloy, it became responsive to heat treatments which provided significant creep strengthening ^[22]. The increase in creep properties were later found to be brought about due to the precipitation of the second phase particle $\text{Ni}_3(\text{Ti,Al}) \gamma'$.

In 1939 a brief was given to The Mond Nickel Company Ltd outlining the material requirements of turbine blades in the new Whittle engine. The Mond Nickel Company Ltd attempted to meet these requirements by considering three types of alloy: 80-20 nickel-chromium, complex nickel-chromium alloys, complex nickel-chromium-iron alloys and austenitic steels. At first resources were focused on looking at modifications to existing 80-20 nickel-chromium alloys; early work going down this path led to the eventual development of the early Nimonic series. Although the modified 80-20 nickel-chromium material met initial requirements, it was soon found that more complex nickel-chromium alloys could provide greater creep strength.

The arrival of World War II greatly increased both the attention and resources put into developing these alloys for use in military jet engines. Before the introduction of investment casting Superalloys were only used in their wrought condition. Components currently being produced in wrought form could often be replaced by cast alternatives, through the implementation of design changes and small alterations in the alloys chemical composition. Cast alloys if engineered correctly are stronger and more economically viable for production.

One of the main advances after the war was the development of better processing technology, one such development was vacuum melting. Vacuum melting allowed for greater control over alloy chemistry of castings produced. The introduction of this technology specifically aided in the removal of undesirable alloy impurities: that had been proved detrimental in the metallurgical development of the 1930's and 1940's. Vacuum melting also increased the amount of control over reactive strengthening and oxidative resisting elements. Other advances with less relevance to this particular research include; directional solidification developed in the 1960's by Frank Versnyder and associates; oxides dispersion strengthening ODS by Anders et al, and; finally advances in single crystal alloys.

Superalloys can be loosely defined as a wide range of high performance materials that combine high strength and corrosion resistance at temperatures at and above 650°C. Superalloys are usually based on group VIII elements and can be divided into three main categories: nickel, cobalt and iron based. Figure 2.1 shows a timeline for the development of this material class and the subsequent improvement in creep properties.

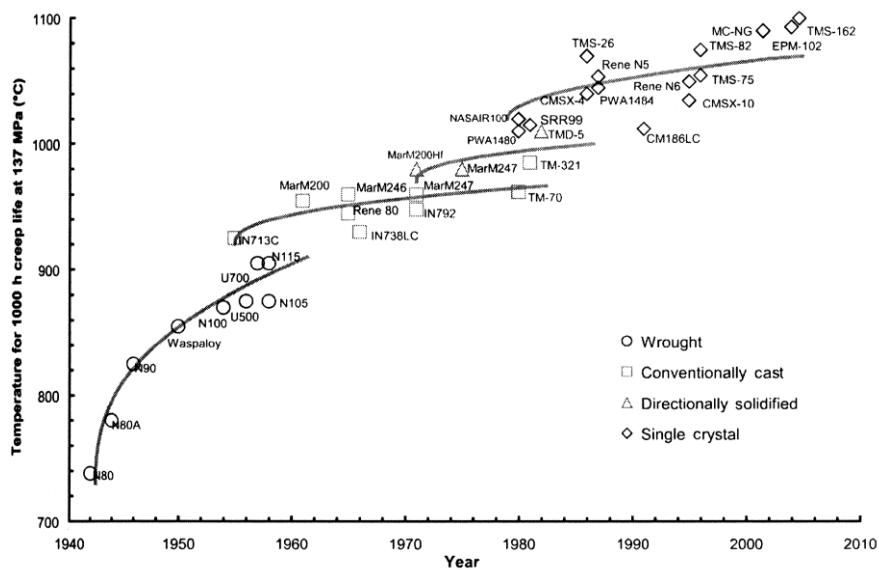


Figure 2.1: Evolution of the high-temperature capabilities of the Superalloys over a 60 year period ^[23]

2.1.1 Nimonic series

Nimonic 263 is a wrought Ni-based Superalloy developed in the 1950's by Rolls-Royce plc for use in gas turbines. It was originally developed with the intention of having the weld ductility and fabrication characteristics of Nimonic 75 and the creep rupture strength of Nimonic 80A^[24]. The alloy was designed as a sheet material that lent itself to fabrication: due to the improved ductility in welded assemblies when compared to its precursors^[25]. Due to Nimonic 263 being developed for sheet applications current uses include; combustion chambers, casings, liners, exhaust ducting and bearing housings^[26]. The first Nimonic alloy developed is now known as Nimonic 75 which has the basic composition: 80-20 nickel chromium with additions of 0.3% titanium and a carbon level of 0.1%. Although performing well it was soon discovered that increasing the additions of titanium provided a considerable improvement in creep properties. In 1941 by increasing the titanium addition to 2.5 wt.% Nimonic 80 was created^[27]. Nimonic 80 was the first alloy in the Nimonic series to exploit precipitation hardening, in which high creep resistance was produced from the controlled precipitation of nickel-titanium or a nickel-aluminium compound. Subsequent developments included the addition of cobalt and further control of the titanium and aluminium contents: resulting again in improved creep resistance. Nimonic 80 was succeeded in 1944 by Nimonic 80A which contained small changes in the amount of titanium and aluminium present again improving the alloy's properties as can be seen in Figure 2.2.

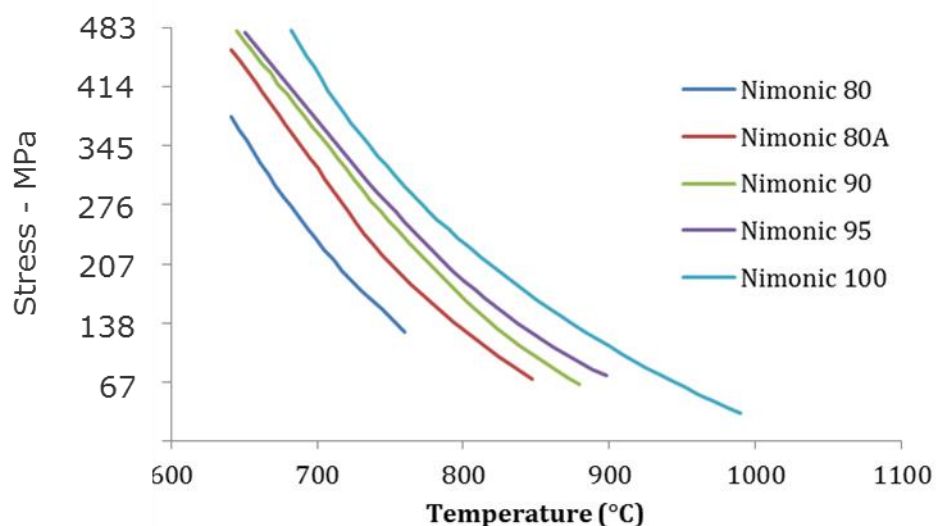


Figure 2.2: The creep rupture strength of Nimonic 80 and the alloys developed thereafter^[27]

The next alloy in the Nimonic series was developed in 1945 containing 20 wt.% addition of cobalt, replacing nickel, and named Nimonic 90. Using improved methods of hot working in 1951 it was found that levels of titanium and aluminium could be further increased and Nimonic 95 was created. In 1955 another alloy was added to the Nimonic series through the inclusion of molybdenum named Nimonic 100. Five years later Nimonic 263, the subject material for this investigation, was invented by Rolls-Royce plc.

Figure 2.2 indicates that each subsequent development in the Nimonic series has brought with it an increase in both creep resistance and the potential operating temperatures.

2.2 Chemistry of Superalloys

As previously discussed, the chemistry of Superalloys has varied since their introduction in the late 30's, this has been for two main reasons: technological / theoretical advancements and material shortages. Figure 2.3 shows a comparative view of trends in Superalloy chemical composition over time. Early Superalloys had significant amounts of iron present, however the iron component in the majority of Superalloys was reduced steadily until the 1950's. The reduction of iron is attributed to the presence of cobalt and nickel, which preferentially stabilised the FCC structure. Due to the development of γ' strengthened alloys titanium and aluminium content was seen to increase from the 1950's to the 1960's, after which it remained steady. Nickel content in Superalloys has decreased steadily over the years for a number of reasons: the cost of the alloy, security of supply and the increased use of cobalt. The nickel shortage during the Korean War in 1950 – 1951 resulted in the introduction and increase of cobalt as an alloying addition. Chromium was present in early Superalloys at roughly 20%, between the 50's and 60's efforts were made to reduce chromium levels, however, problems with hot corrosion arose and the levels were again increased.

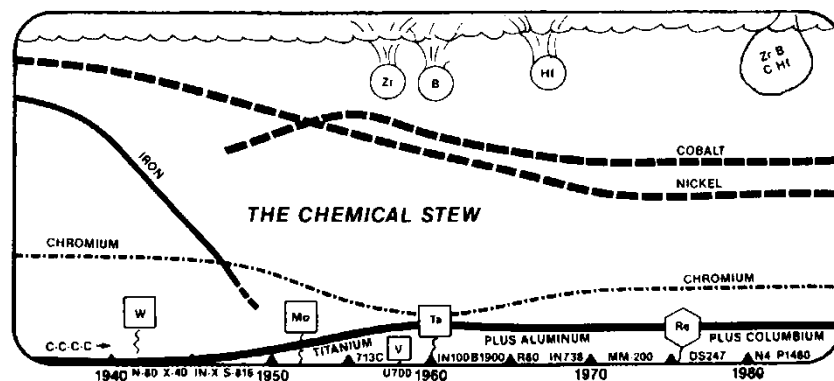


Figure 2.3: A qualitatively comparative view of trends in Superalloy chemical composition [28]

When looking at Superalloy compositions Table 2.1 demonstrates how the elements contained can be classified into both major and minor roles.

Table 2.1: Classification of elements present in Superalloys ^[28]

Elements	Ni	Co	Fe	Cr	Mo, W	Cb, Ti	Ta, Al	C, B, Zr, Hf
Matrix class	X	X	X	X	X			
γ' class						X	X	
Grain boundary class								X
Carbide class				X	X	X		
Oxide class				X			X	

The matrix class consists of elements that prefer and make up the Face Centered-Cubic (FCC) austenitic γ matrix. These elements are from groups VI, VII and VIII and include nickel, cobalt, iron, chromium, molybdenum and tungsten. The γ' class consists of elements that are contained within or result in the precipitation of Ni_3X . These elements are from groups III, IV and V, including aluminium, titanium, columbium, tantalum and hafnium. The grain boundary class includes elements that tend to segregate at grain boundaries e.g. Boron, Carbon, Zirconium. The carbide class include the following elements that encourage carbide formation; chromium, molybdenum, tungsten, niobium, tantalum and titanium. The final class includes elements that promote the growth of a protective oxide that protects the alloys from corrosion; elements in this class include chromium and aluminium.

Table 2.2 shows bulk chemical composition of the subject alloy Nimonic 263. The elemental additions detailed in the table are carefully balanced against each other to ensure that each element is effective. The role of each element varies; ultimately, each element will aid in providing the optimum microstructure to produce the desired chemical and mechanical properties.

Table 2.2: Chemical composition range of Nimonic 263 according to Special Metals ^[25]

Element	Wt. %
Carbon	0.04 – 0.08
Silicon	0.40 max.
Manganese	0.60 max.
Sulphur	0.007 max.
Silver	0.0005 max
Aluminium	0.60 max.
Boron	0.005 max.
Bismuth	0.0001 max.
Cobalt	19.0 – 21.0
Chromium	19.0 – 21.0
Copper	0.20 max.
Iron	0.70 max.
Molybdenum	5.6 – 6.1
Lead	0.0020 max.
Titanium	1.9 – 2.4
Aluminium and Titanium	2.4 – 2.8
Nickel	<i>Balance</i>

2.2.1 Alloying Additions – Effects and Typical Quantities

Chromium is present at a concentration of ~ 20 wt.% resulting in a high level of corrosion resistance; one of the reasons for this is due to the formation of a surface layer of Cr_2O_3 . It has been found that the threshold addition for the continuous oxide layer to form is approximately 9 wt.%. Aluminium is also known to provide an increase in corrosion resistance when added.

Heavy elements such as molybdenum, tungsten, niobium and tantalum are effective matrix hardeners. The problem with using heavy elements is that they increase the density of the alloy, which may make it unsuitable for some applications where component weight is an issue. If chromium, molybdenum and tungsten are present in excessive amounts they can also result in the formation of topologically close-packed phases (TCP), which although has a beneficial effect on oxidation resistance and creep strength, can encourage brittleness in alloys. Brittle components can fail prematurely in service or during installation if subjected to heavy impact. It is due to this brittleness that chromium, molybdenum and tungsten must be limited as alloying additions.

Aluminium and titanium are added to aid in the formation of γ' , which results in improved high temperature properties. The volume fraction of γ' usually increases with the development of each new alloy, this is illustrated in figure 2.4 below. The increase in volume fraction is also accompanied by changes in Cr and Al-Ti-Ta-Nb, illustrated in Figure 2.5

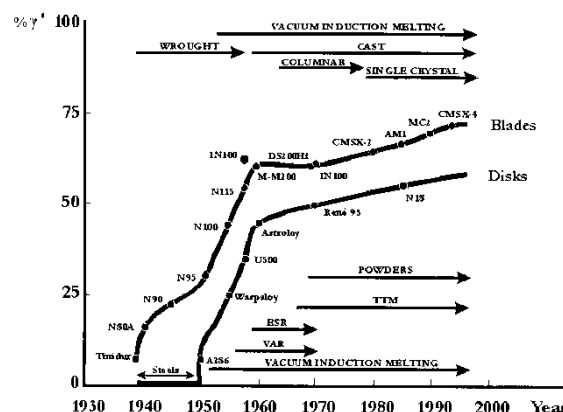


Figure 2.4: Variation in the γ' volume fraction and the related processing ^[29]

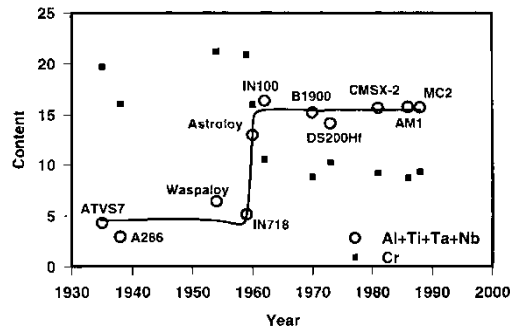


Figure 2.5: Variation in the contents of γ' forming element and chromium in nickel-base Superalloys ^[29]

Additions of iron, titanium, aluminium and carbon result in improved high temperature properties brought about through the controlled precipitation of secondary phases and the solute strengthening mechanism. Titanium in particular can also help refine the grain size by helping to precipitate stable carbides ^[30].

Many early Superalloys contained high cobalt contents, some as high as 20 wt.%. In the 1970's the price of cobalt increased dramatically due to the Shaba conflict in Zaire ^[31], because of this increase its role as an alloying element was closely examined. It was found after investigation that cobalt had little effect on solute strengthening, the reason being it had a similar atomic size to the material's bulk element nickel. However, cobalt is found to increase the volume fraction of γ' contained within the alloy at low temperatures and also increases the solubility temperature of gamma prime precipitates ^[30].

Carbon is present in Superalloys to aid in the formation of carbides which precipitate out both in the matrix and along grain boundaries. Early work noted that the grain boundary carbides lowered the ductility and therefore the carbon levels were reduced ^[21,25]. Further studies found that at very low levels of carbon, both ductility and creep life were reduced. It has since been decided that carbides formed as a result of the carbon addition have a beneficial effect on rupture strength at high temperatures in polycrystalline materials.

Minor alloying additions and trace elements are also present in very small quantities, to help optimise the alloys castability and other properties. The presence and levels of these elements are highly regulated and can be classified in two categories; detrimental and beneficial. Table 2.3 shows how alloying elements can be split into both detrimental and beneficial classes, they are further narrowed by the type of detriment or benefit.

Table 2.3: Classification of impurities and trace elements in nickel-based Superalloys ^[32]

Class	Type	Elements
<i>Detrimental</i>	Residual gases	O, H, N, Ar, He
	Non-metallic impurities	S, P
	Metallic impurities	Pb, Bi, Sb, As, Se, Ag, Cu, Tl, Te
<i>Beneficial</i>	Refining aids	Ca, Mg, Ce, La
	Minor alloying additions (ppm)	B, Hf, Mg, C
	Alloying additions (<1.5wt.%)	Hf, Zr

The roles of the more prominent alloying elements are summarised in Table 2.4.

Table 2.4: Roles of each alloying element in Superalloys ^[33]

Effect	Iron-base	Cobalt-base	Nickel-base
Solid-solution strengtheners	Cr, Mo	Nb, Cr, Mo, Ni, W, Ta	Co, Cr, Fe, Mo, Ta, Re
FCC matrix stabilisers	C, W, Ni	Ni	-
Carbide form	-	-	-
MC	Ti	Ti	W, Ta, Ti, Mo, Nb, Hf
M ₇ C ₃	-	Cr	Cr
M ₂₃ C ₆	Cr	Cr	Cr, Mo, W
M ₆ C	Mo	Mo, W	Mo, W, Nb
Carbonitrides: M(CN)	C, N	C, N	C, N
Promotes general precipitation of carbides	P	-	-
Forms γ' Ni ₃ (Al, Ti)	Al, Ni, Ti	-	Al, Ti
Retards formation of hexagonal η (Ni ₃ Ti)	Al, Zr	-	-
Raises solvus temperature of γ'	-	-	Co
Hardening precipitates and/or intermetallics	Al, Ti, Nb	Al, Mo, Ti, W, Ta	Al, Ti, Nb
Oxidation resistance	Cr	Al, Cr	Al, Cr, Y, La, Ce
Improve hot corrosion resistance	La, Y	La, Y, Th	La, Ta
Sulphidation resistance	Cr	Cr	Cr, Co, Si
Improves creep properties	B	-	B, Ta
Increases rupture creep strength	B	B, Zr	B
Grain-boundary refiners	-	-	B, C, Zr, Hf
Facilitates working	-	Ni ₃ Ti	
Retard γ' coarsening	-	-	Re

2.3 Microstructure of Nickel Based Superalloys

The microstructure of a nickel-based Superalloy is made up of the following; a γ matrix containing γ' precipitates and other phases including carbides, borides and TCP-type phases. The grain size varies in Superalloys depending on the particular alloy and the mechanical and thermal processing they have been subjected to. It can be seen in the graph in Figure 2.6 that there is some relationship between creep rate and grain size, the graph shows that as grain size increases the alloys creep rate decreases. Nimonic 263 is a typically large grained alloy with a grain size of $\sim 100\mu\text{m}$.

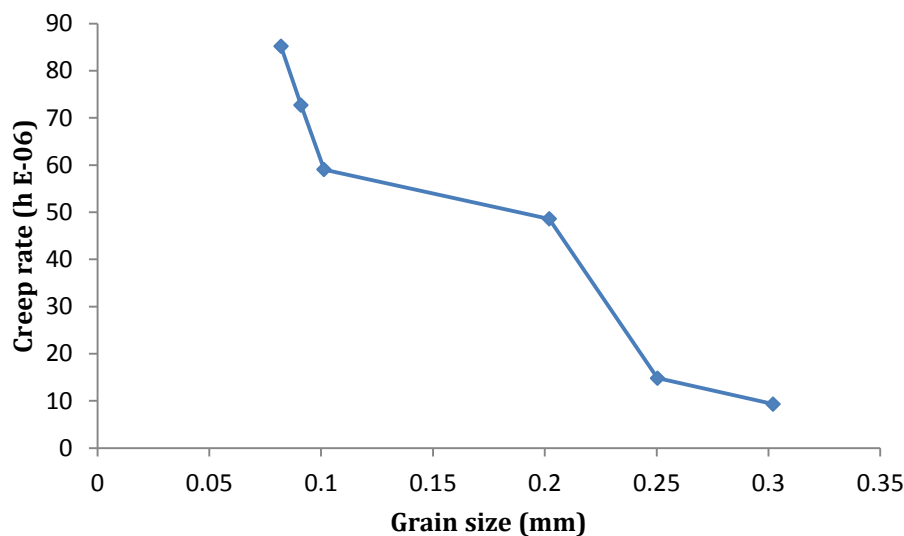


Figure 2.6: Variance in creep rate to grain size in typical Superalloy ^[30]

The relationship between grain size and component thickness is also very important to the strength of Superalloys. Creep deformation occurs due to grain boundary sliding. Before grain boundary sliding, individual voids will grow until eventually a crack opens up. The larger the grain size of a component the less grain boundary area present for voids to form, and therefore the more difficult it is for grain boundary sliding to occur. Large grained alloys are not suitable for smaller components, instead a sensible compromise should be looked for. An exception to this is single crystals materials, in which a small component can have an infinite grain size, where creep deformation is more difficult due to zero boundaries being present.

2.3.1 The γ matrix

Nickel-Based Superalloys have a gamma matrix, containing a bulk nickel composition with high percentage of solid solution elements, such as cobalt, iron, chromium and refractory metals such as molybdenum and tungsten. The γ matrix has a face centred cubic (FCC) crystal structure, an example of which can be seen in Figure 2.7. Nickel has a low modulus of elasticity and a low diffusivity, both of which are essential for good creep resistant materials.

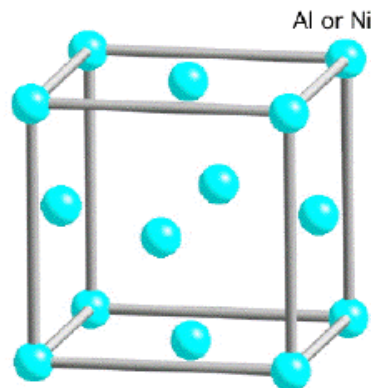


Figure 2.7: Schematic of a nickel FCC crystal structure ^[34]

Nickel based Superalloys are highly corrosion resistant materials, that can operate at $0.9T_m$ for up to 100,000 hours (at lower temperatures) ^[28]. The stability of such alloys is down to the following:

- High tolerance of nickel for alloying without phase instability owing to its nearly filled third electron shell
- Corrosion protection is increased due to the tendency of chromium additions to form Cr_2O_3 rich protective scales. This has a low cation vacancy content, thereby restricting the diffusion rate of metallic elements outward, and oxygen, nitrogen, sulphur and other atmospheric elements inward
- High temperature formation of Al_2O_3 rich scales with exceptional oxidation resistance.

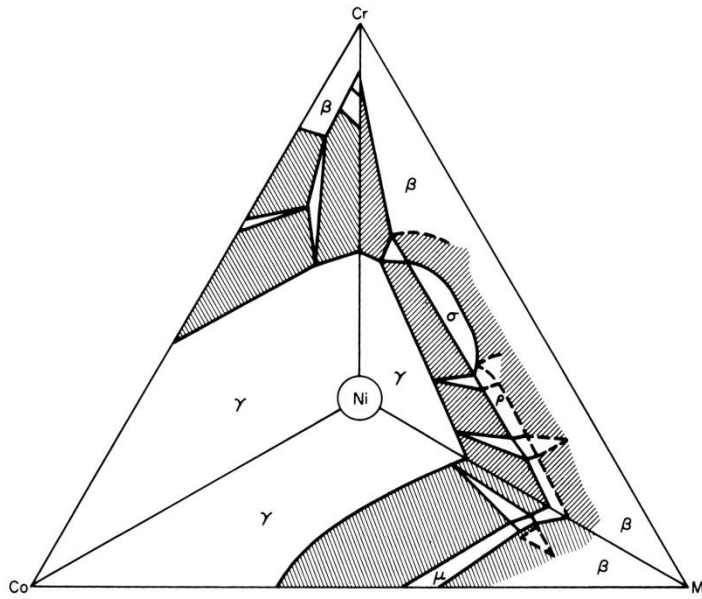


Figure 2.8: Quaternary phase diagram (Co, Cr, Mo, Ni system) ^[21,25]

Figure 2.8 shows the Ni-Co-Cr-Mo quaternary phase diagram displaying the possible phases of formation; in addition to the γ matrix a number of other phases and particles can form. This can be seen by the band of compounds separating the FCC austenitic quaternary space from the BCC quaternary space. This band of separation contains topologically close packed (TCP) phases which are hard, brittle and consequentially avoided ^[21]. The formation of the β type phase is more likely to occur in coatings rather than substrate materials due to the higher Mo content. The figure emphasises the importance controlling an alloy chemistry can have its final microstructure.

One strengthening mechanism present in the γ matrix is solid-solution strengthening, which is caused through the addition of elements with varying atomic size. The strengthening occurs due to lattice distortion, and it is the case that the larger difference in size, the greater the strengthening effect; this is true for differences up to 10% (Hume Rothery). Table 2.5 highlights the percentage difference in atomic diameter from nickel for elements commonly found in Nimonic 263.

Table 2.5: % difference of each alloying element from nickel

Element	% different in atomic diameter from nickel
Fe	3
Co	1
W	13
C	-27
Cr	3
Ti	9
B	-21
Al	6
Mo	12

Solid solution strengthening is said to strengthen the γ matrix due to the following:

- Effect on the local modulus in a grain
- Effect on local atom arrangements in grain
- Limit diffusion in atoms
- Change stacking fault energy

Elements with high melting points such as molybdenum and tungsten produce a matrix with strong lattice cohesion that will experience reduced diffusion at elevated temperatures, this is one of the reasons for molybdenum's inclusion in Nimonic 263. At higher temperatures where diffusion and dislocation cross-slip readily occur, atoms which diffuse slowly such as molybdenum and tungsten are useful solid solution additions. The reduction in diffusion brought about by the addition of molybdenum or tungsten will limit the rate at which second phase particles can coarsen, thus increasing the alloys resistance to creep. Chromium is effective as a solid solution strengthener at additions between 10 – 25 wt.%, molybdenum is effective in the range of 0 - 9 wt.%, the same is true of tungsten, although cost and density limits the use of the latter two.

Some elements are introduced to lower the stacking fault energy (SFE) in the alloy, which makes it more difficult for dislocations to move in new directions. When dislocations, moving through a matrix with a lower-SFE encounter obstacles, they have more difficulty

avoiding them by movement onto a new plane. This is also true for elements such as cobalt which decreases the stacking fault energy between partial dislocations.

Atomic clustering or short range order is another strengthening mechanism that occurs in the γ matrix. It is observed with the following elements; molybdenum, tungsten, chromium and aluminium. Short range order strengthening breaks down above $0.6T_m$ due to increased diffusion ^[29] .

2.3.2 Precipitates

The γ matrix is further strengthened due to precipitation strengthening or hardening through the precipitation of second phase particles. The most common precipitates to form in Nickel-Based Superalloys include:

- A_3B compounds
- Intergranularly forming primary carbides, nitrides or carbonitrides of the general form $M(C, N)$ where M is usually titanium
- Chromium-rich grain boundary carbides like M_7C_3 and $M_{23}C_6$
- Other grain boundary carbides such as M_6C

A table listing some of the phases contained within Nimonic 263 is given in table 2.6.

Table 2.6: Phases present and crystal structures of Nimonic 263 ^[35]

Phase	Major Composition	Basic crystal structure	Pearson Symbol	Lattice parameter, nm
γ'	$(Ni,Co)_3(TiAl)$	Ordered fcc ($L1_2$)	cP4	$a_0 = 0.3561$ to 0.3568
η	$(Ni,Co)_3Ti$	Hexagonal ($D0_{24}$) Hexagonal	hP16	$a_0 = 0.5093$ to 0.5118 $c_0 = 0.8307$ to 0.8348
MC	$(Ti,Mo)C$	FCC	cF8	$a_0 = 0.4300$ to 0.4700
$M_{23}C_6$	$(Cr,Mo)_{23}C_6$	FCC	cF116	$a_0 = 1.048$ to 1.080
M_6C	$(Co,Ni)_3Mo_3C$	Diamond cubic	cF112	$a_0 = 1.085$ to 1.175
μ	$(Co,Ni)_7Mo_6$	Rhombohedral	hR13	$a_{hex} = 4.762 \pm 0.001$ $c_{hex} = 25.615 \pm 0.005$ ^[36]

2.3.3 A_3B Phases

In A_3B compounds electronegative elements such as nickel, cobalt and iron compose part 'A' whereas electropositive elements such as aluminium or titanium compose part 'B'. In many Nickel-Based Superalloys the precipitate is of the general formula $Ni_3(Ti,Al)$, although the exact composition varies depending on the titanium and aluminium contents of the subject alloy.

Gamma prime (γ') phase is coherent with the matrix and has an ordered $L1_2$ FCC crystal structure, which exhibits long range order. An example of this structure can be seen in Figure 2.9, with the substitution of Al/Ti atoms at the vertices of the crystal structure.

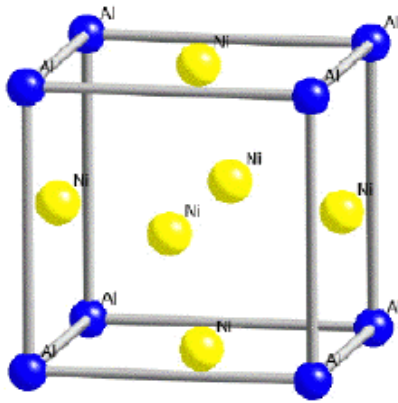


Figure 2.9: Schematic illustrating the $L1_2$ lattice structure of γ' phase ^[34]

γ' precipitates have a lattice mismatch with gamma phase of approximately 0.1%, when mismatch is defined as the difference between γ matrix and γ' precipitate lattice parameters ^[28]. The mismatch results in a coherency strain that can contribute to the hardening of the alloy. The degree of mismatch between the phases can also determine the morphology of the γ' precipitates. Low values of lattice mismatch (0 – 0.2%) will result in spherical γ' particles, increasing values of mismatch (0.5 – 1.0%) will result in cubic γ' and finally high degrees of lattice mismatch (>1.25%) will result in plate form γ' . The shape of this phase can also be determined by the alloys thermal history e.g. coarsening or rafting. The morphology of γ' can also be related to its composition i.e. spherical shapes are common in iron-nickel-base alloys and also in some of the older nickel base alloys such as Nimonic 80A and Waspalloy. In more recently developed alloys the morphology of γ' is often cubic. The compatibility of both the FCC γ matrix and the γ' precipitates (approximately 0.1% mismatch) enables

homogenous nucleation of precipitates with low surface energies. The precipitation of these particles play a large part in Superalloys ability to operate up to $0.9T_m$ as mentioned earlier in the literature review.

The γ' precipitate is the principal strengthening precipitate in many nickel-base Superalloys and was first determined in 1957 by Betteridge and Franklin, using X-ray diffraction ^[29].

The precipitation of γ' in γ is a continuous process involving three main stages; nucleation, growth and ripening. When exposed to high temperatures for long periods of time γ' will change morphology from spherical to cubic before adopting more complex cubic arrangements. This growth mechanism can be seen below in Figure 2.10.

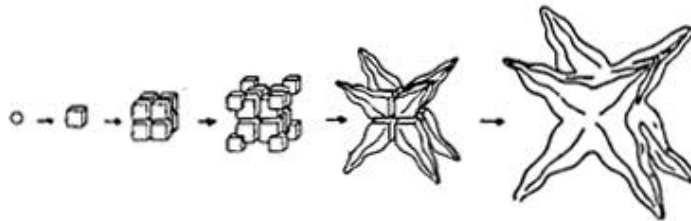


Figure 2.10: Typical growth mechanism of γ' ^[29]

Wang et al 2009 studied a Nimonic 263 sample that had undergone the following heat treatment: 1150°C/30min then water quenched followed by a secondary heat treatment of 800°C/8h then air cooled. γ' was present in the microstructure of this sample in a fine spherical form (14-16nm) and was distributed uniformly in the matrix with a volume fraction of approximately 10%. During this study it was also noted that there was a denuded γ' zone along grain boundaries; the formation of this precipitate free zone is due to the precipitation of $M_{23}C_6$ and MC carbides during aging ^[26].

At elevated temperatures precipitates such as γ' will grow or coarsen over time at the expense of smaller ones, average size is said to increase while the volume fraction will remain fairly constant. The driving force for coarsening is the reduction of interfacial area that occurs as a particle grows. Growth occurs through taking solute atoms from the matrix to form larger precipitates that will exist in a preferential low energy state. The rate of coarsening occurs depends on the diffusive behaviour of these solute atoms.

LSW theory refers to the work published by Lifshitz, Slyozov^[37] and Wagner^[38] on diffusion controlled coarsening. Diffusion based models, like LSW theory, assume precipitates to be spherical, sparsely dispersed throughout the matrix with their mean separation far exceeding the average size^[39]. In LSW theory, there is threshold diameter, R_c , any particles larger than R_c will grow or coarsen and any below will shrink or be consumed. The important output from LSW theory for this research is the relationship between time (t) and particle radius (r) shown below in Equation 2.1:

$$r \propto t^{1/3} \quad (\text{Eq 2.1})$$

Theory states that the coarsening behaviour of the gamma prime phase in Nimonic 263 should follow Wagners theory of Ostwald ripening shown in Equation 2.2^[28]:

$$h^3 = \frac{64\gamma_e D C_e V_m^2 t}{9RT} \quad (\text{Eq 2.2})$$

Where: t is time, γ_e is the specific $\gamma' - \gamma$ interfacial free energy, D is the coefficient of diffusion of γ' solutes in γ , C_e is the equilibrium molar concentration of γ' solute in γ , V_m is the molar volume of γ' , R is the molar gas constant, T is temperature and h is the particle size.

Assuming that diffusion is the rate controlling factor it has been shown that this coarsening behaviour can be simplified as shown in Equations 2.3 and 2.4^[40] where r is radius, X_e is the equilibrium solubility of very large particles :

$$(r^3) - r_0^3 = kt \quad (\text{Eq 2.3})$$

where:

$$k \propto D\gamma X_e \quad (\text{Eq 2.4})$$

Equation 2.3 again shows important the relationship between annealing time (t) and particle radius (r) is as per Equation 2.1.

Rafting of γ' can also occur when an alloy is subjected to both high temperature and an externally applied stress. Rafting usually occurs in high volume fraction alloys and it is not currently known if this phenomenon will be observed in Nimonic 263.

Eta phase (η) is another A_3B phase that can be found in iron-nickel, cobalt and nickel-base Superalloys. The formation of η tends to occur in alloys with high titanium/aluminium ratios and at long exposure times. Eta may form either intergranularly in a cellular form or as acicular platelets in a Widmanstätten pattern. Eta particles can prove to be a problem if precipitation occurs along grain boundaries: due to the resultant reduction in notch stress, lowering creep rupture strength. The formation of this phase is therefore not desired when alloys are used in applications where a good creep resistance is required.

Some work has been carried out to suggest that the Eta particles occur due to the transformation of gamma prime. This transformation to Ni_3X cannot occur in γ' with sufficiently high aluminium contents, however, transformation can occur when the titanium and/or niobium and/or tantalum contents are sufficiently high. Pearson and Hume-Rothery found a relationship between the stability of Ni_3X compounds and their size, they can be ranked in decreasing order of stability; Ni_3Al , Ni_3Ti and Ni_3Nb (or Ta). η phase have been found to form from the transformation of Ti rich γ' particles. The transformation has been found to occur when the titanium-aluminium ratio was raised to 5:1; although transformations have been seen to occur at ratios as low as 3:1 in some alloys. It is possible to retard this transformation through the introduction of boron. Equilibrium segregation of the boron to grain boundaries retards the nucleation of cells^[41]. Looking at the predicted phases for Nimonic 263 in Figure 2.11(b) it can be seen that a higher fraction of γ' is predicted when the η phase has been suspended for calculation, this indicates that at equilibrium the η phase will preferentially occur over a fraction of γ' phase.

The effect of the Eta phase on the properties on nickel base alloys is currently not fully understood. Some literature states that it can be detrimental to the mechanical strength of nickel base superalloys^[28,42], part of this is attributed to the reduction of γ' precipitates due to Eta transformation. Research conducted by Shingledecker^[43] on alloy Inconel 740 suggested that when present at low volume fractions, approximately 0.02 - 0.03, Eta phase has no effect on creep strength or ductility. Another study by Choi et al.^[44] found that precipitation of intergranular Eta phase reduced the room temperature ductility of the alloy,

but didn't affect creep rupture life or high temperature ductility. Nimonic 263 specific research was carried out by Kim et al^[45] in which tensile creep tests were performed on isothermally aged plate. The research concluded that coarsening of the γ' phase and the formation of the Eta phase resulted in a reduction of tensile strength and creep rupture life of the alloy.

2.3.4 Carbides

Carbides form in Superalloy microstructures due to the addition of minor elements such as carbon, boron, zirconium and hafnium. Grain boundary carbides strengthen the alloy by increasing grain boundary cohesion and inhibiting grain boundary sliding, yet permitting stress relaxation. The precipitation of such carbides has a beneficial effect on the alloys rupture strength at high temperatures. Their existence can also influence the ductility and chemical stability of the matrix through the removal of reactive elements. A range of carbides are present in Nimonic-263, with each type of carbide discussed in more detail below.

MC precipitates are formed from the combination of carbon with reactive and refractory metals. 'M' elements can be titanium, tantalum, niobium, hafnium, thorium or zirconium. MC carbides are dense and form with a closely packed FCC structure, which confers substantial strength and stability. TiC is the common precipitate present in Nimonic 263, this particular carbide has some solubility for nitrogen, zirconium and molybdenum and due to this carbides such as Ti-Mo readily form. MC carbides usually form during freezing and are distributed heterogeneously throughout the alloy at both inter and transgranular locations. MC carbides have also been known to form during hot working and ageing. During heat treatment and ageing MC carbides can act as carbon reservoirs for the precipitation of other carbides such as $M_{23}C_6$ and M_6C . The MC phase is stable up to temperatures of 1200 - 1260°C.

$M_{23}C_6$ precipitates are present within Nimonic 263 in a number of forms including globules, platelets, lamellae and cells. $M_{23}C_6$ carbides form in high chromium alloys during low temperature heat treatment and during service (760 - 980°C). $M_{23}C_6$ carbides usually form along grain boundaries but can also precipitate within grains and other areas such as; twin lines, stacking faults and at twin ends. In this case 'M' is usually chromium, but nickel-cobalt, iron, molybdenum and tungsten can substitute. The presence of these carbides greatly

increase the creep rupture strength of nickel alloys, through the prevention of grain boundary sliding.

M_6C is a randomly distributed FCC structured precipitate carbide that is generally formed at higher temperatures than $M_{23}C_6$ (815 - 980°C). The carbide precipitates in a blocky form and under certain conditions it can occur in the Widmanstätten intragranular morphology. M elements are generally molybdenum or tungsten, however, there is some solubility for chromium, nickel, niobium, tantalum and cobalt. Due to the presence of refractory elements this carbide is stable at higher temperatures, which makes it more beneficial when present as a grain boundary precipitate ^[28].

2.3.5 Borides

Borides are present in some Superalloys, usually in very small quantities, typically 50 - 500 ppm. Grain boundary tearing or sliding is produced when an alloy is subjected to creep rupture loading; this tearing can be retarded by the addition of boron, which travels to the grain boundaries. The boron is present as borides of the form, M_3B_2 , which are hard refractory particles. These particles are observed at and along grain boundaries with shapes varying from blocky to half-moon in appearance ^[28].

2.3.6 TCP Phases

TCP phases form in alloys where the composition has not been carefully controlled, the formation of these phases can occur during either heat treatment or service. TCP phases are composed of close-packed layers of atoms forming in 'basket weave' nets aligned with the octahedral planes of the FCC matrix. These phases are generally thought of as detrimental, appearing as thin linear plates often nucleating along grain boundary carbides. Common TCP phases present in nickel alloys are μ and σ ; the formula is $(Cr,Mo)_x(Ni,Co)_y$, where x and y can vary from 1 to 7. Mu phase (μ) is observed in alloys with high levels of molybdenum or tungsten that have been subjected to long exposure times, the phase forms as coarse irregular Widmanstätten platelets ^[33].

2.4 Evolution of Carbides (Carbide reactions)

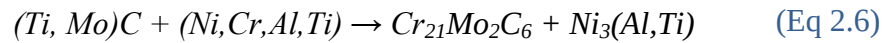
At temperatures below 980°C the majority of carbon in Superalloys exists as high temperature carbide MC. During heat treatment and thermal exposure the MC carbides

decompose, and the carbon contained within diffuses into the alloy causing a number of significant reactions.

An important reaction when considering Nimonic 263 is the formation of $M_{23}C_6$ and γ' from the MC carbide.



or more specifically:

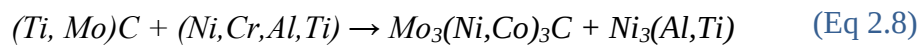


The following equations are based on observations made by Sims and Phillips^[28] in a study of phase transformations at grain boundaries. The carbide reaction shown by equations 2.5 and 2.6 usually occur at about 980°C, however, they have been known to react at temperatures as low as 760°C.

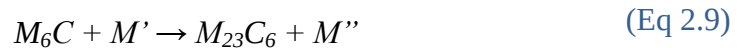
The carbide M_6C can also form in a similar reaction:



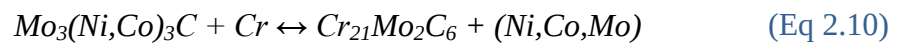
or more specifically



Both M_6C and $M_{23}C_6$ can also interact forming each other



or more specifically

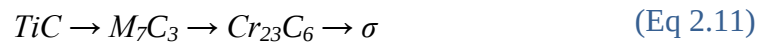


The above carbide reactions take place throughout the alloy. The carbide reactions displayed in Equations 2.5 and 2.6 as mentioned are very important producing both $M_{23}C_6$ and γ' which both significantly strengthen the alloy. The $M_{23}C_6$ carbides produced, inhibit grain boundary

sliding, whilst the subsequent γ' formation surrounds the carbides and the boundary area with a ductile, creep resistant layer.

On formation of $M_{23}C_6$, chromium is depleted from the matrix. This depletion raises the solubility for γ' near the grain boundary, which can leave the denuded zones eluded to earlier in this review by Wang et al; this was shown in a study into Inconel X-750 by Raymond utilising Huey tests.

Mihalisin suggests that carbon is slowly depleted through the following sequence of carbide reactions ^[46]:



2.5 Heat Treatment of Superalloys

The processing of Superalloys is a very important procedure in which both mechanical and chemical properties can be tailored through the production of certain microstructures. When heat treating an alloy the following needs to be taken into account: the alloys constitution; phase stability, structural effects, and; the properties required.

Sheet Nimonic 263 is subjected a standard heat treatment before going into service, this heat treatment consists of two separate stages: solution annealing at 1150°C for 2 hours, followed by an ageing or precipitation hardening heat treatment of 800°C for 8 hours. Solutioning is when all solute atoms are dissolved to form a single phase solid solution. The solutioning temperature for Nimonic 263 is typically in the range of 1040 – 1230 °C. Solution annealing is carried out for two main reasons: firstly to relax any of the strains induced during the forging process and secondly to dissolve any precipitate phases formed during production, mainly γ' and carbide phases. Ageing is then carried out to reintroduce such phases in a manner where size, distribution and composition can be controlled.

2.6 Precipitation hardening

The major contribution to the strength of Nickel-Base Superalloys is provided through the presence of coherent stable intermetallic compounds such as γ' . Other phases such as borides and carbides produce little strengthening, although they may provide significant effects to

creep properties through precipitation at grain boundaries. Precipitation hardening in Nickel-Based Superalloys is affected by the following properties^[28]:

- Volume fraction f of γ' ,
- Radius r_0 of γ' ,
- Solid-solution strengthening of both γ and γ'
- Presence of hyperfine γ' .
- Antiphase boundary (APB) and fault energy of γ'
- Coherency strains
- $\gamma - \gamma'$ modulus mismatch
- Existence of order in particles

The low surface energy of the $\gamma' - \gamma$ matrix interface contributes to the alloys long-term stability at elevated temperatures.

γ' precipitates strengthen the alloy by impeding the generation and movement of dislocations. For a matrix dislocation to move through or 'shear' a γ' particle it must create the corresponding stacking fault or antiphase boundary, this requires a significant amount of energy and therefore opposes dislocation movement^[29]. Dislocations are numerous and complex, especially at high temperatures when thermally activated processes play a major role in by-passing particles. The effectiveness of dislocation impedance is dependent upon the volume fraction of the γ' phase and its distribution. This highlights the importance of any research carried out which characterises the evolution of the γ' phase in Nimonic 263 at intended service conditions. Particle strengthening models of low volume fraction alloys like Nimonic 263 suggest that the stress required to shear a precipitate increases with particle size. This only occurs up until particles reaches a critical size, in which dislocation are able to bypass the particles through a phenomenon called dislocation bowing or bending.

2.7 Phase Diagram Calculations for Ni-Based Superalloys

Thermodynamic calculations can be carried out to determine what fraction of phases are at equilibrium through a determined temperature range. Figure 2.11 shows the result of some calculations carried out by Zhao et al. predicting a γ matrix containing: μ , η , γ' , $M_{23}C_6$ and

MC. The calculations below were calculated using Thermocalc software and its dedicated databases.

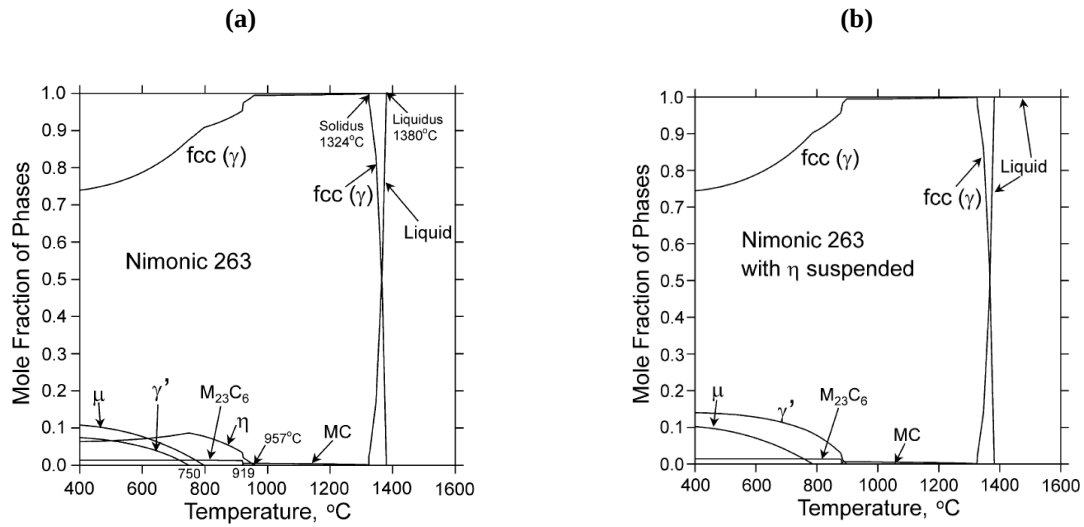


Figure 2.11: (a) Calculated phase fraction of Nimonic 263 alloy, (b) Calculation with η phase suspended ^[35]

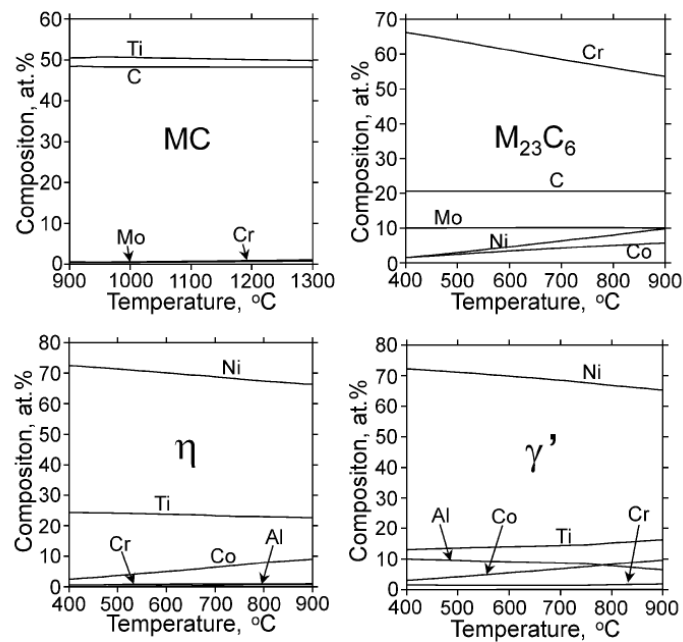


Figure 2.12: Calculated composition of main precipitate phases in Nimonic 263 ^[35]

The chemical composition of the phases present in the alloy have also been calculated and are shown in Figure 2.12. Equilibrium calculations will provide an important tool when predicting the alloys microstructure and the potential effect of changes in chemistry. The calculations, particularly the ‘calculated compositions’ of precipitate phases, will aid in identification of the alloys phases during the experimental portion of this work.

2.8 Physical and Mechanical Properties of Nimonic 263

If Nimonic 263 is to be used in next generation plant it is important to have an understanding of some important physical properties. Table 2.7 indicates the physical properties observed in Nimonic 263.

Table 2.7: Physical properties of Nimonic 263^[25]

Property	Value
Density (g/cc)	8.36
Liquidus temperature (°C)	1355
Solidus temperature (°C)	1300
Specific Heat (J/kg°C ⁻¹)	461

For use in Ultra Super Critical (USC) plant the creep properties of Nimonic 263 are critical. The creep rupture properties of an extruded section are displayed in Table 2.8. Further information detailing the creep characteristics of Nimonic 263, including creep curves, are displayed in the next section

Table 2.8: Creep properties of Nimonic 263 through a range of temperatures and exposures^[25]

Heat treatment 2h / 1150°C/WQ + 8h / 800°C / AC					
Temperature (°C)	Stress, MPa, to give rupture in				
	30 h	100 h	300 h	1000 h	3000 h
550	(726)	695	680	633	(587)
600	641	618	595	556	(510)
650	479	541	510	471	(432)
700	510	448	386	317	(263)
750	378	317	263	224	(178)
800	263	216	178	142	(116)
850	165	133	103	77	(59)
900	86	74	54	42	(34)

(Values in parentheses are extrapolated from isothermal curves)

2.9 Effects of Creep

Pipes or tubes used to transport superheated heated steam to and from the turbine are subjected to both high temperatures and pressures, due to this these components often suffer creep. Creep is defined as the time dependent component of plastic deformation when under constant stress. The creep properties of a material are measured using a creep test which in turn produces a creep curve. Creep curves in the majority of γ' precipitation strengthened alloys show an initial stage of small and short primary creep, followed by a long accelerated creep stage where the strain rate, $\dot{\epsilon}$, increases linearly with strain, ϵ :

$$\dot{\epsilon} = \dot{\epsilon}_0 (1 + C\epsilon) \quad (\text{Eq 2.12})$$

where $\dot{\epsilon}_0$ is the extrapolated strain rate at the beginning of the test, and C a parameter controlling the shape of the creep curve. An example of a typical creep curve is shown below in Figure 2.13, with areas of primary, secondary and tertiary creep labelled

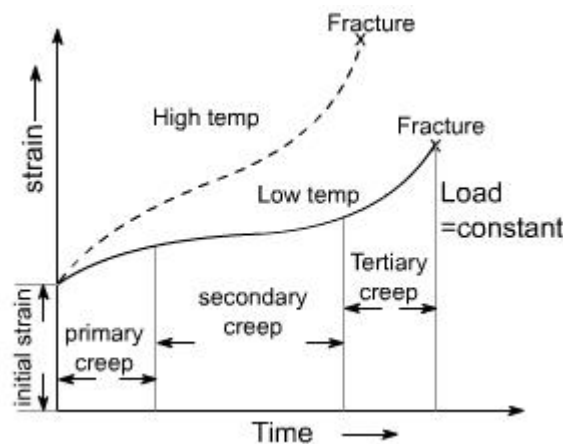


Fig 2.13: Typical creep curve ^[47]

An investigation by Maldini, Angella and Lupinc ^[48] conducted some creep testing on Nimonic 263 over the temperature range of 600 - 950°C to investigate the importance of γ' volume fraction to the alloys creep strength. Nimonic 263 contains 10% γ' precipitates from room temperature up to 800°C, at 900°C this is reduced to approximately 3% before decreasing to zero its solvus temperature of 920°C ^[49].

The creep curves produced from a study into the ‘shape of creep curves in nickel base superalloy C263’, again by Maldini, Angella and Lupinc are shown below in Figures 2.14^[49]. The creep curves show specific creep data for C263 which can be compared to simplified creep curve in Figure 2.13. The results showed that similarly to other nickel base superalloys primary creep in C263 is very small. The results also confirm the relationship between temperature, pressure and the alloys creep rate. Although creep can occur at any temperature it has traditionally been associated with elevated temperatures, usually higher than $0.4T_m$, where T_m is the absolute melting temperature of a material^[50]. For alloy 263 with a solidus temperature of 1300 $0.4T_m$ is $\sim 520^\circ\text{C}$ ^[25].

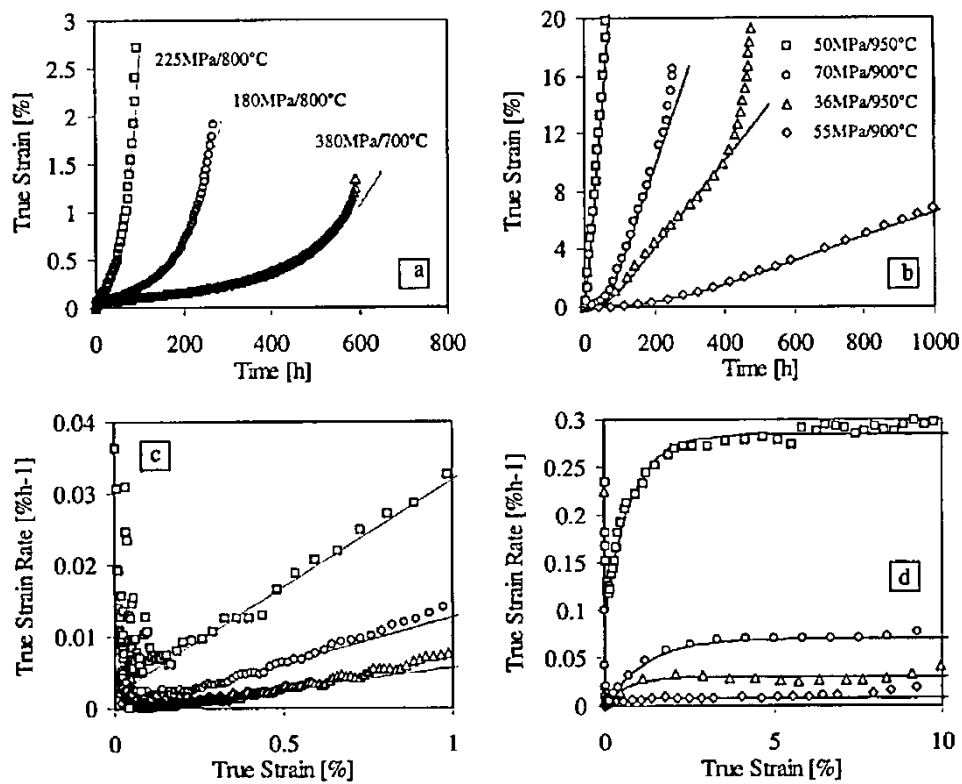


Figure 2.14: shows the creep curves for 7 different conditions^[48]

The above creep curves show the relationship between temperature and creep. Materials exposed to elevated temperatures will suffer the onset of creep much earlier, resulting in premature failure.

2.10 Effect of processing on Nickel base superalloys / Nimonic 263

Nickel base superalloys like Nimonic 263 are available in a number of forms such as forged, cast or welded. The form of material used will depend on the particular application, type of component or stage in the product's life cycle. Forgings or extrusions are often used for long simple components such as rails, bar or one of the components that makes up part of this research, pipes. Forging of nickel base superalloys is difficult due to the high temperatures and tight range in which hot working of these alloys is possible. Forging of the Nimonic series is reported to occur at around 1200°C, this will, however, vary slightly between alloys. A paper by Brooks states that the forging temperature of C-263, the Haynes variant of Nimonic 263 is 1150°C with a range of 1100 - 1170°C^[51]. In addition to forging temperature other parameters such as extrusion speed can have significant effects on the final forging. Too slow an extrusion speed can result in a drop in the extrusion temperature resulting in not only possible mechanical damage to the forging but also a variation in properties due to the temperature gradient throughout the billet. Too fast an extrusion speed can result in a rise in temperature causing intergranular incipient melting^[27].

It is often necessary for nickel base components to be joined together to form more complex assemblies. Although mechanical means can be used to achieve this, a welding process is often used. Welding is the fusion of two materials, this can be done using a range of different processes. Most commonly, welding is carried out through the introduction of heat to the intended materials of fusion. The heat may be generated by a number of different means e.g. creation of an arc, friction or combustion of gas etc. The most common method to weld nickel base alloys is using an arc welding process, of which there are many different types. Due to the high cost and quality associated with the use of nickel alloys it is likely that the gas tungsten arc welding (GTAW) process is used. The GTAW process has the advantages that it is clean, maintains a high degree of control and the resultant weld is often stronger than those produced using alternative processes^[52]. In addition to joining materials together welding can be used as a repair technique.

When welding nickel alloys, consideration has to be given to the effect of segregation brought about through the non-equilibrium cooling of the weld pool. A segregated weld microstructure can have significant on the precipitation products present in the solidified weld metal, which can affect a welds mechanical properties and corrosion resistance. The welding process can also have an effect on the materials to be joined through the introduction

of a heat affected zone (HAZ). The heat affected zone is an area of the parent material which has not been fused but has undergone a metallurgical change as a result of the heat generated during the welding process^[52].

Superalloys are also often used in the cast form when forging or fabrication of a component is not practical. Casting of superalloys can prove problematic due to the complex mix of elements present in each alloy and the large number of potential precipitates which can form.

Chapter 3

Experimental Methods

3.1 Introduction

This research programme was primarily focussed on characterising the microstructural evolution of Nimonic 263 in a number of different conditions, including forged thick section pipe, a number of different weldments, some mechanically tested samples and also experimental castings. In addition to the different forms of materials studied, the alloy microstructures were also evaluated as a function of different heat treatments including pre-service heat treatments such as solutioning and precipitation hardening, and different ageing temperatures and exposure times. A series of different experimental techniques, covered in this section, were used to critically evaluate the alloys microstructure and properties.

3.2 Materials

The alloy Nimonic 263 has been studied in a number of different forms and conditions. To cover each sample set the experimental section has been broken down to describe each form e.g. isothermally aged, welded and cast separately.

3.2.1 Isothermally Aged Samples / Forged Thick Section Pipe

The samples examined in this research were sourced from a forged thick section pipe of the following dimensions; 310 mm outside diameter, 170 mm bore diameter (resulting in a wall thickness of 70 mm) and 3140 mm length. The pipe material was produced at Special Metals (cast ALT2224) and extruded by Wyman Gordon, using a vertical forging process. At the current time it is believed that there are only two of these Nimonic 263 pipes in existence, one of which is shown in two views in Figure 3.1. Others experimental pipes may exist but are not known to the Supergen Research Programme.



Fig 3.1: Pictures showing a Nimonic 263 header pipe after forging

The specific chemistry of the pipe used for the research, detailed in chapter 4, was analysed in three locations; bore, mid wall and outside diameter using spectrographic atomic absorption test method and overall showed very little change. The Al content did, however, vary from 0.31 wt.% in the bore to 0.37 wt.% in the outer diameter. The chemical analysis of the three different sections and the mean chemistry are shown in Table 3.1. The effect of chemical variation along the length of the pipe was not taken into account.

Table 3.1: Chemical composition of Nimonic 263 in different locations through pipe wall, average and nominal (wt.%)

Material	Element, wt.% (balance is Ni)							
Location	C	Al	Co	Cr	Fe	Mo	Ti	N
Bore	0.06	0.31	19.87	20.41	0.46	5.89	2.11	0.006
MW	0.07	0.32	19.84	20.31	0.45	5.94	2.08	0.006
O.D.	0.06	0.37	19.94	20.52	0.44	5.73	2.13	0.005
<i>Average</i>	<i>0.06</i>	<i>0.33</i>	<i>19.89</i>	<i>20.41</i>	<i>0.45</i>	<i>5.85</i>	<i>2.11</i>	<i>0.006</i>

Samples studied in this research were provided by several different industrial partners, and due to the extensive number of samples used in each chapter a table has been included at the end of each experimental section to indicate the following:

- Sample reference number – Each sample is assigned a number for identification
- Sample origin – e.g. E.On, Doosan Power Systems etc.
- Form – e.g. section of pipe, creep samples etc.
- Heat treatment – e.g. any solutioned, precipitation hardening or ageing heat treatment
- Finally, any notes giving further description to the sample are also included

Samples were cut to a suitable size and mounted in the desired orientation for analysis; some of the samples in this study have been cut from the pipe in the orientation shown in Figure 3.2. The sections removed typically measure 15 mm x 8 mm x 70 mm and are subsequently referred to as ‘sticks’.

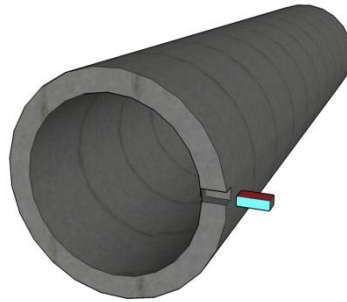


Fig 3.2: Schematic diagram indicating the location in the pipe from which the samples have originated

3.2.2 Heat Treatment of Forged Thick Section Pipe

Sections were cut from the pipe in order to produce a series of samples for metallurgical analysis. All samples underwent a solution heat treatment (ST) at 1150°C for 2 hours, before being quenched to room temperature in water. The majority of the samples have also been subjected to a precipitation hardening heat treatment (PH) at 800°C for 4 hours. A schematic diagram of the time temperature profile for the standard heat treatment and additional ageing heat treatments is shown in Figure 3.3.

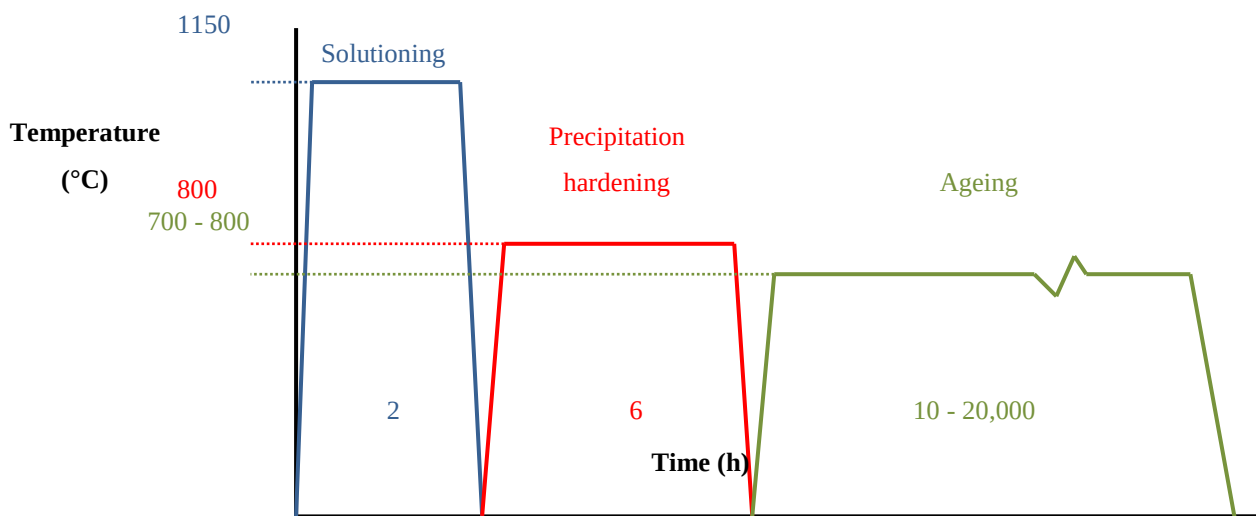


Figure 3.3: A schematic diagram showing time temperature profile for heat treatments

After having undergone the standard heat treatments some samples were aged at a series of different temperatures and exposure times, as shown in Table 3.2. Ageing of the samples was carried out under atmospheric conditions in the dedicated furnaces at both E.On Engineering and Doosan Power Systems. Potential variations between furnaces at the different companies were not felt to be significant as very little difference was found between pre-service conditions of different origins. No thermal plots were provided for heat treatments relating to either industrial partner. The samples aged at 800°C for 0.25 and 4 hours were produced to study the early γ' precipitation in the alloy and in the case of the 4 hour sample, repeat the pre service precipitation heat treatment on solutioned material.

Table 3.2: Ageing heat treatment sample matrix

Ageing temperature (°C)	700	725	750	800
Ageing time (h)	8, 100, 1000, 3000, 10,000, 20,000	10,000	8, 100, 1000	0.25*, 4*, 100, 1000

*No precipitation heat treatment (4h at 800°C)

In addition to the heat treatments carried out in industry, additional samples were aged in Loughborough's heat treatment facilities. A Bahr-Thermoanalyse DIL 805 dilatometer was used to carry out some of the more precisely controlled heat treatments on the Nimonic 263 samples. A dilatometer was used due to the accuracy of heat treatments that can be achieved. It also has the ability to measure additional information, such as the change in length of the samples, during heat treatment.

For the dilatometer to function correctly the temperature of the sample must be known throughout the heat treatment. To measure temperature accurately a thermocouple was used, the particular thermocouple was a 'Type S platinum-rhodium', which has a composition of 90% platinum and 10% rhodium, and was attached to the sample using a small spot welding unit. Once the thermocouples were attached and connected into the control computer, the heat treatment could be carried out. The samples are held in position by a weighted alumina rod either side; alumina was chosen as it has a low coefficient of thermal expansion and will not be heated directly from the induction coil. Having a low coefficient of thermal expansion in the rod limits the error that is generated when measuring the expansion of the sample. In addition to providing accurate heating to the samples, the dilatometer can also carefully control cooling rates. Cooling is controlled by a series of different gases, which can be administered at varying flow rates depending on the desired rate of cooling. In the case of this investigation the cooling gas is not important, however it should be noted that nitrogen was used for each test. Each heat treatment required a simple programme to be written detailing the exact temperature of each heat treatment step, and depending on the nature of the step either the heating / cooling rate, and finally the exposure time. Before commencing heat treatment the chamber must be put under vacuum to create a neutral environment for each sample. In addition to heat treating the forged thick section origin material the dilatometer has been used for both welded and cast samples.

A complete list of the samples used in the isothermally aged chapter is included below in Table 3.3.

Table 3.3: Sample matrix for Chapter 4 microstructural characterisation of isothermally aged Nimonic 263

Sample ID	Origin	Form	Heat treatment				Notes / description
			Solutioned	Precipitation hardened	Ageing time (h)	Ageing temp (°C)	
1	DPS	Pipe section	ST	~	~	~	09/152
2	DPS	Pipe section	ST	PH	~	~	09/160
3	E.On	Pipe section	ST	PH	8	700	08/133 Produced from bar 15/4
4	E.On	Pipe section	ST	PH	100	700	08/201 Produced from bar 15/4
5	E.On	Pipe section	ST	PH	1000	700	08/453 Produced from bar 15/4
6	E.On	Pipe section	ST	PH	10000	700	Produced from bar 15/4
7	E.On	Pipe section	ST	PH	8	750	07/737 Produced from bar 15/6
8	E.On	Pipe section	ST	PH	100	750	08/115 Produced from bar 15/6
9	E.On	Pipe section	ST	PH	1000	750	08/205 Produced from bar 15/6
10	E.On	Pipe section	ST	PH	10000	750	Produced from bar 15/6
11	E.On	Pipe section	ST	~	~	~	Bar 14/3 (solution treated sample)
12	E.On	Pipe section	ST	PH	~	~	Bar 15/8 (precipitation hardened sample)
13	DPS	Pipe section	ST	PH	3000	700	
14	DPS	Pipe section	ST	PH	10000	700	
15	DPS	Pipe section	ST	PH	20000	700	
16	DPS	Pipe section	ST	PH	100000	700	Not available
17	DPS	Pipe section	ST	PH	3000	725	
18	DPS	Pipe section	ST	PH	10000	725	
19	DPS	Pipe section	ST	PH	20000	725	
20	DPS	Pipe section	ST	PH	100000	725	Not available
23	E.On	Pipe section	ST	~	0	~	Produced from bar 14/3 O
24	E.On	Pipe section	ST	PH	0	~	Produced from bar 15/8 O
25	E.On	Pipe section	ST	~	0	~	Produced from bar 14/3 I
26 / 49	E.On	Pipe section	ST	PH	100	800	Produced from bar 15/3
27	E.On	Pipe section	ST	PH	1000	800	Produced from bar 15/3
28	E.On	Pipe section	ST	~	100	700	Produced from bar 15/1
29	E.On	Pipe section	ST	~	1004	700	Produced from bar 15/1
30	E.On	Pipe section	ST	~	0.25	750	Produced from bar 14/4
31	E.On	Pipe section	ST	~	8	750	Produced from bar 15/2

32	E.On	Pipe section	ST	~	1004	750	Produced from bar 15/2
33	E.On	Pipe section	N	~	~	~	LECO N chemistry test
34	E.On	Pipe section	ST	~	~	~	Bar 14/1 (solution treated sample)
35	E.On	Pipe section	ST	PH	10000	700	Bar 15/7 (standard PH 8h)
36	E.On	Pipe section	ST	~	10000	700	Bar 15/1 (no PH or regulated heat rate)
37	E.On	Pipe section	ST	PH	10000	700	Bar 14/10 (4h PH fast heating)
38	E.On	Pipe section	ST	~	10000	750	Bar 15/2 (no PH)
39	E.On	Pipe section	ST	PH	10000	750	Bar 15/6 (4h PH)
40	SM	Rolled bar	ST*	~	~	~	ST 20mm diameter annealed and ground bar
41	SM	Rolled bar	Y	~	0.25	800	Produced from special metals bar
42	SM	Rolled bar	Y	PH	~	~	Produced from special metals bar
43	SM	Rolled bar	ST* + ST	~	~	~	Produced to check solution treatment correct
49	SM	Rolled bar	ST*	~	104	800	
50	SM	Rolled bar	ST*	~	1500	800	
51	SM	Rolled bar	ST*	~	2000	800	
52	SM	Rolled bar	ST*	~	5000	800	
53	SM	Rolled bar	ST*	~	10000	800	
116	SM	Rolled bar	ST	~	10000	800	Rejuvenation 2h @ 1150°C
117	SM	Rolled bar	SR	~	10000	800	Rejuvenation 3h @ 980°C
120	SM	Rolled bar	ST*	~	10000	800	Rejuvenation 2h @ 1150°C + PH
121	SM	Rolled bar	ST*	~	10000	800	Rejuvenation 3h @ 980°C + PH

The table uses the following abbreviations:

- Solution heat treatment
 - ST – 2 h @ 1150°C
 - ST* - 0.5 h @ 1150°C
 - SR – Stress relieved 3 h @ 980°C
- Precipitation hardening heat treatment
 - PH – 4 h @ 800°C
- SM – Special Metals, DPS – Doosan Power Systems, E.On – E.On engineering

3.2.3 Welded Nimonic 263 Sample Conditions

To study the effect of welding Nimonic 263 on an industrial scale, full scale Nimonic 263 forgings were welded. Two different sets of welded samples were analysed in this research designated IP (I) and IP (II). The IP (I) were sourced from E.On Engineering and IP (II) sourced from Doosan Power Systems. Production of the IP (I) welded samples which were used for the majority of the work involved milling a 15 mm channel into the circumference of a forged pipe of dimensions: 360 mm external diameter, 240 mm internal diameter and 5 m in length. The channel was then filled back up with a Nimonic 263 filler material, as shown in Figure 3.4 (a). The resultant weld was made up of 20 passes, welded with an overall heat input of 5.9 kJcm^{-1} and a feed rate 21 cm/min. The weld passes were approximately arranged 5 high and 4 wide, although this varies slightly between each weld. A macro overview from one of the welded samples can be seen below in Figure 3.4 (b).

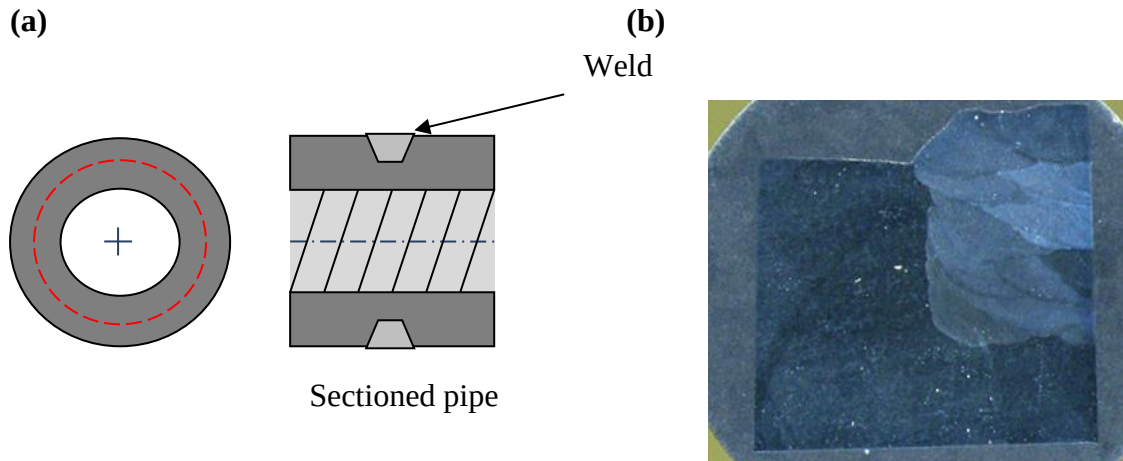


Figure 3.4 – (a) Diagram showing a section view of the welded samples and (b) a macrograph of the stress relief welded sample highlighting the multipass weld structure

The parent material or pipe used to produce the welded samples was well within the alloy's nominal composition, designed by Special Metals. This parent pipe does show a slight variation in chemical composition to that of the pipe studied in the isothermally aged chapter, although this is not thought to be significant. The weld filler material, however, showed large variances from the Special Metals nominal composition. Both weld compositions are shown in Table 3.4 in addition to the nominal composition set by Special Metals. Any elemental compositions above specification have been highlighted in red, those below in blue and those that fall within the limits have been coloured green. Details regarding the welding and origins of IP (II) and associated parent material are unavailable, although this is thought to originate

from the original pipe material used in Chapter 4. Both IP(I) and IP(II) sample were produced using the GTAW welding process. No welding procedures (WPS) have been provided for either sample set.

Table 3.4 – Composition of welded samples

Elemental composition (wt.%)	C	Si	Mn	Cr	Co	Mo	Ti	Al	Fe	N
Nominal composition (set by Special Metals)	0.04 – 0.08	0.4 max	0.6 max	19.00 – 21.00	19.00 – 21.00	5.6 – 6.1	1.9 – 2.4	0.6 max	0.7 max	-
Weld material IP (I)	0.075	0.71	0.073	18.62	18.31	5.39	2.71	0.64	0.75	-
Nimonic 263 pipe material IP (I)	0.051	0.1	0.15	19.5	19.93	5.76	2.28	0.52	0.31	-
Weld material IP (II)	0.067	0.24	0.35	20.02	19.7	5.78	2.24	0.51	0.43	-

There were three different post weld heat treatments considered in this work. The first of these was a stress-relief heat treatment at 980°C for 3 h aimed at reducing any thermomechanical stresses after welding. This heat treatment was also considered as a resolution heat treatment to dissolve any second phases formed during welding. The second heat treatment considered was a hardening treatment typically 810°C for 4 h. The hardening heat treatment is designed to strengthen the weld and its surrounding parent metal through the controlled precipitation of the γ' phase. Finally, the third sample set referred to as ‘fully processed’ combined both heat treatments by carrying out the stress relief followed by the hardening heat treatment. To thoroughly characterise the microstructural behaviour of the welded samples it was necessary to carry out further heat treatments to the as-received samples and repeat some of the pre-service heat treatments on the as-welded material. The four as-received conditions: as-welded, stress relieved, hardened and fully processed were isothermally aged to study its effect on the alloys microstructural evolution. Due to the limited amount of weld material available, one ageing temperature of 750°C was chosen for all four conditions. An additional set of samples from the stress relieved condition were aged at 800°C to further its microstructure at a higher ageing temperature. These heat treatments are detailed in Table 3.4 along with the as received weld samples.

The IP (II) sample set was comprised of 5 samples; as-welded and then aged at 700 and 725° for 3000 and 10,000 h. A breakdown of all the samples used in the welded Nimonic 263 chapter are shown in Table 3.5.

Table 3.5 – Sample matrix for Chapter 5 microstructural characterisation of welded Nimonic 263

Sample ID	Origin	Form	Heat treatment				Notes
			Solutioned	Precipitation hardened	Ageing time (h)	Ageing temp (°C)	
54	E.On	Welded pipe	~	~			As welded thick section
55	E.On	Welded pipe	SR	~			980°C 3h thick section
56	E.On	Welded pipe	~	wPH			810°C 4h thick section
57	E.On	Welded pipe	~	~			As welded (half welded section slice A)
58	E.On	Welded pipe	SR	~			Welded 980°C 3h (half welded section slice A)
59	E.On	Welded pipe	~	wPH			Welded 810°C 4h (half welded section slice A)
60	E.On	Welded pipe	~	~			As welded EBSD sample slice B
61	E.On	Welded pipe	SR	~			Welded 980°C 3h EBSD sample slice B
62	E.On	Welded pipe	~	wPH			Welded 810°C 4h EBSD sample slice B
63	E.On	Welded pipe	SR	wPH			Welded 810°C + 980°C thick section
64	E.On	Welded pipe	SR	wPH			Welded 810°C + 980°C (half welded section slice A)
65	E.On	Welded pipe	SR	wPH			Welded 810°C + 980°C EBSD sample slice B
66	E.On	Welded pipe	SR	~			As welded with 980°C heat treatment carried out by Lboro
67	E.On	Welded pipe	~	wPH			As welded with 810°C heat treatment carried out by Lboro
68	E.On	Welded pipe	~	~			Re solutioned as welded parent
69	SM	Rolled bar	~	~			Re solutioned gordons bar
70	SM	Rolled bar	ST* + SR	wPH			Fast cool
71	SM	Rolled bar	ST* + SR	wPH			Slow cool
72	E.On	Welded pipe	~	~	3	1000	weld metal
73	E.On	Welded pipe	SR	~			Fast cool weld metal
74	E.On	Welded pipe	SR	~			Slow cool but produced from old 1000°C sample
75	E.On	Welded pipe	SR	~			Slow cool produced from as welded weld metal
76	E.On	Welded pipe	~	~	25	750	As welded ageing sample
77	E.On	Welded pipe	~	~	100	750	As welded ageing sample
78	E.On	Welded pipe	~	~	1000	750	As welded ageing sample
79	E.On	Welded pipe	~	~	5000	750	As welded ageing sample
80	E.On	Welded pipe	SR	~	25	750	Stress relieved ageing sample
81	E.On	Welded pipe	SR	~	100	750	Stress relieved ageing sample
82	E.On	Welded pipe	SR	~	1000	750	Stress relieved ageing sample

83	E.On	Welded pipe	SR	~	5000	750	Stress relieved ageing sample
84	E.On	Welded pipe	~	wPH	25	750	Hardened ageing sample
85	E.On	Welded pipe	~	wPH	100	750	Hardened ageing sample
86	E.On	Welded pipe	~	wPH	1000	750	Hardened ageing sample
87	E.On	Welded pipe	~	wPH	5000	750	Hardened ageing sample
88	E.On	Welded pipe	SR	~	25	750	Stress relieved + Hardened ageing sample
89	E.On	Welded pipe	SR	~	100	750	Stress relieved + Hardened ageing sample
90	E.On	Welded pipe	SR	~	1000	750	Stress relieved + Hardened ageing sample
91	E.On	Welded pipe	SR	~	5000	750	Stress relieved + Hardened ageing sample
92	E.On	Welded pipe	~	~	100	750	Furnace heat and cool
93	E.On	Welded pipe	~	~	100	750	Fast cool removed from furnace to air
97	DPS	Welded pipe	~	~	~	~	As welded: IP (II)
98	DPS	Welded pipe	~	~	~	~	700°C 3kh: IP (II)
99	DPS	Welded pipe	~	~	~	~	700°C 10kh: IP (II)
100	DPS	Welded pipe	~	~	~	~	725°C 3kh: IP (II)
101	DPS	Welded pipe	~	~	~	~	725°C 10kh: IP (II)
102	E.On	Welded pipe	SR	~	250	800	Stress relieved 800°C aged set
103	E.On	Welded pipe	SR	~	1000	800	Stress relieved 800°C aged set
104	E.On	Welded pipe	SR	~	5000	800	Stress relieved 800°C aged set
105	E.On	Welded pipe	SR	~	110	750	Furnace heat and cool 110h weld cracking
106	E.On	Welded pipe	SR	~	1	750	1h wq furnace weld cracking
107	E.On	Welded pipe	SR	~	145	750	WQ 148h weld cracking

The table uses the following abbreviations:

- Solution heat treatment
 - ST* - 0.5 h @ 1150°C
 - SR – 3 h @ 980°C
- Precipitation hardening heat treatment
 - wPH – 4 h @ 810°C

3.2.3 Cast Nimonic 263

A step block of the dimensions shown in Figure 3.5 was cast in Nimonic 263 using a traditional sand casting method. The as cast step block was given a solution heat treatment of $1100^{\circ}\text{C} \pm 20^{\circ}\text{C}$ for 6 hours before ramping to $1200^{\circ}\text{C} \pm 20^{\circ}\text{C}$ for 12 hours followed by a water quench. After the solution heat treatment the step block was cut into two pieces as shown in Figure 3.5, and one of these pieces was then given an ageing heat treatment of $800^{\circ}\text{C} \pm 15^{\circ}\text{C}$ for 8 hours followed by air cooling.

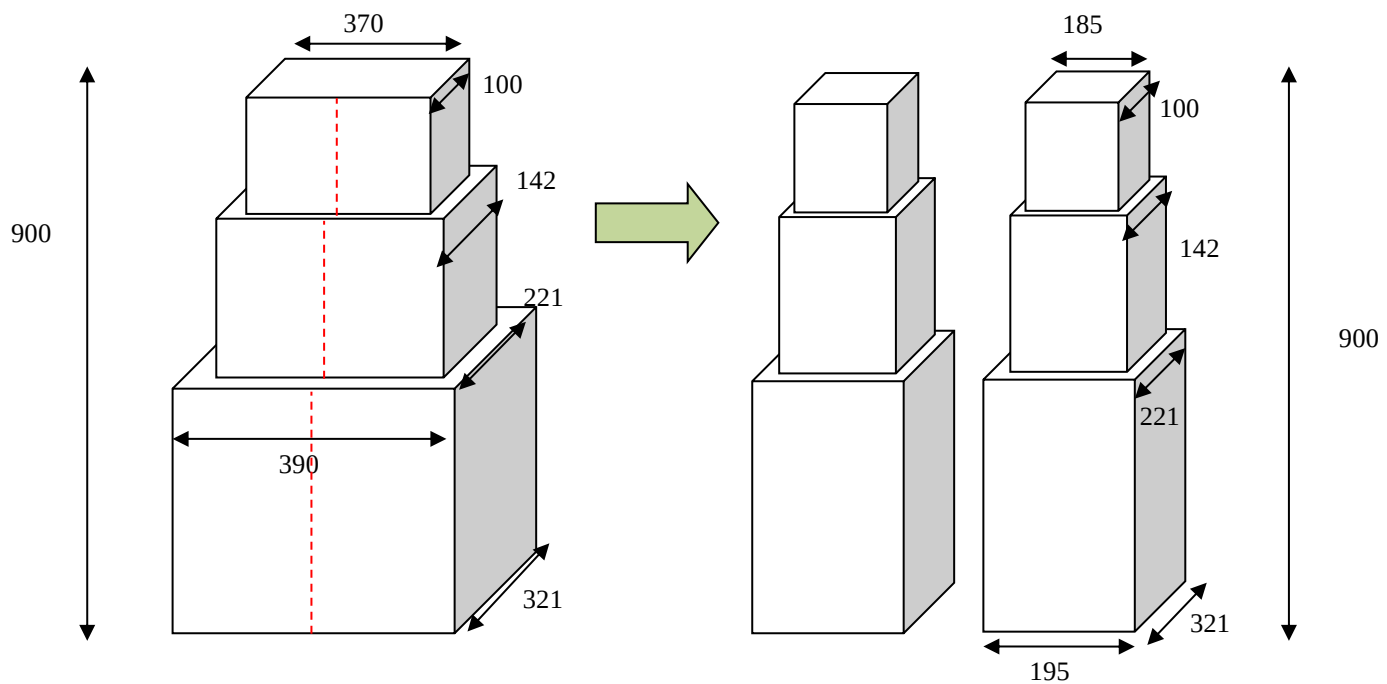


Figure 3.5 – A schematic diagram indicating the dimensions of the cast step block before and after sectioning (units are in mm)

The composition for Nimonic 263 casting as supplied by Goodwins Steel Castings has been compared to the nominal composition from Special Metals and is shown below in Table 3.6. The numbers are coloured in green as they are within the limits set by Special Metals, any outside of the limits would have been coloured red.

Table 3.6 – Chemical composition of cast Nimonic 263 compared to nominal composition

Elemental composition (wt.%)	C	Si	Mn	Cr	Co	Mo	Ti	Al	Fe	N
Nominal composition (set by Special Metals)	0.04 – 0.08	0.4 max	0.6 max	19.00 – 21.00	19.00 – 21.00	5.6 – 6.1	1.9 – 2.4	0.6 max	0.7 max	-
Composition of cast 263 material	0.057	0.34	0.37	19.85	19.59	5.61	2.05	0.42	0.07	0.007

The as cast samples studied were removed from the bottom of the feeders as indicated with the red dashed lines in Figure 3.6.

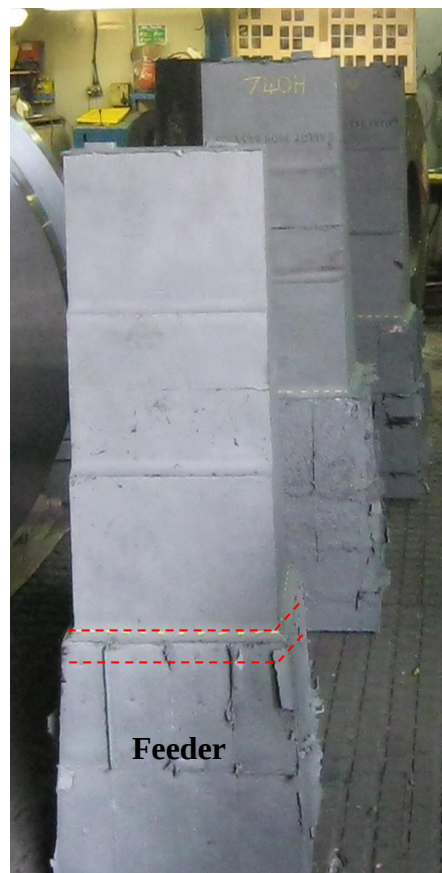


Figure 3.6 – Photograph showing one of the typical step block castings produced with the location of the samples used in this research highlighted in red.

After sectioning a piece of the Nimonic 263 fully processed test bar, a number of samples were produced for subsequent ageing. 8 samples were produced at approximate dimensions of 10 mm x 20 mm x 10 mm. Ageing was carried out in a furnace with exposure to air at two ageing temperatures of 700°C and 800°C for 100, 1000, 2000 and 5000 h. Samples were air cooled after reaching the desired time of exposure. A breakdown of all the samples used in the cast chapter can be seen in Table 3.7.

Table 3.7 – Sample matrix for Chapter 6 microstructural characterisation of cast Nimonic 263

Sample ID	Origin	Form	Heat treatment				Notes
			Solutioned	Precipitation hardened	Ageing time (h)	Ageing temp (°C)	
94	GW	Test block	cST	cPH	~	~	As cast test block
95	GW	Test block	cST	cPH	~	~	Centre
96	GW	Test block	cST	cPH	~	~	Edge
108	GW	Test block	cST	cPH	100	700	
109	GW	Test block	cST	cPH	1000	700	
110	GW	Test block	cST	cPH	2000	700	
111	GW	Test block	cST	cPH	5000	700	
112	GW	Test block	cST	cPH	100	800	
113	GW	Test block	cST	cPH	1000	800	
114	GW	Test block	cST	cPH	2000	800	
115	GW	Test block	cST	cPH	5000	800	
118	GW	Step casting	~	~	~	~	As cast 263
119	GW	Step casting	cST	~	~	~	ST 263
122	GW	Step casting	cST	cPH	~	~	Produced from piece of ST step casting (119)
123	GW	Test block	cST	cST	1200	20	
124	GW	Test block	cST	cST	1200	30	Solution investigation
125	GW	Test block	cST	cST	1200	40	Solution investigation
126	GW	Test block	cST	cST	1200	50	Solution investigation
127	GW	Test block	cST	cST	1200	165	Solution investigation

The table uses the following abbreviations:

- Solution heat treatment
 - cST – 6 h @ 1100°C + 12 h @ 1200°C
- Precipitation hardening heat treatment
 - cPH – 8 h @ 800°C

3.4 Sample preparation

Depending on the experimental work undertaken samples may have to be cut into smaller pieces for mounting, this is done using a more precise cutting system. The samples were cut using a Struers Accutom-5 with a water cooled Al_2O_3 cutting disk. Due to the hardness of Nimonic 263 the machine is operated at low cutting speeds at approximately 0.03 mm/min to minimise the heating and deformation during cutting. Once cut to the correct size the sample were mounted in conductive Bakelite (MetPrep Conducto-Mount) using an automatic mounting system (Struers ProntoPress-10). After mounting the samples need to be prepared for metallurgical analysis using a series of grinding and polishing stages. Depending on the cutting method used the sample may need to be finished to remove any cutting marks or damaged areas. The next step was carried out using a TegraPol-25 automated polisher, with the use of a TegraForce-5 multiple specimen holder. The grinding stages are lubricated using a water feed and include: 200, 600 and 1200 grit. Three separate polishing stages were then carried out for 12 minutes, with the aid of a TegraDoser-5 to dispense the dedicated polishing solutions. Three different combinations of pads and polishing solutions were used: Plan - 9 μm , Mol - 3 μm , and Floc - 1 μm . Certain microscopic techniques, such as EBSD, will require an additional polishing stage using a colloidal silica chemical polish of 0.04 μm for between 20 - 40 minutes. This polishing stage combines mechanical polishing with chemical etching and is known as a chemo-mechanical polishing process. The aim of this stage is to highlight the grain structure, remove any remaining fine scratches or deformation left from prior polishing stages. After polishing, cleaning of the sample is imperative as any foreign debris will be present when analysed using electron microscopy. The samples are cleaned with methanol for about 2 - 3 minutes before being dried. After preparation the samples were mounted on small stubs using a conductive adhesive ready for analysis. The samples were then etched depending on the experimental technique being used and the particular features to be analysed; Fry's reagent (CuCl - 200 g, HCl - 1 l and water - 1 l) was used to highlight the gamma prime precipitates and Kallings no. 2 (CuCl_2 - 2 g, HCl - 40 ml and ethanol - 40 - 80 ml) was used to preferentially attack the grain boundaries and in turn reveal the alloy's grain structure.

3.5 Thermodynamic Calculations

Thermodynamic calculations were carried out using the mean chemical composition of Nimonic 263 to ascertain which phases were expected to be present at thermodynamic equilibrium and their fraction through a temperature range of 400 - 1600°C. Calculations

were extended to show the change in chemical composition of each phase against temperature.

The calculations were produced using ‘Metallurgical and Thermochemical Databank’ MTDATA^[53] version 4.81 developed by the National Physical Laboratory (UK), in conjunction with the Thermotech Ni-Data database^[54]. MTDATA is a thermodynamic modelling software package that allows equilibria to be calculated for multicomponent systems of interest. Equilibria is calculated from critically assessed data for each phases binary and ternary subsystems^[53].

MTDATA uses a principle calculation module called MULTIPHASE, inputs required for the MULTIPHASE module include: composition, temperature and pressure. The equilibrium state is calculated in terms of the distribution of components and species between the stable phases. The module can also determine the volume or pressure of the system. MTDATA specifically calculates equilibria using an algorithm providing true Gibbs energy minimisation through solution of a non-linear optimisation problem with linear constraints.

To provide reliable and accurate thermodynamic predictions an accurate and extensive series of databases are accessed by a programme using an integral data management system. When producing thermodynamic calculations for Nimonic 263 the parameters in Table 3.7 were used. It can be noticed that nitrogen has been suspended due to the limitations of the current database.

Table 3.7: List of elements and phases that were allowed for thermodynamic calculations.

Alloy	Allowed Elements	Allowed Phases
Nimonic 263	Co, Cr, Mo, Ti, Al, Fe,	γ^* , $M_{23}C_6$, Liquid, MX^* , η ,
	C, Ni, N	γ' , μ , M_6C

*Two miscibility gaps were allowed for the FCC phase to calculate both MX and the matrix γ

Figure 3.9, shows a flow diagram illustrating how the different software modules are used for data retrieval, assessment and calculation in the MTDATA software package.

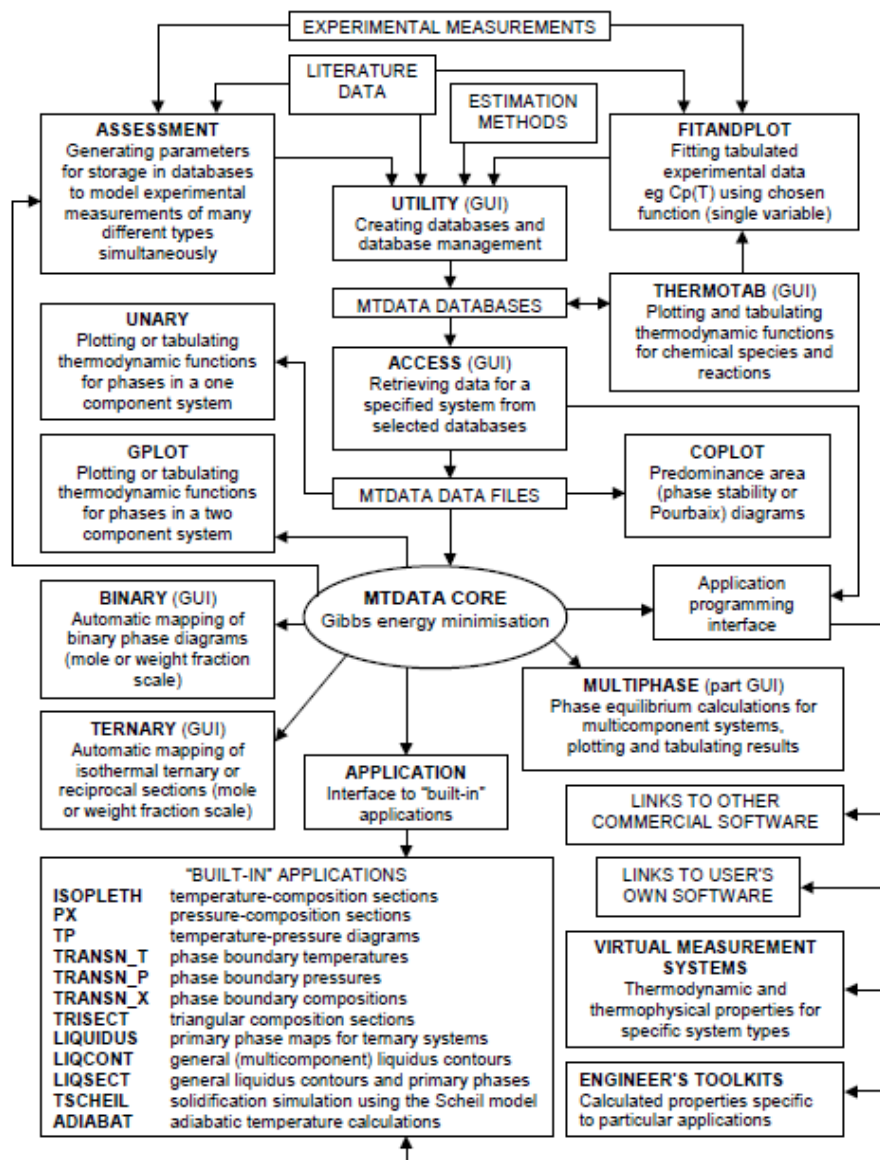


Fig 3.9: MTDATA structure overview [53]

3.5.1 Non-Equilibrium Calculations

Non-equilibrium solidification is often associated with more traditional processing routes such as casting or welding. This type of solidification can also occur in forged products although to a lesser extent. To model this type of solidification an expression termed the ‘Scheil equation’ is used. For equilibrium solidification described by the lever rule the composition of the solid (C_s) as a function of the fraction of solid transformed (f_s) is given by the equation:

$$C_s = \frac{kC_0}{f_s(k-1) + 1}$$

Where k is the partition coefficient which is constant during solidification, and C_0 is the composition of the original liquid alloy. This can be re-arranged to give:

$$f_s = \left(\frac{1}{1-k} \right) \left(\frac{T_L - T}{T_f - T} \right)$$

Where T_L and T_f are the equilibrium liquidus and solidus temperatures. When dealing with equilibrium solidification two assumptions are made i) that solute diffusion in the solid phase is small enough to be considered negligible ii) that diffusion in liquid is extremely fast and thus complete. These two assumptions allow Eq. 1 to be rewritten as:

$$C_s = kC_0(1 - f_s)^{k-1}$$

and Eq. 2 as:

$$f_s = 1 - \left(\frac{T_f - T}{T_f - T_L} \right)$$

Figure 3.10 shows a graphical representation of the modelling of a non-equilibrium solidification simulation using the Scheil method. A liquid of composition C_0 is cooled just below the liquidus T_1 . It precipitates out a solid with the composition C_1^S and the remaining liquid changes its composition to C_1^L . After further cooling to T_2 precipitation of the solid phase occurs from the liquid C_1^L this time with the composition C_2^S . After precipitation of the solid phase C_2^S the liquid composition will now be C_2^L . The precipitation of solid C_2^S precipitates around the original precipitation of solid C_1^S . This process continues indefinitely with the liquid becoming further enriched with solute until eventually the eutectic composition is achieved and the final solidification occurs^[55].

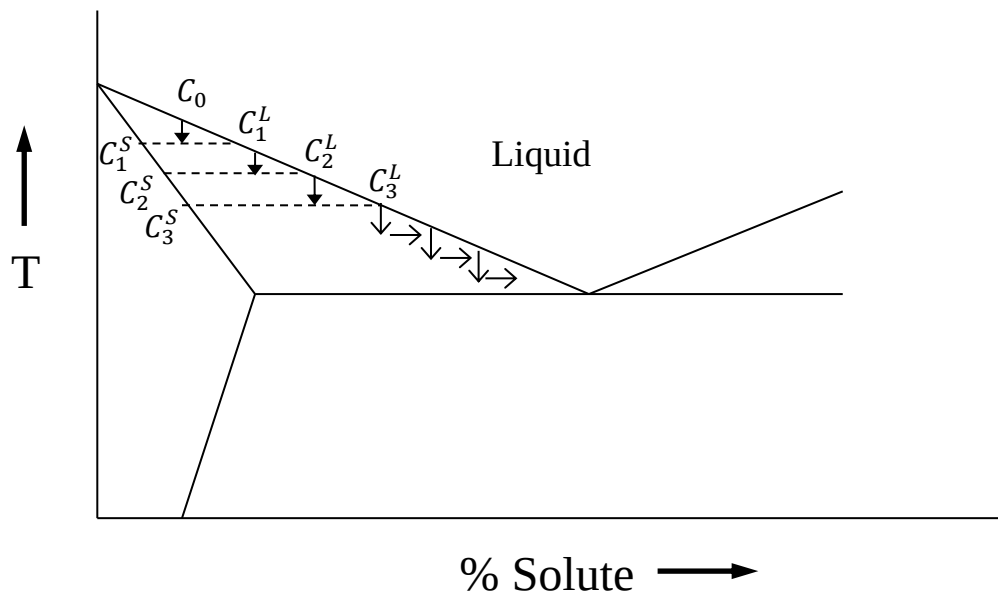


Figure 3.10: Diagram showing solidification occurring under ‘Scheil’ conditions^[55]

3.6 Hardness Testing

After heat treatment the hardness of each of the samples was determined. Mounted samples prepared up to the 1 μm polish stage, were tested for their hardness using a Mitutoyo AVK-C macro Vickers hardness testing unit at a load of 10 kg applied for 10 s. Samples were tested 10 times to ensure that the hardness of each sample was fully evaluated. In parts of the research hardness traverses have been carried out along a length of material, in this work each data point relates to an individual test. This varies from other samples where an average of several tests make up one data point.

3.7 Optical Microscopy

Initial assessment of the alloys microstructure was carried out using both bright and dark field optical microscopy. Prepared samples etched with Kallings No2 were analysed using a Reichert-Jung MeF3, inverted metallurgical microscope and images were collected using a Q-imaging Micropublisher 5.0 digital camera. Optical microscopy was used to help evaluate the alloys grain structure and size.

3.7.1 Grain Size Measurements

The grain size of the etched samples was measured from optical micrographs, using the mean linear intercept method ^[56]. The grain size is measured by determining the number of grain boundary interceptions along a line of a finite and known length. The linear intercept grain size, L_1 , can be calculated using equation 3.1:

$$L_1 = \frac{\sum L}{M \sum x} \quad (\text{Eq 3.1})$$

where M is the magnification, $\sum L$ is the total length of the n traverses, and $\sum x$ is total number of interceptions of the n traverses.

The boundary interceptions were recorded along both horizontal and vertical lines for all samples. The magnification used for production of optical micrographs was approximately x100. In order to achieve statistically significant results, care was taken to space the test lines sufficiently far apart so that two adjacent lines do not cross the same grain – this, however, proved difficult due to the large grain size of Nimonic 263.

3.8 Electron Microscopy

When an electron beam is directed towards a target it interacts in a number of different ways. The different interactions, shown in Figure 3.11, can be exploited to ascertain various types of information. The specific electron interactions in each sample depend on the material type, topography and thickness. For example a thinner sample will result in more transmitted electrons, as is the case when analysing a TEM thin foil.

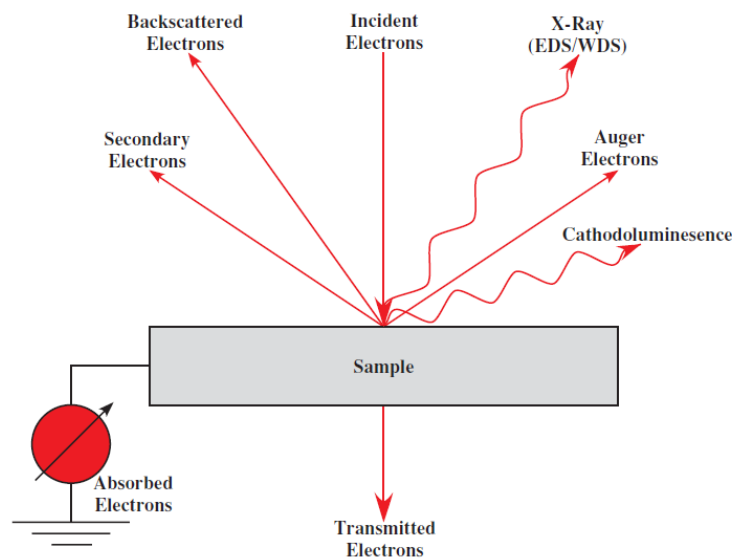


Figure 3.11: Diagram highlighting the different interaction of an incident scanning electron beam with a solid sample ^[57]

3.8.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) enables the resolution of smaller features not observable by other techniques such as optical microscopy. In this research a Carl Zeiss (Leo) 1530VP Field Emission Gun Scanning Electron Microscope (FEGSEM), operating at an accelerating voltage up to 20 kV, has been used in conjunction with a Pegasus combined electron backscatter diffraction (EBSD) and energy dispersive X-ray (EDX) system for both imaging and chemical analysis. The FEGSEM system has a much higher spatial resolution than standard SEM systems due to the higher current density of the electron beam produced. The systems electron source is a thermally assisted field emission source, which has a tungsten tip of a few microns in diameter. The SEM was operated in a voltage range of 5 - 20 kV and at a working distance between 1 - 15 mm, depending on the detector being used. The FEGSEM system can be operated in two modes high voltage (HV) and variable pressure (VP), this research will use only the HV mode. Three detectors are used in HV mode:

secondary electron (SE), In-lens and electron back scatter (QBSD). In this research only three of these modes were utilised, a brief description of each follows.

Imaging using the SE detector provides imaging at an attainable resolution of less than 10 nm, using this detector also provides a good depth of field when scanning across a surface at long working distances. It is also used as an electron source for the EDX analysis and the construction of EDX maps.

In-lens mode utilises true secondary electrons, reducing the topographic effect created when using secondary electrons. Figure 3.12 shows the three types of secondary electron and explains how they affect image quality.

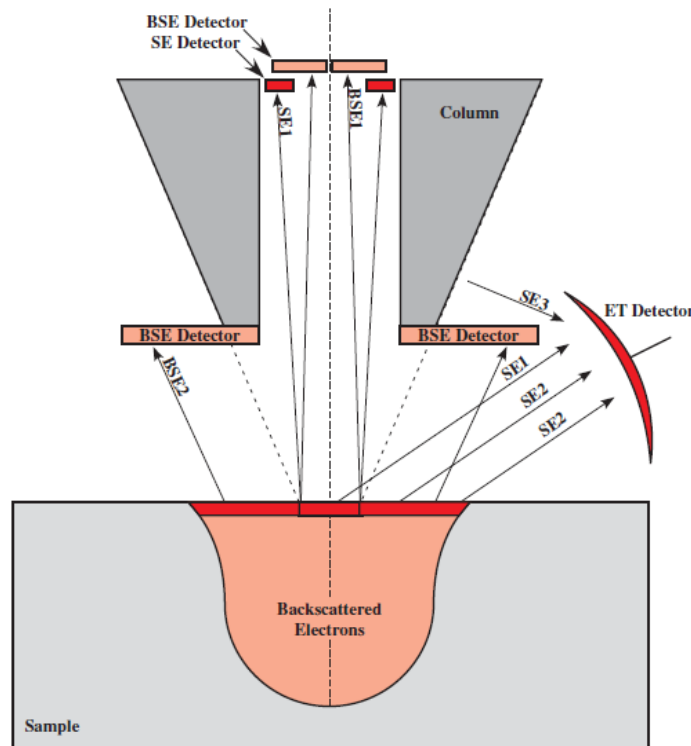


Fig 3.12: Schematic showing the electrons interaction and detectors within an SEM chamber [57]

When operating the SEM using the in lens detector an increased number of true secondary electrons are detected. The smaller working distance also reduces the effect of reflected electrons from both the column and the chamber. Due to some γ' precipitates being present at diameters <10 nm it is paramount that interference of additional secondary electrons are reduced. In-Lens mode was used in this research at an operating voltage of between 5 - 10 KV with working distances between 1 and 3 mm.

When an electron beam interacts with a solid sample a fraction of them will be scattered by the target material, the fraction of scattered electrons depends greatly on atomic number of the area it comes into contact with. This phenomena is sometimes termed ' $\bar{Z}$ contrast', the higher the $\bar{Z}$ value the more electrons are scattered, meaning that high atomic numbers such as Ni will appear light and low atomic numbers such as C will appear dark. In this research the FEGSEM was operated in back scatter mode to distinguish between similar sized and shaped precipitates by utilising atomic number contrast.

3.8.2 Energy Dispersive X-ray Analysis

In both TEM and SEM, energy dispersive X-ray analysis (EDX) can be used to identify the chemistry of certain phases. X-rays are emitted when incident electrons with sufficient energy interact with the sample, ejecting an electron from an inner shell. To complete the now unbalanced shell an electron migrates from the K or L shell, this migration results in an excess of energy which is released as an X-ray. Each element will release an X-ray of different energies, which can be detected allowing for quantification. Although software can auto index the peaks it should be noted that some peaks overlap creating erroneous results. When using this technique it should also be understood that the penetration depth of the electron beam generating the X-rays can go beyond the target feature. The effect this has will depend on the parameters being used in the microscope and the size of the precipitate or phase being analysed. Figure 3.13 indicates how an electron beam can penetrate the specimen.

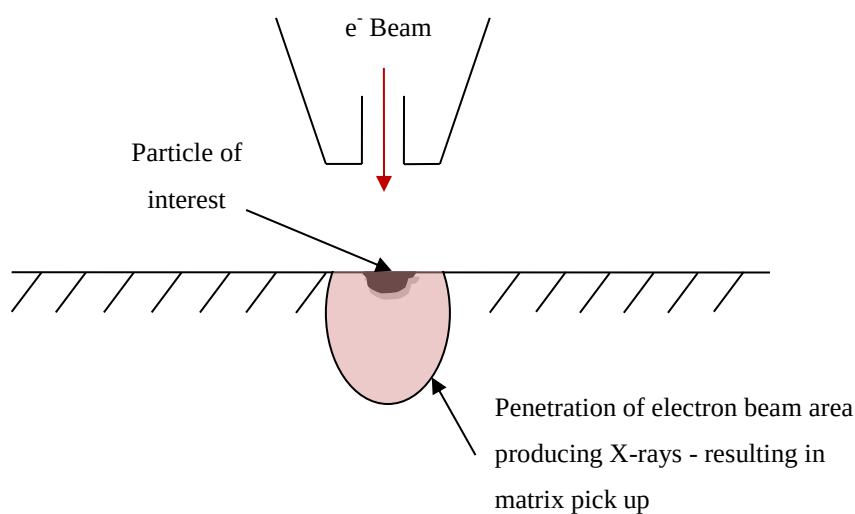


Figure 3.13: Penetration of electron beam resulting in matrix pick up or interference from other phases

3.8.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was used to study γ' and grain boundary precipitates at high magnifications in Nimonic 263. A TEM operates using an emission source of either: tungsten or lanthanum hexaboride, tungsten filaments are usually preferred due to their more robust nature. High voltages are applied to the emission source and electrons are emitted due to thermionic emission. The emitted electrons are focused into a beam and manipulated by a series of electromagnets or lenses. A series of different electromagnetic lenses are used to concentrate the electron beam before producing an image. Three different apertures are also used to further focus the beam depending on the type of analysis being carried out; condenser, objective and diffraction. Once focused the electron beam is passed through a chamber under vacuum containing the sample. After passing through the sample the electrons fall on the target plate creating an image. The TEM can be used to ascertain information regarding the precipitates present including: particle composition, size, crystallography and through imaging a distribution of particles. The TEM used in this research was a Jeol JEM 2000FX equipped with an Oxford Instruments EDX system with an ultra-thin polymer window. The system is operated at an acceleration voltage of 200 kV. During analysis a series of digital images were captured at both high and low magnifications to show typical microstructures and the features contained. The digital camera system attached to the Jeol JEM 2000FX is an Erlangshen camera produced by Gatan. For imaging and EDX the single tilt holder is used. When carrying out diffraction the double tilt holder is used which tilts the specimen along two different axes to ensure optimum diffraction conditions are achieved.

EDX analysis is generally done at spot size 5, however for smaller particles a larger spot size can be used to ensure that the whole particle is encompassed. During EDX analysis software written by INCA was used to quantify elements. During EDX analysis the software illustrates the peak elements detected during analysis, an example of this can be seen in Figure 3.14.

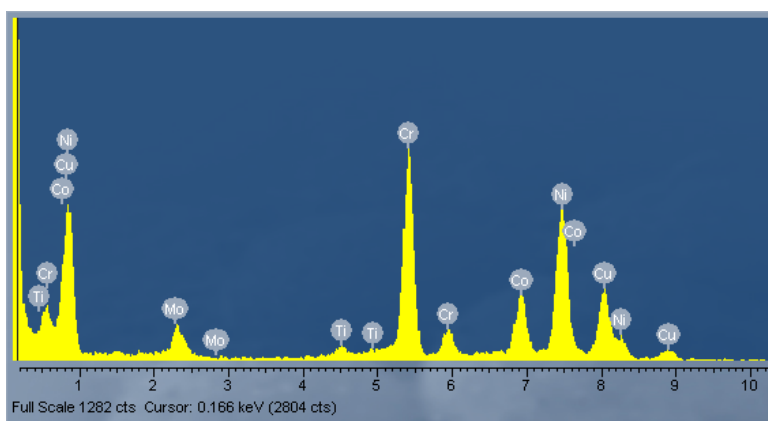


Figure 3.14: Example of spectrum produced using INCA software

The program allows for elements to be added and removed from analysis. Large copper peaks are often present in extraction replicas and in-situ lift outs, due to them being mounted on copper grids: it is therefore very useful to be able to discount the existence of such elements. Although EDX can give an indication whether a certain low atomic number element like Carbon or Nitrogen is present it is also difficult to quantify, so during quantification these elements are often removed. The element beryllium is also removed when using the double tilt holder as the cap that secures the sample in place is made from this element.

3.8.4 Selected Area Diffraction

To gain information about the crystal structure of a precipitate or phase, selected area diffraction (SAD) can be carried out using the TEM. Crystal information when combined with chemical composition can help conclusively identify a phase. Firstly, the phase or precipitate to be analysed is tilted using the double tilt holder until it is diffracting strongly, the darker the precipitate appears the more strongly it is diffracting. The next stage is to isolate the precipitate using the selected area aperture, there are three different size diffraction apertures and it is important that an aperture size suitable to the target precipitate is chosen. The objective aperture is then removed before diffraction mode is then engaged producing a pattern. The pattern produced will vary depending on the crystallographic nature of the phase and any interference of the surrounding phases; in the case of many patterns both the desired precipitate and the surrounding matrix are displayed. Indexing or solution of the pattern requires knowledge of what the precipitate or phase could potentially be. Figure 3.15 shows a schematic of the technique and a labelled basic diffraction pattern.

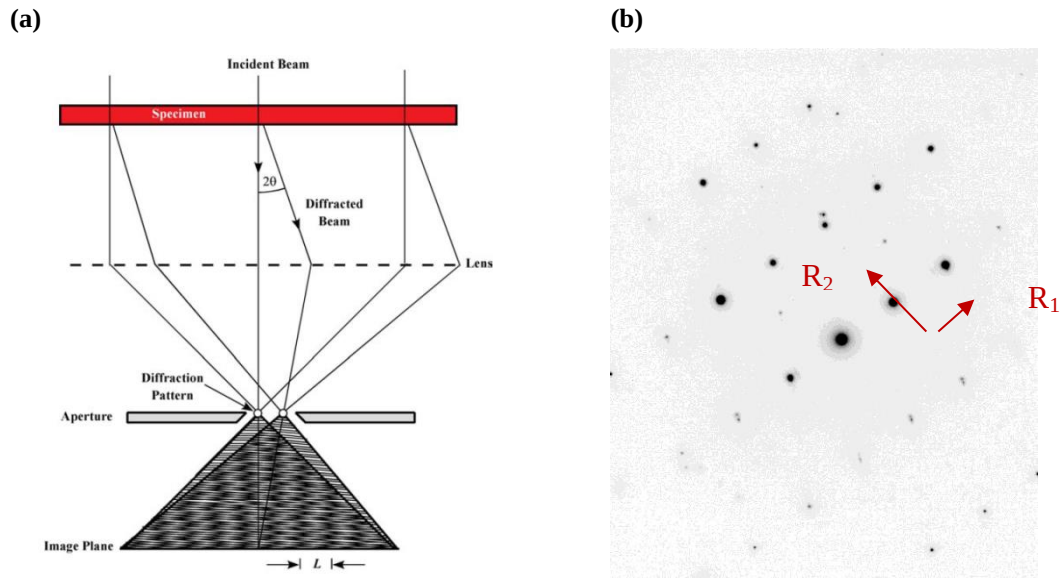


Fig 3.15: (a) Schematic of the diffracting incident beam, (b) Typical diffraction pattern with $R_1 R_2$ measurements shown^[57]

Figure 3.15(a) shows the incident beam being diffracted by an angle of 2θ creating the diffracted spots the distance 'R' from the transmitted spot. The distance ' R_{hkl} 1 and 2', shown in Figure 3.15(b), between the transmitted spots is related to the spacing ' d_{hkl} ' for the Bragg hkl indices, the camera length 'L' and the wavelength of the transmitted electron beam through the following equation:

$$R_{hkl} d_{hkl} = L\lambda \quad (\text{Eq 3.2})$$

where $L\lambda$ is defined as the camera constant. The wavelength of an electron is determined from the acceleration voltage using the following equation:

$$\lambda = \sqrt{\frac{h}{2m_e eV}} \quad (\text{Eq 3.3})$$

Where V is the acceleration voltage, e is the charge on an electron, m_e is the mass of an electron and h is Planck's constant. For the acceleration of 200 kV, as used in this research, the electron wavelength λ is calculated to be 0.025 Å.

The diffraction patterns can also be resolved using the MSDOS based computer programme 'Practical Crystallography version 1.6' developed by H. K. D. H. Bhadeshia at Cambridge

University^[58,59]. The SAD technique will sometimes require the use of the double tilt TEM holder. The double tilt holder rotates the sample through two axes, optimising the diffraction contrast of the precipitate and producing a diffraction pattern with little interference from other phases.

3.4.1 TEM Sample Preparation Techniques

To produce samples for analysis in the TEM three different techniques were used: electro polished thin foils; in-situ lift out, and; carbon extraction replicas. Each technique was chosen depending on the particular feature to be investigated and the specific information to be analysed e.g. EDX, diffraction and imaging.

Electro polished thin foils were prepared by cutting thin sections from heat treated samples using the Struers Accutom-5. Discs of 3 mm diameter were then punched out of the thin sheets ready to be ground down to $\approx 100 \mu\text{m}$. The discs were then ground using a manual polishing rack, in conjunction with a bespoke holder designed to grip 3 mm discs. The discs were then electropolished to perforation using a 10% perchloric acid in methanol electrolyte at -40°C and 30 V, using a double-jet electropolisher, the principle of which is displayed in Figure 3.7.

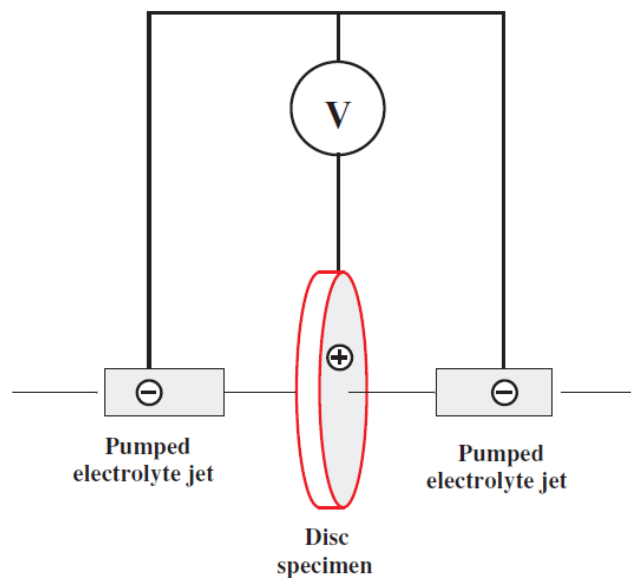


Fig 3.7 Schematic illustrating the principles of the double jet electropolishing unit ^[57]

To ascertain chemical and crystallographic information from second phase particles without interference from the Ni-rich matrix a carbon extraction replica can be used. In the extraction replica technique, the samples were first etched using Kalling's No2 to preferentially etch away the matrix. Samples are then coated with a thin layer of carbon using a Quorum Carbon Evaporator. The evaporator deposits carbon through the application of current and the subsequent arcing of two carbon rods under vacuum. Once the carbon layer is deposited, small squares are cut into the surface using a razor blade. The carbon replicas were then removed using an electrolytic etch consisting of 10% HCl in methanol at 5 V. The electrolytic etch causes the carbon layer to break free from the substrate, removing with it the second phase precipitates. After immersion in 10% HCl in methanol the sample is placed into methanol to clean, followed by distilled water in which the extractions float off ready to be mounted on a 3 mm copper grid for examination in the TEM. The basic process of carbon extraction is detailed in Figure 3.8.

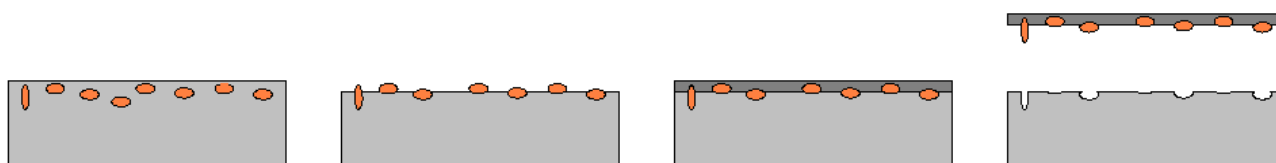


Figure 3.8 showing Carbon extraction including etching, and carbon evaporation

3.9 Dual Beam Focused Ion Beam/Electron Beam Microscopy

To image and produce in-situ lift outs a Fei Nova Nanolab 600 dual beam focused ion beam field emission gun scanning electron microscope (FIB/FEG-SEM) was used. This equipment allows images to be taken with either the ion beam or a standard FEGSEM. Ion beam imaging was used to look at the size of the second phase particles in addition the crystallographic structure of the surrounding matrix. The FIB uses a gallium ion source; the ion beam is formed when gallium metal is placed in contact with a tungsten needle and then heated. The gallium then begins to wet the tungsten and the electric field causes ionisation and the field emission of gallium ions. Helium sources can also be used, which are far less destructive, meaning that complex sectioning of samples is more difficult. Advantages of helium sources include higher resolution imaging and the possibility of increased dwell time without introducing any channelling contrast. The ion beam impacts the sample surface

causing electrons to be emitted and then detected to produce the image. Second phase the particles such as carbides and nitrides show up darker as they emit fewer electrons due to the ceramic nature of particles. This technique can also be used to reveal any crystallographic contrast between grains: due to grains absorbing different amounts of gallium ions, depending on orientation some grains will appear darker than others.

The in-situ lift out technique was carried out using a Fei Nova 600 Nanolab Dual Beam system. The technique involves finding a specific grain boundary or area of interest, depositing a layer of protective platinum and then milling a trench either side using the ion beam. The area between the two trenches is then further thinned using the ion beam at a much lower current. The thinned region is then removed using an Omniprobe manipulator and welded onto a copper TEM grid, before being thinned to electron transparency at ≈ 100 nm. A series of images breaking down the process is shown in Figure 3.16.

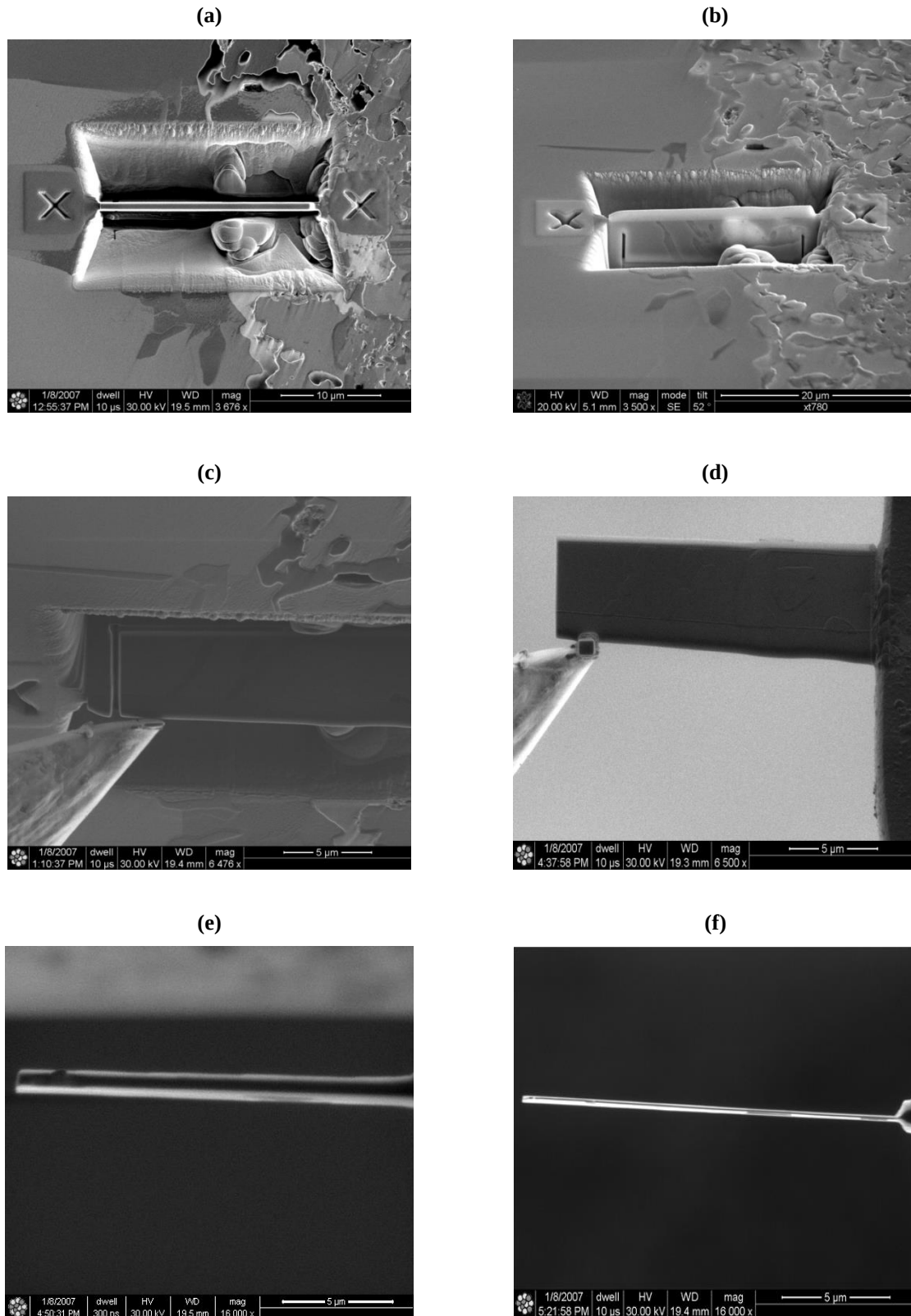


Fig 3.16: Images showing the process of producing an 'in-situ lift out', (a) Pt layer deposited and trenches milled either side, (b) U-shaped cut, (c) sample removed from trench using omniprobe, (d) sample attached to copper tem holder, (e) before final thinning, (f) after final thinning ≈ 100 nm

3.10 Image analysis to determine area fraction and average particle size

After the collection of electron micrographs image processing was conducted using the UTHSCSA Image Tool software. Prior to any image analysis the software has to be calibrated to the magnification of the intended images for use. To do this an image with a scale bar at the correct magnification is imported. A line is then drawn along the length of the scale bar and its known length is input into the software. For image analysis images first have to be cropped to remove the scale bar, this was done using the CS4 version of Adobe Photoshop software.

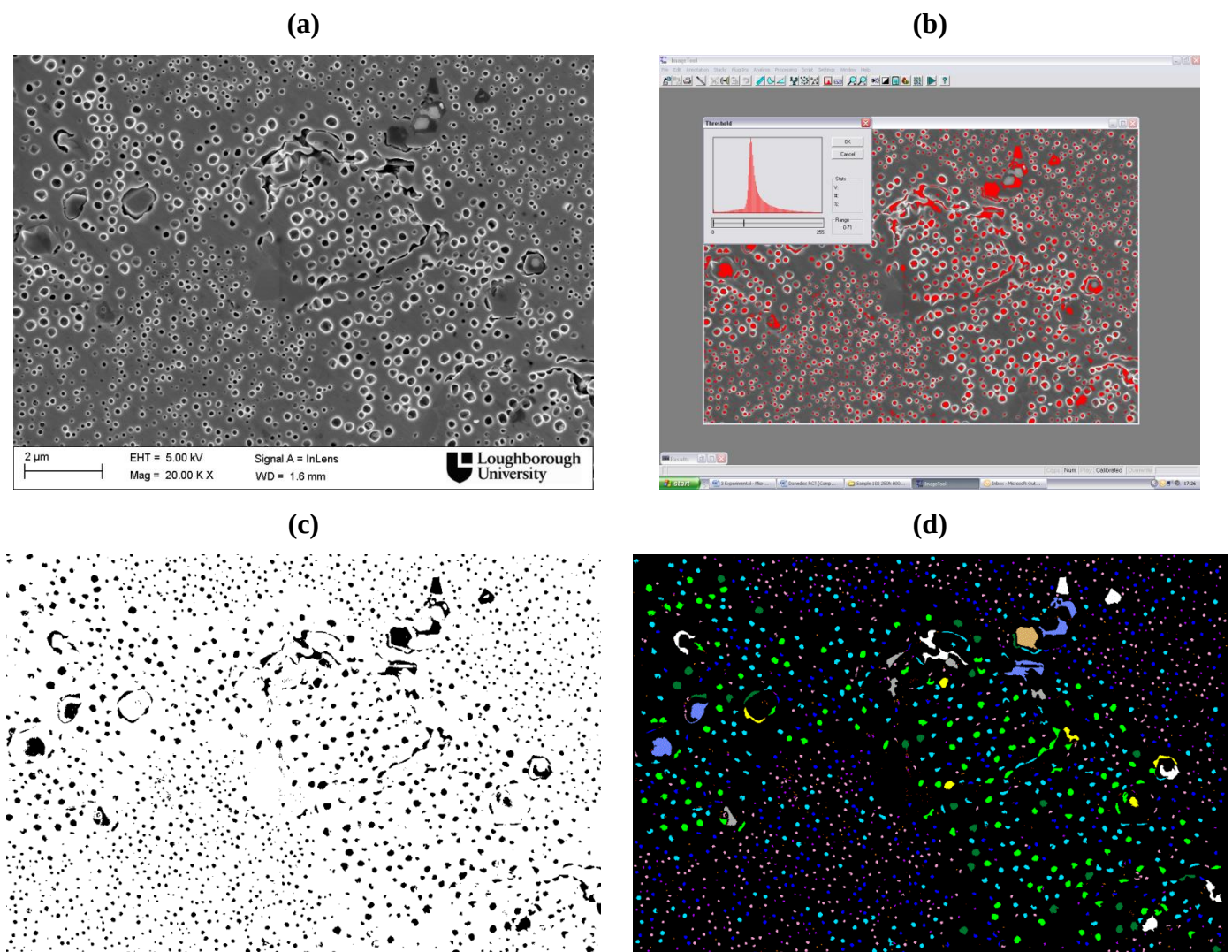


Fig 3.17 – Images documenting the image analysis process used in the research showing in particular (a) original micrograph, (b) cropped image during thresholding, (c) black and white image after thresholding and (d) fully processed image

Photoshop was also used to remove individual features not representative of the microstructure, an intended region of interest and to alter / remove areas of shadowing. The

cropped image was imported to the image tool program to carry out a process termed thresholding. Thresholding is when features of a certain contrast are highlighted in an image, this is shown in Figure 3.17 (a) and (b). The thresholded image is then converted to a black and white image shown in Figure 3.17 (c). From this image black and white image pixels are counted to give an area fraction of the thresholded region or particles. After thresholding the image can be further processed using the image tool software to quantify the particle size distribution. A tool is used to identify the number of individual objects contained in the image. An object is defined as a stand-alone collection of pixels, and it is for this reason that such care is taken preparing the images for analysis. It was sometimes necessary to raise the maximum number of objects to ensure that all features were processed, on average in each image between 2000 – 3000 objects were processed. To quantify the particle size distribution, a size classification is used to create range of precipitate size groups for which each object can be placed. During this research different size classifications and ranges have been used depending on the sample in question, to ensure good statistics are gathered for analysis. In addition to the raw data an image is also produced which colour codes each object / particle based on the size range it has fallen into. Such an image can be seen in Figure 3.17 (d) in which the collection of larger precipitates running through the centre have been differentiated against compared to those in the surrounding areas. For each sample between 5 – 10 images were processes depending on statistics. The software is very versatile, its capabilities include the ability to measure elongated precipitates using the major axis command and conversely minor axis length. These two features were considered when investigating the evolution of an elongated precipitate present after long term ageing in Nimonic 263. The main limitation of the software is the individual programme it uses to define an object. This was the problem that prevented it being used to study the Eta phase, as due to the overlapping and inter connective nature of the elongated phase the software could not distinguish between individual needles.

3.11 Electron Backscatter Diffraction (EBSD)

The EBSD technique was utilised during this study as a supplemental method to accurately measure the alloys grain size and compare results with those generated from optically based measurements. It was also used to render information on grain size when etching the alloy was problematic, meaning optical microscopy was limited. The samples were polished as per the sample preparation instruction in Section 3.4, including the additional polishing step using colloidal silica. The samples were mounted on a specimen holder which is pre tilted to 70° and an incident electron beam is directed at the sample. Electrons reflected from the sample fluoresce a phosphor screen creating a diffraction pattern. Each diffraction pattern is captured using a CCD camera, the resultant patterns are indexed based on a reference, in this case nickel. This process continues as the beam is scanned across the samples target area. The number of patterns collected, sometime referred to as points, will depend on the target area and step size.

EBSD scans in this research were typically performed with an accelerating voltage of 20 kV and an aperture size of 50 µm. Due to the large grain size present in Nimonic 263 a large sample area of 2500 by 5000 µm was chosen to ensure the scanned area was representative of the bulk microstructure. A step size of 4 µm was used to reduce the run time whilst maintaining an effective resolution. Collection and analysis of the EBSD data were carried out using the Orientation Information Microscopy software TSC OIM 5.31. The crystallographic file used for indexing was for pure nickel, which has a face centred cubic structure with a lattice parameter $a=0.356$ nm. With the use of this package the data was subsequently analysed allowing grain sizing and other measurements such as; grain misorientation and grain boundary length. Specifically in this research the software was used to categorise different grain sizes and colour them accordingly, showing clearly the distribution of grain size in the alloys macrostructure.

Chapter 4

Microstructural characterisation of isothermally aged Nimonic 263

4.1 Introduction

This chapter discusses the microstructural characterisation of Nimonic 263 in the as-received, precipitation hardened and aged conditions. The aim of the work in this chapter was to establish the overall microstructure present in Nimonic 263 in each pre service condition. The next part of the research was then to study how the microstructure will evolve when experiencing some of the likely conditions present in A-USC plant. The aim of this part of the research programme was to contribute to a life assessment methodology in which a microstructural assessment could inform decisions about when a particular component or area needs to be replaced or repaired.

The microstructure has been assessed using both theoretical and experimental techniques. Thermodynamic modelling was utilised to predict the fraction and chemical composition of each phase present at equilibrium conditions, and their variation with temperature. The thermodynamic modelling was extended to simulate the effect of non equilibrium cooling and the associated segregation. Electron microscopy techniques, both SEM and TEM, were used to carry out high resolution imaging of the alloys different phases. The chemistry of the alloys different phases and precipitates were investigated using the dedicated EDX systems attached to each microscope. Samples were first cut from a pipe in the as received condition before undergoing precipitation heat treatment and isothermal ageing using high temperature furnaces. The specific ageing temperatures and exposure times are described in detail in the experimental section. Isothermally aged samples were produced to help understand how the alloy evolves under controlled temperatures. The effect of other factors such as load and welding are considered in later chapters. Three main ageing temperatures were chosen for investigation: 700, 750 and 800°C with ageing times ranging from 0.25 and 20,000 hours. Finally, the alloys potential for rejuvenation is explored through an investigation in which long term aged material is subjected to two different rejuvenation heat treatments.

4.2 Sample conditions

The composition of the forged Nimonic 263 pipe is repeated from the experimental section and is shown below in Table 4.1, this composition will form the basis of Thermodynamic calculations. The table shows the pipe composition in three distinct areas.

- Bore – inside of pipe
- MW – Middle wall or ½ t
- OD – Outside diameter or outside of pipe

Table 4.1 – Composition of Nimonic 263 forged pipe (wt.%)

Material location	Element, wt.% (balance is Ni)							
	C	Al	Co	Cr	Fe	Mo	Ti	N
Bore	0.06	0.31	19.87	20.41	0.46	5.89	2.11	0.006
MW	0.07	0.32	19.84	20.31	0.45	5.94	2.08	0.006
O.D.	0.06	0.37	19.94	20.52	0.44	5.73	2.13	0.005
Average	0.06	0.33	19.89	20.41	0.45	5.85	2.11	0.006
Nominal	0.04 – 0.08	0.6 max	19 - 21	19 - 21	0.7 max	5.6 – 6.1	1.9 – 2.4	-

4.3 Thermodynamic Equilibrium Calculations

Thermodynamic equilibrium calculations were produced using the commercial thermodynamic equilibrium software package MTDATA, in conjunction with the critically assessed thermodynamic database for Ni-based alloys provided by NPL. The calculations were carried out to predict the phase stability and the fraction of each phase present at equilibrium. The mean composition from Table 4.1 in the experimental section was used to produce the thermodynamic phase calculations shown in Figures 4.1 (a) and (b). The composition used is within the values specified by Special Metals in the nominal Nimonic 263 composition. The calculations predicted the formation of the following six phases: gamma prime γ' , gamma γ , MC and MX, Eta phase η , $M_{23}C_6$ and the Mu phase μ . Calculations were initially carried out allowing all phases to exist, and then subsequently with η phase suspended because it was known to be extremely slow to form, and therefore the latter calculation is expected to give a more realistic prediction for shorter ageing times and non equilibrium conditions. Each calculation predicted the formation of γ , γ' , MX, $M_{23}C_6$ and Mu phase although the precipitation temperature and the fractions formed of each phase varied. The calculations predicted FCC γ as the bulk component or matrix of the alloy at 73 wt.%. The most significant difference between the two calculations was the predictions involving γ' precipitation. The calculation allowing of all phases, predicts γ' to form at 745°C and to be present at a fraction of 6.76 wt.% at 400°C. In the calculations with η suspended, γ' was found to form at 925°C and is present at a fraction of 13.9 wt.% at 400°C. Figures 4.1(a) and (b) show that the fraction of γ' decreases with an increase in temperature until dissolution. With η suspended, $M_{23}C_6$ was predicted to form at a reduced fraction; this may be due to the slightly higher Cr content in the increased fraction of γ' over the suspended η . The calculations also predicted the presence of MX and Mu phase in small quantities.

Figures 4.3(a – c) show that the compositions of the γ' , MX and η precipitates can be seen to be relatively consistent as a function of temperature. Figure 4.3(a) indicates that the γ' phase is calculated to be a Ni-Ti-Al rich precipitate with small amounts of Co and Cr. Figure 4.3(b) shows the calculation for the MC phase which contains half Ti and half C with a small fraction of Mo. Figure 4.3(c) shows the Eta phase to be predicted to be Ni-Ti rich, with both elements decreasing slightly in favour of Co when temperature is increased. Figure 4.3(d) shows $M_{23}C_6$ to be a Cr rich phase, in which Cr decreases with temperature in favour of Ni and Co.

A small change was noticed between the Al contents (0.31-0.37 wt.%) in the bore and the outside diameter as mentioned in the experimental section. This was deemed important due to sensitivity of γ' formation to the Ti-Al ratio in the alloy. Additional calculations (allowing for all phases) predicted that the difference in Al is likely to result in a small difference in the amount of γ' in each region, with corresponding fractions of 0.032 and 0.039 predicted to form in the bore and outside diameter respectively.

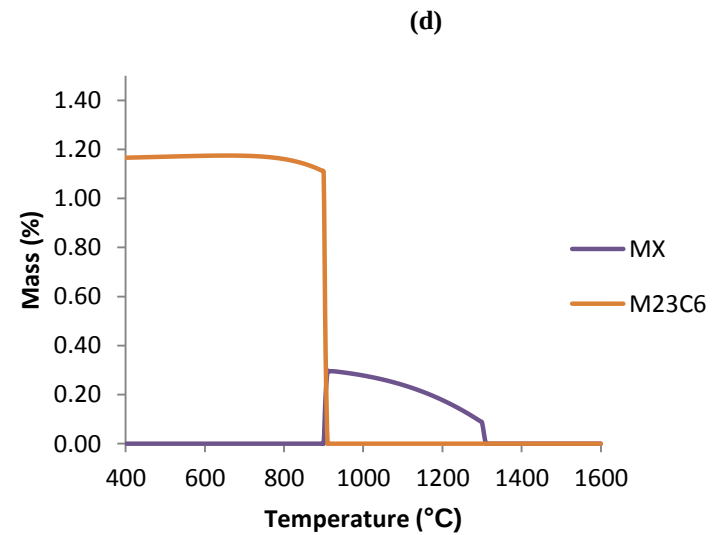
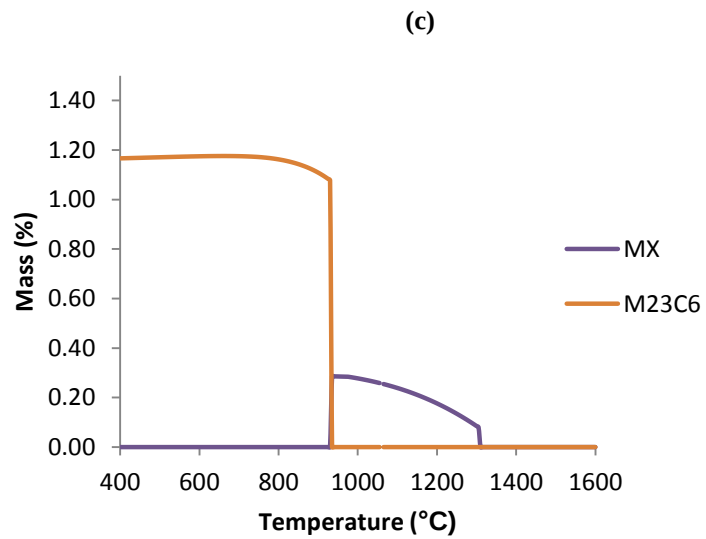
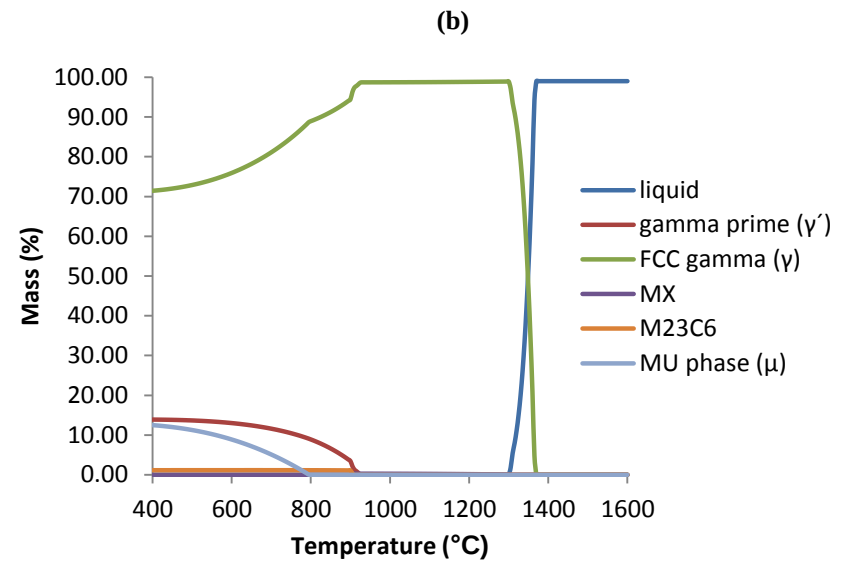
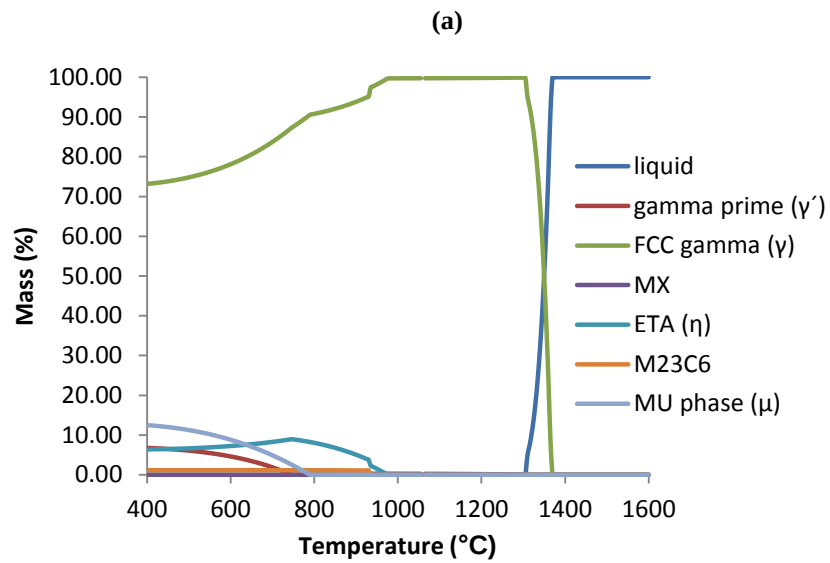


Figure 4.1: (a), (c) Nimonic 263 predicted phases against temperature in equilibrium conditions, (b), (d) predicted phases with Eta phase suspended from the calculations

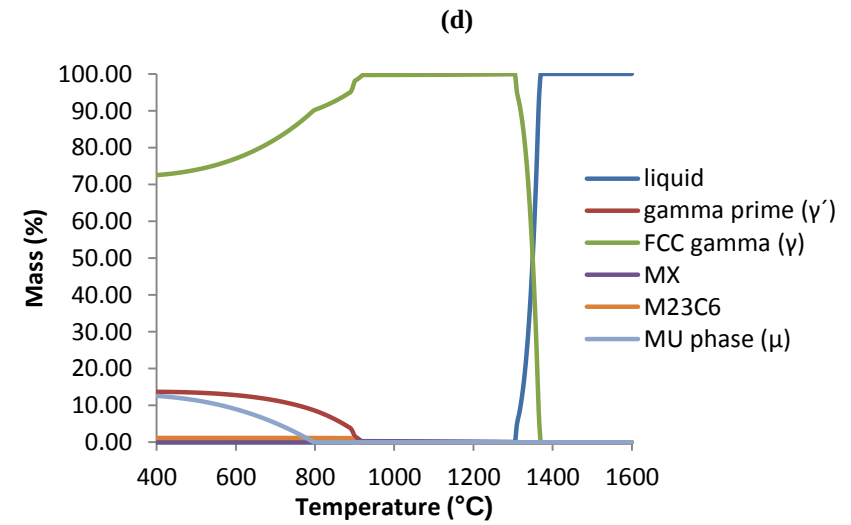
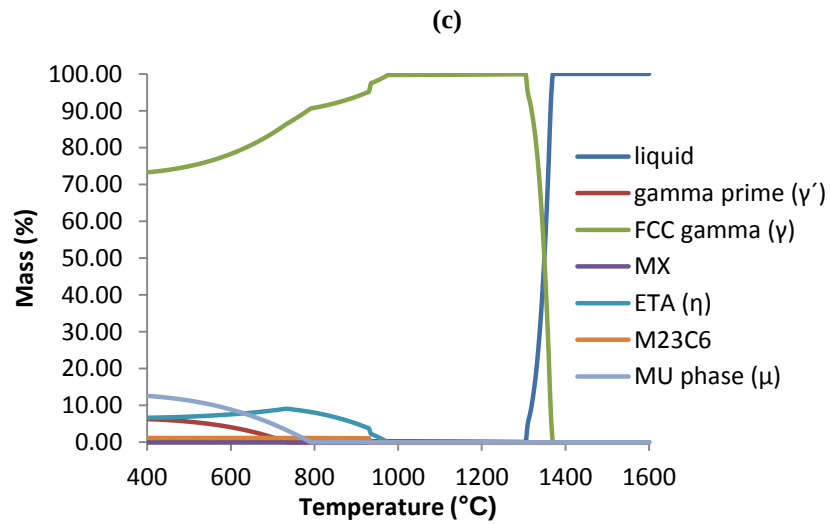
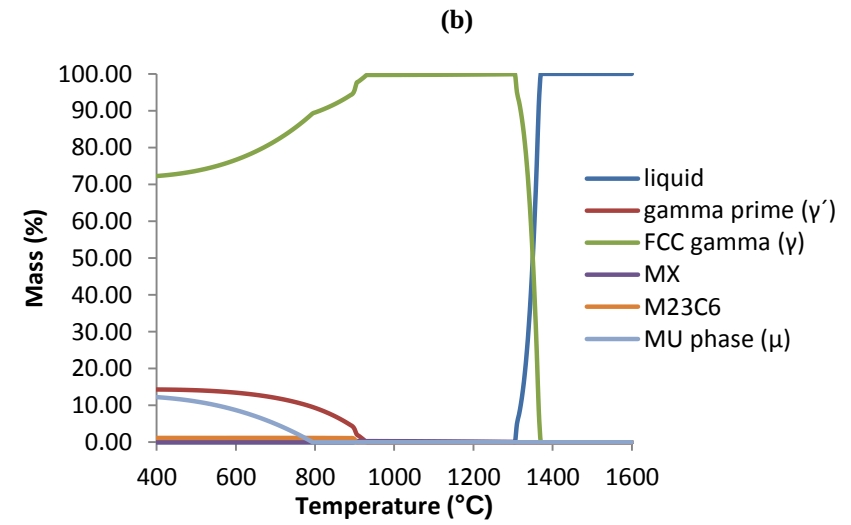
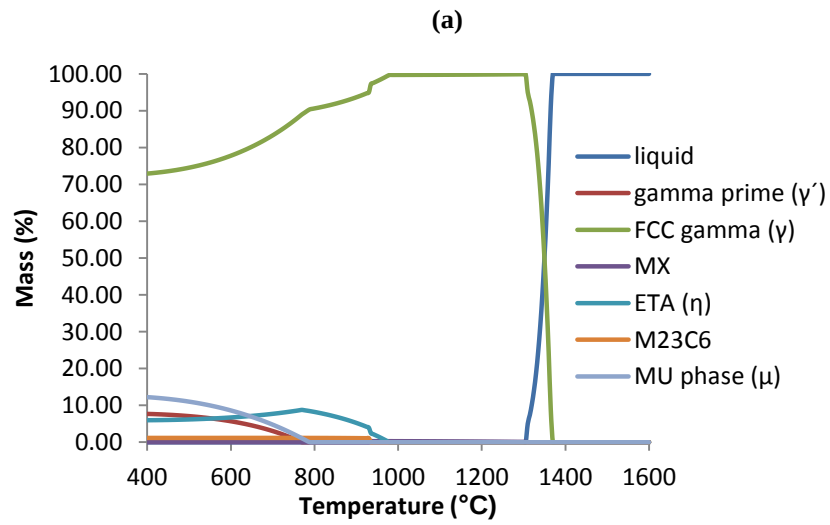


Figure 4.2: (a) Predicted microstructure allowing for all phases with O.D. composition, (b) predicted microstructure with Eta phase suspended with O.D. composition, (c) Predicted microstructure allowing for all phases for bore composition, (d) predicted microstructure with Eta phase suspended for bore composition,

In addition to predicting the phases present, the composition of each phase can also be calculated as a function of temperature, as shown in Figures 4.3(a – e).

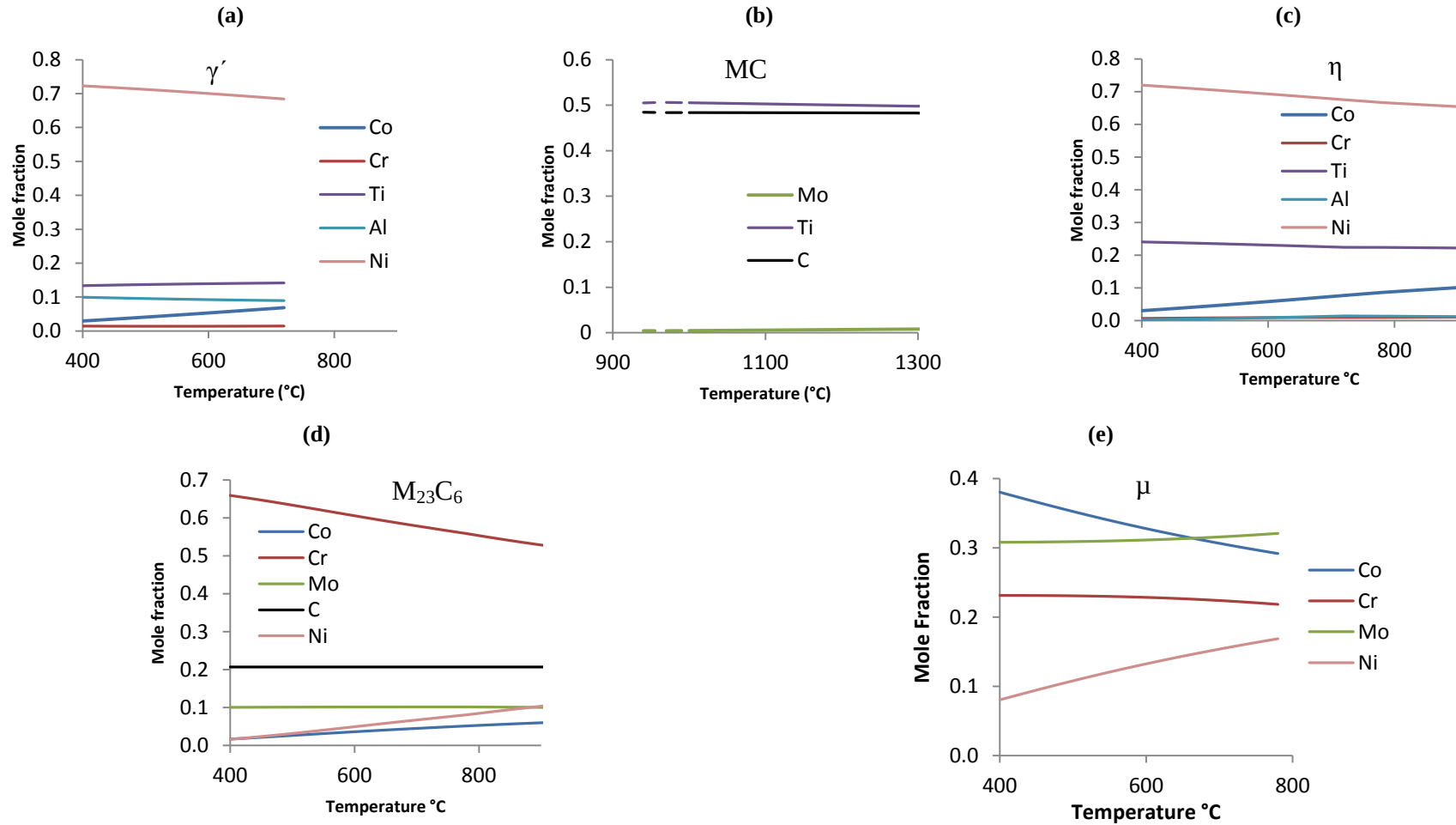


Figure 4.3: Phase composition calculations for average Nimonic 263 composition: (a) γ' , (b) MC, (c) η , (d) $M_{23}C_6$ and (e) μ phase as a function of temperature

The compositional difference between the bore and the outside diameter, noted earlier in the chapter, and the resultant thermodynamic calculations showed a difference in the precipitation trends of the gamma prime and Eta phase. Based on that result a sensitivity study was conducted using MTDATA to study the effect of aluminium content on these two precipitation products. The average composition in Table 4.1 was again used as a basis for the calculations. The aluminium content was varied by 0.1 wt.% in each calculation and was balanced against nickel content. For example with the average composition in Table 4.1 the content of nickel and aluminium was 50.89 and 0.33 wt.%, whereas in the calculation for 0.6 wt.% aluminium the nickel was 50.62 wt.%. The other phases present showed little or no sensitivity to changes in the aluminium content although the matrix gamma phase did decrease at high aluminium content to make way for the increased fraction of the gamma prime phase.

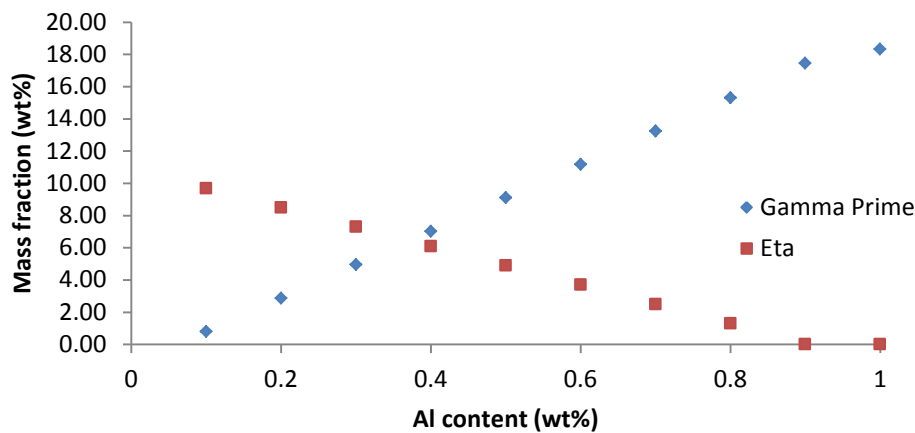


Figure 4.4: Predicted precipitation gamma prime and Eta phase with varying aluminium content (balanced against nickel)

Figure 4.4 shows the effect of aluminium content on the precipitation products present in Nimonic 263. The graph shows quite clearly that as the aluminium content increases then so does amount of gamma prime predicted to be present. In the reverse situation as the aluminium content goes down then so does the amount of the predicted gamma prime. The graph also shows that the precipitation of the gamma prime and Eta phase are clearly linked to each other with one preferentially precipitating in favour of the other. Finally, although the Eta phase is predicted in the equilibrium calculations it is well understood that this phase takes a long time to form and is not very representative of the early microstructure. The above calculation does, however, help to predict possible precipitation problems for low aluminium content areas within Nimonic 263 after long term exposure.

4.3.1 Thermodynamic non equilibrium calculations

Non-equilibrium solidification is often associated with more traditional processing routes such as casting or welding. This type of solidification can also occur in forged products although to a lesser extent. To model this type of solidification the Scheil method discussed in the experimental section is used.

Using a starting composition in Table 4.1 Scheil calculations were performed. Figure 4.5 describes how the mass of the liquid phase varies with temperature thus modelling the solidification of the liquid phase. The graph shows that solidification in Nimonic 263 occurs between 1370 and 1200°C. The large solidification temperature range will mean that the composition of the liquid phase will vary significantly as it solidifies under ‘Scheil’ conditions.

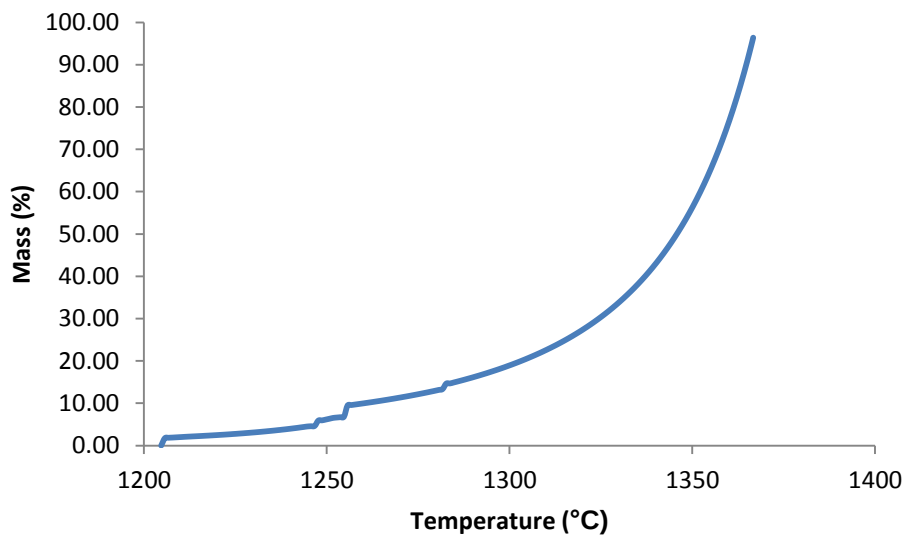


Figure 4.5: Solidification temperature range of liquid phase

Figure 4.6 shows the change in composition of the liquid phase with temperature, as it solidifies. In Figure 4.6 (a), nickel content can be seen to decrease from 0.52 at the start of solidification to 0.42 at the end of solidification. The same is true of cobalt decreasing from 0.19 at the start of solidification to 0.15 at the end. Chromium content decreased from 0.20 to 0.18 during solidification. Titanium content increased from 0.021 at the start of solidification to 0.079 at the end. Molybdenum content also showed significant change, 0.059 at the start of solidification with the composition of the final liquid found to contain a fraction of 0.164. This result indicates that Ti and Mo do not solidify at the same rate as other elements in the alloy, causing elevated levels in some of the last liquid phase to solidify. Figure 4.6 (b) is an

expanded version of Figure 4.6 (a) displaying mass fraction values up to 0.010, enabling the meaningful display of changes in aluminium, iron and carbon. The graph shows that iron preferentially solidifies due to the decrease in iron content during solidification from 0.0045 to 0.0023. The same is true of aluminium, decreasing from 0.0033 to 0.0005 throughout solidification; this decrease could prove significant due to the importance of aluminium when forming γ' .

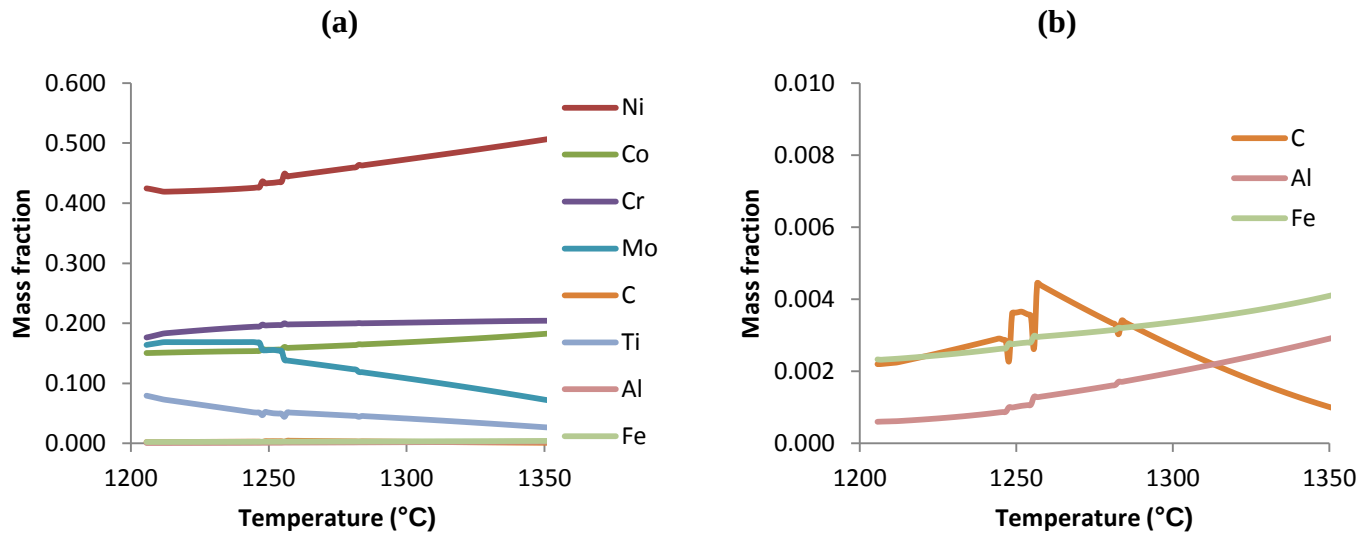


Figure 4.6: Change in composition of liquid phase during solidification (a) all phases and (b) expanded view to highlight Al, C and Fe

To model the effect of the chemical segregation in the liquid phase further calculations were carried out using the equilibrium method. The composition of the last liquid to form was used to get an idea of the two different precipitation extents. The segregated composition at this temperature is: 42.46 wt.% Ni, 15.05 wt.% Co, 17.64 wt.% Cr, 16.39 wt.% Mo, 0.22 wt.% C, 7.94 wt.% Ti, 0.06 wt.% Al and 0.23 wt.% Fe. Calculations were carried out as before, allowing for all phases and using the above composition. The phase prediction can be seen in Figure 4.7. The calculation allowing for all phases shows a large amount of Eta precipitation to be predicted within the segregated regions at a peak level of 38.7 wt.% at approximately 700°C. Attention should also be drawn to the relatively small amount of γ' predicted to form at 5.8 wt.% in comparison. Large amounts of the Mu phase are also calculated to form with 36.1 wt.% predicted to exist.

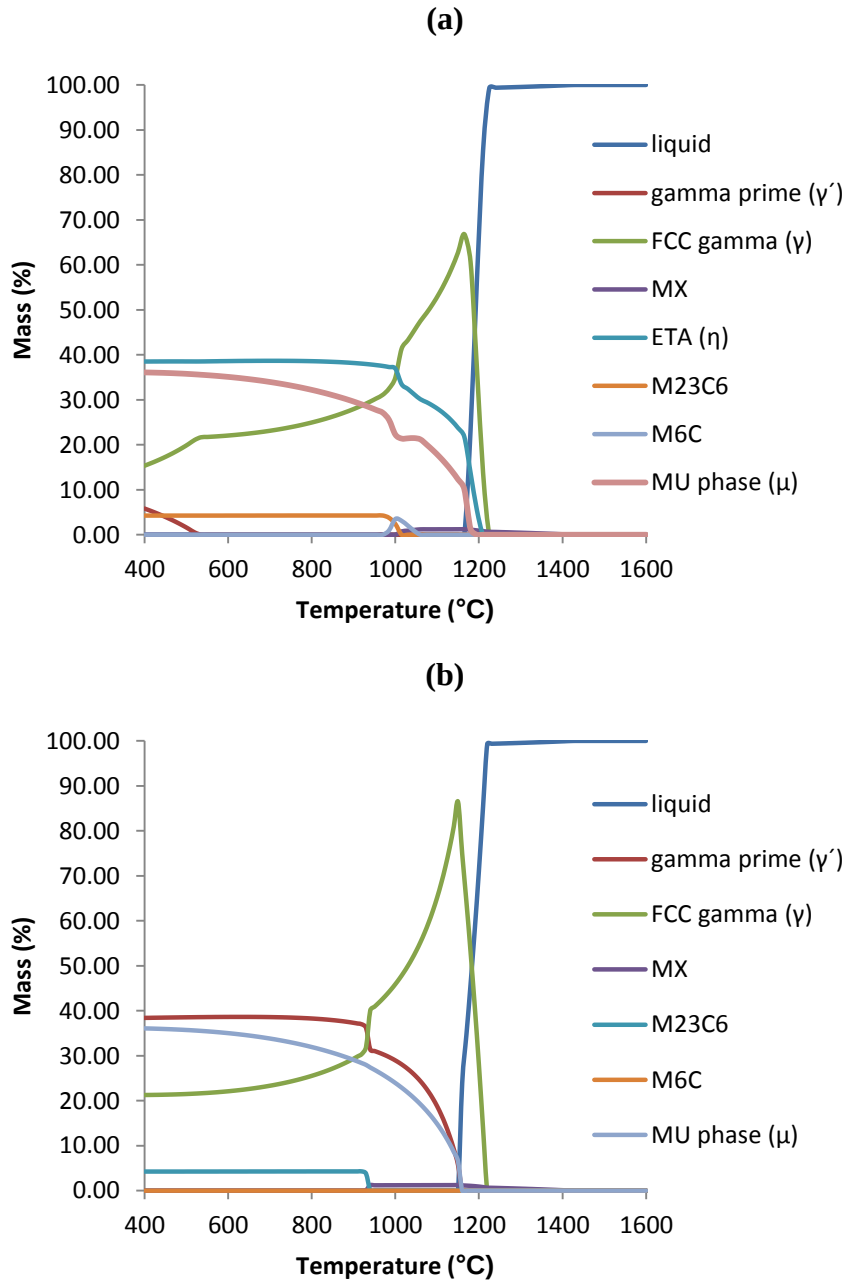


Figure 4.7: Predicted phases against temperature in equilibrium conditions for segregated region (a) allowing for all phases and (b) Eta phase suspended

The increase in Mu phase is likely to be due to the large increase in Mo content within the segregated regions. With the Eta phase suspended γ' would be expected to precipitate in large quantities. The calculation also showed an increase in the amount of MX and $M_{23}C_6$ predicted to occur at 1.2 and 4.3 wt.% respectively. It is again thought that banding of the MX phase will be observed throughout the samples microstructure due to their concentrated formation in segregated areas. The segregated composition also predicts the M_6C phase

which is not previously observed using the average composition. This phase is present at approximately 4.5 wt.% between the temperatures of 985 and 1045°C. To help explain the precipitation of M_6C phase, the calculation also shows a corresponding ‘bump’ of a similar mass to the M_6C phase across the same temperature range within the Mu phase.

Figure 4.7 (b) shows the prediction for segregated composition with the Eta phase suspended. The results shows that similarly to previous results suppression of the Eta phase increases the amount of γ' to be predicted from 5.81 wt.% in the calculation allowing for all phases to 38.41 wt.% in the Eta suspended calculation. The suspended calculation also predicts no M_6C phase to be present as a result the ‘bump’ in the prediction of Mu phase is no longer evident. $M_{23}C_6$ is also found to dissolve at a lower temperature 930°C compared to 1000°C in the calculation for all phases.

4.4 Hardness as a function of temperature

To evaluate the impact of pre-service heat treatments and ageing on the mechanical properties of Nimonic 263 a series of hardness tests were conducted. As covered in the experimental section hardness testing carried out used the Vickers method with a 10 kg load.

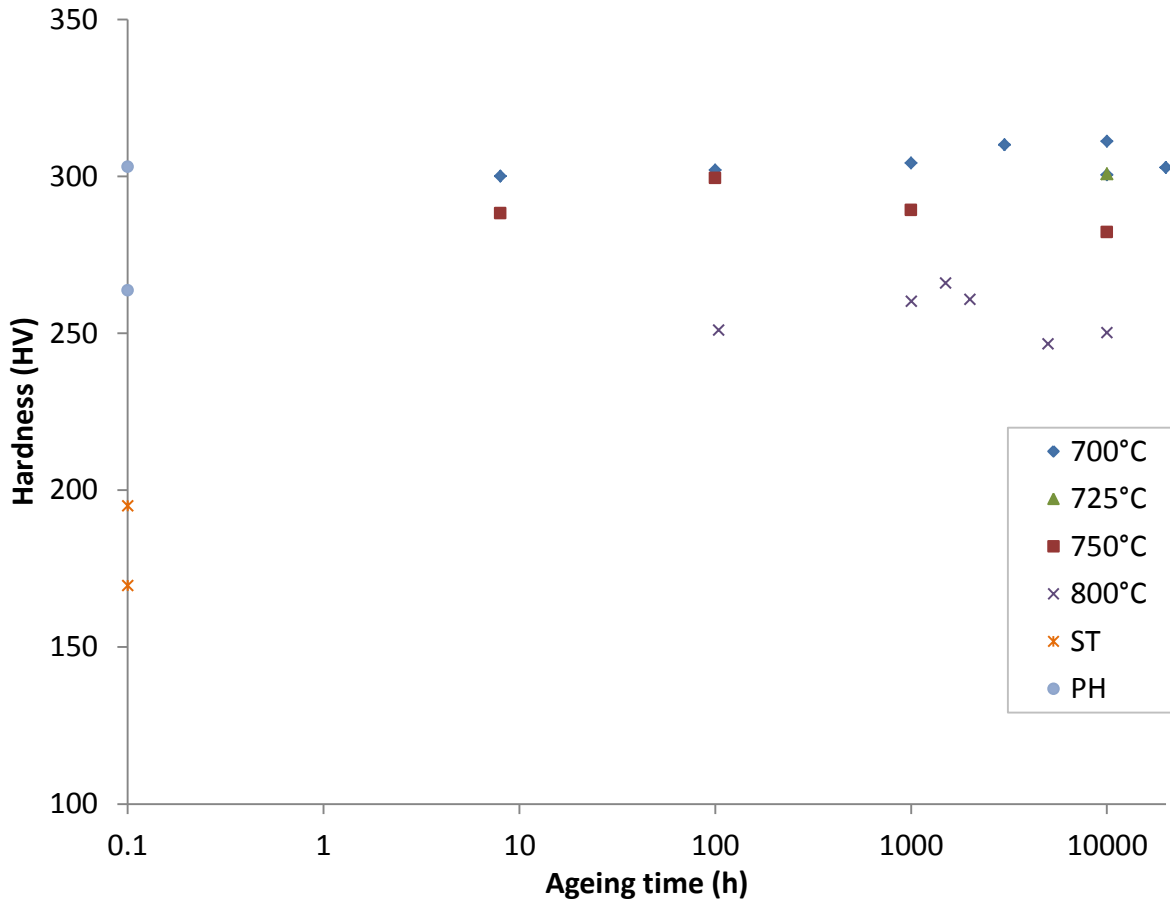


Figure 4.8: Plot showing hardness of pre-service conditions and against ageing temperature and time

The results from hardness testing are shown in Figure 4.8. The plotted hardness values are based on the average of 3-5 indents and the variation is negligible. In the solution treated condition Nimonic 263 has a hardness of approx 180 HV. The precipitation hardened samples can be seen to have hardened by approximately 100 HV from the solution treated condition. This increase was due to the precipitation of strengthening phases such as the gamma prime phase and grain boundary $M_{23}C_6$, which has formed during the 4 hour heat treatment at 800°C. The effect of ageing at a series of different temperatures was also evaluated. Ageing at 700°C can be seen to have had very little overall effect on the hardness of the alloy,

although a small and steady increase in hardness was recorded from ≈ 300 HV to 311 in the 10,000 h sample. The long term ageing results at 20,000 h shows the material to soften slightly to around 303 HV. Based on the profile of the curve it would be expected that the material hardness would further soften with more exposure albeit gradual. Ageing at 725 and 750°C show unchanged hardness properties in short term ageing, although the 10,000 hour samples were seen to soften to 301 and 282 HV respectively, representing a small decrease in hardness when compared to the 700°C aged sample. Ageing at 800°C showed a drop in hardness to 247 HV when aged for 5000 hours. After 10,000 hours ageing the hardness was recorded at 250 HV, meaning no further drop in hardness was observed.

4.5 Grain size and distribution

Optical microscopy of the samples showed that there was a significant number of twins present with a bimodal grain size of large equiaxed grains and banded regions of smaller grains; an example optical micrograph is shown in Figure 4.9. The banded regions are thought to form during extrusion. Grain sizes were determined using a linear intercept method, and increased from 85 μm in the solution treated sample to 109 μm in the long term ageing treatment at 700°C representing a total increase of 24 μm , as shown in Figure 4.10.

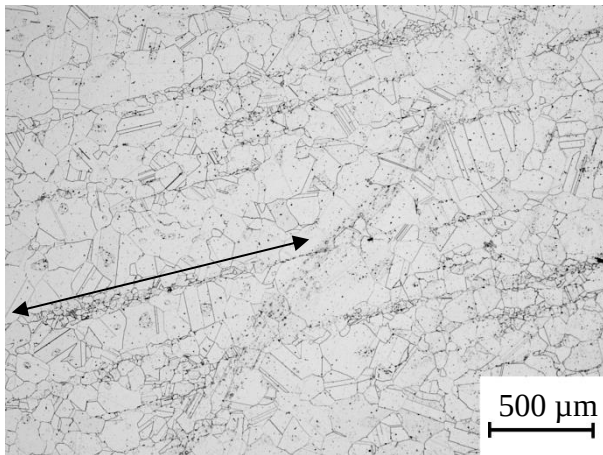


Figure 4.9: Optical image of solution treated sample showing the bimodal grain size distribution present in 263 (line highlighting one of the banded regions and its direction)

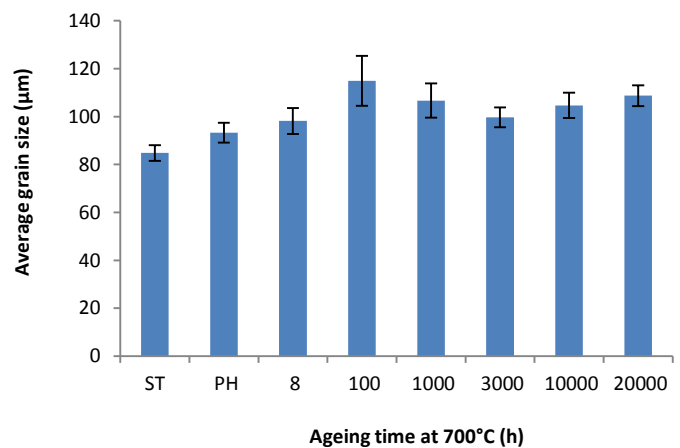


Figure 4.10: Plot indicating the change in average grain size with ageing at 700°C

Figures 4.11(a) and (b) show dark field optical microscope images in which it can be seen that the banded regions are more visible and possible to quantify. The banded regions in several images were traced and analysed in terms of their area fraction using image analysis software. After analysis, a clear reduction in the area fraction of the banded regions between the precipitation hardened and the long term aged samples were noted, from 5 % in the precipitation hardened sample down to 2 % in the long term aged sample. Although a slight increase in the overall grain size was observed, the two dark field micrographs show that the bulk grain size is still large and little change has occurred. The reduction in area fraction of banded grains and the overall increase in bulk grain size suggest that coarsening of the banded regions may have occurred. At higher temperatures such as 750 and 800°C very little change was observed in bulk grain size. Observations also showed that the banded regions reduced similarly to results in the 700°C sample set.

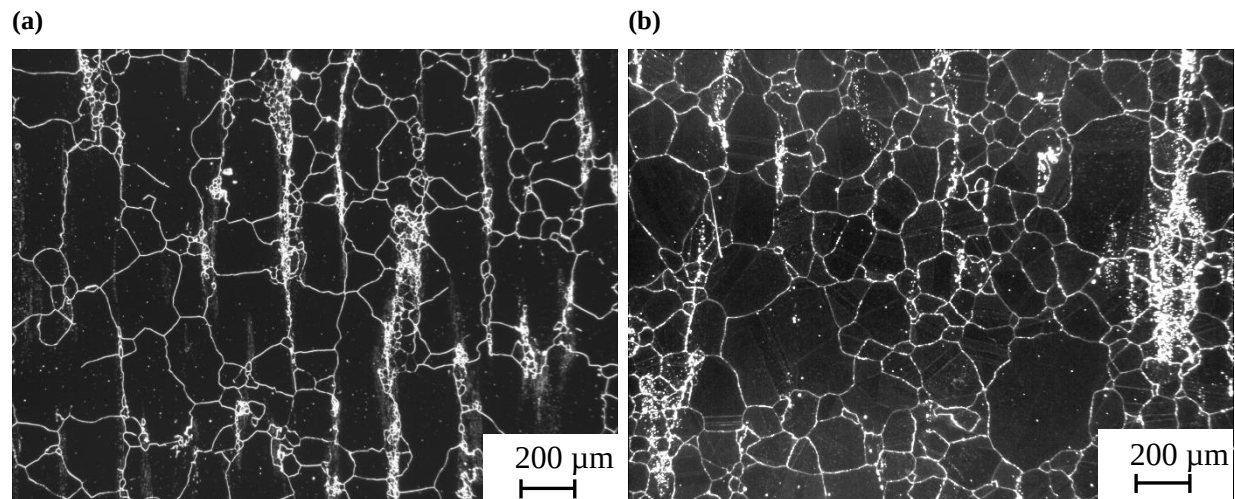


Figure 4.11: (a) Dark field image of sample having undergone standard heat treatment of 1150°C for 2 h and 800°C for 4 h, (b) Dark field image of sample having undergone standard heat treatment, then 20,000h of ageing at 700°C

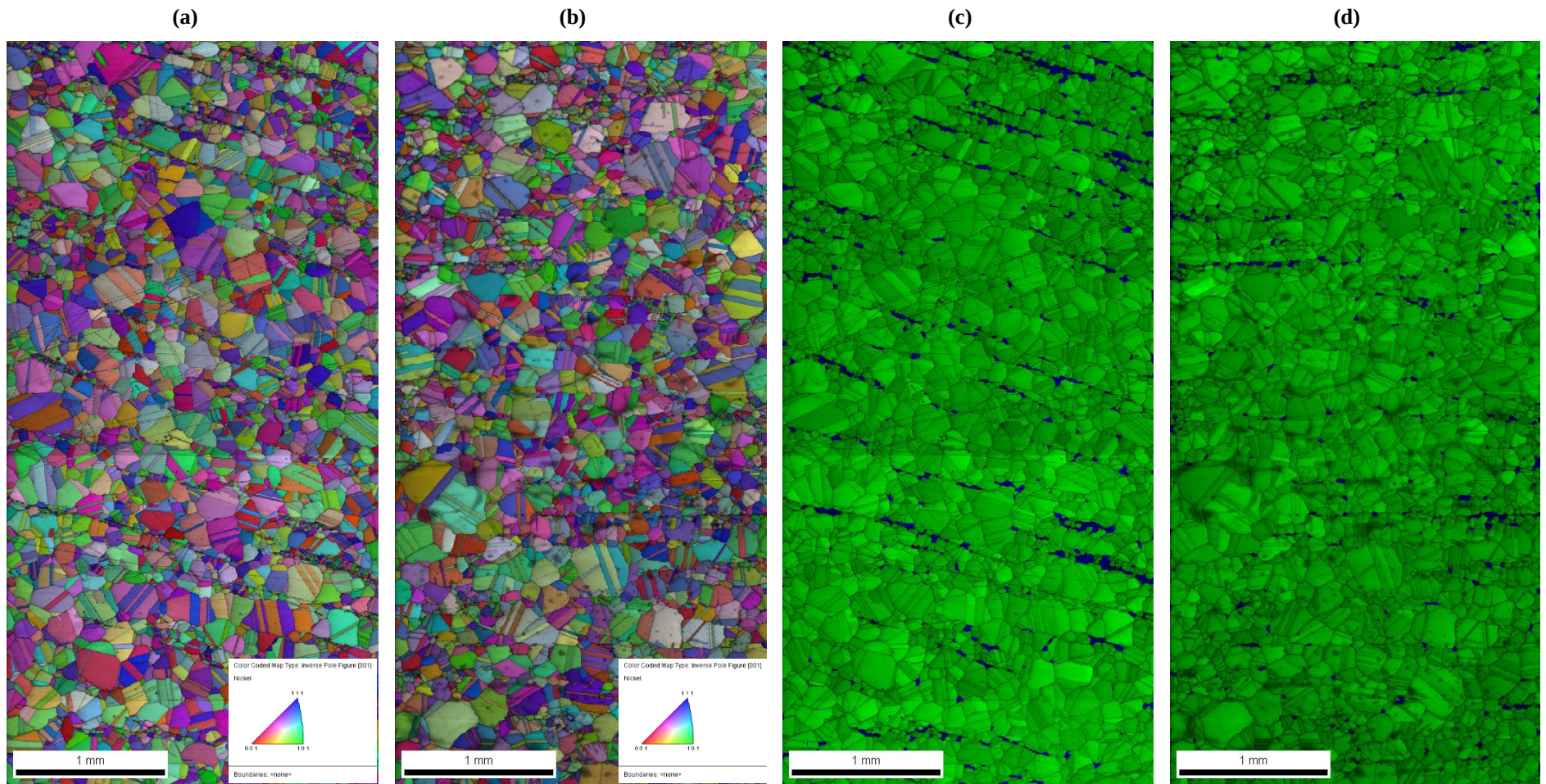


Figure 4.12: (a) IPF (Inverse Pole Figure) maps from EBSD scan for (a) solution treated sample, (b) long term aged sample, (c) and (d) show the isolation of grains below 35 μm in blue and those above in green for both the solution treated and long term aged samples respectively

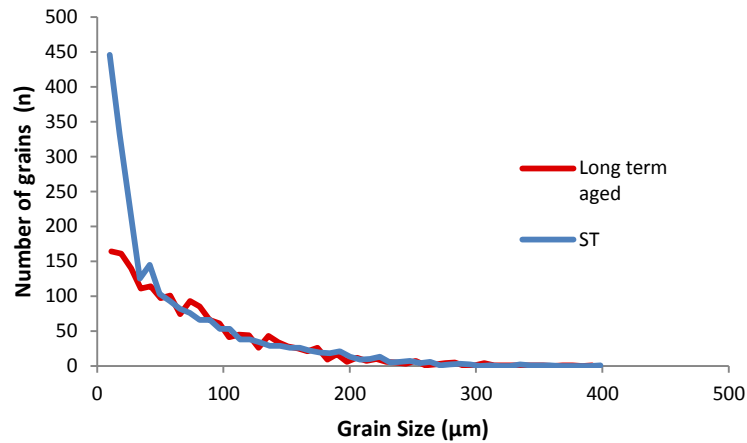


Figure 4.13: Plot showing the grain size distribution of both the solution treated and the 700°C sample aged for 20,000 h

EBS D scans were carried out to further investigate the coarsening of the banded regions in both the solution treated and the 700°C long term aged sample. The IPF maps showing the crystallographic orientation of the grains in each sample can be seen in Figures 4.12(a) and (b). It is possible to observe the banded grains in the IPF maps; however, this was further highlighted using the analysis software to isolate the observed grains into two groups; those above 35 μm and those below. Using these constraints; all grains below 35 μm are coloured blue and any above in green, the resultant maps are shown in Figures 4.12(c) and (d). The two maps show the banded regions to reduce after long term ageing, confirming the work carried out using dark field optical microscopy. Figure 4.13 shows the grain size distribution for both samples, it can be seen that both show a similar distribution, however, there are an increased number of smaller grains in the solution treated sample indicative of a bimodal grain size distribution.

4.6 MX precipitation

Large precipitates were observed throughout the alloy, examples of which can be seen in Figures 4.14, 4.15, 4.16 and 4.17. The precipitates can be characterised into three groups: large dark precipitates, lighter banded precipitates and bands of sub-micron spherical precipitates. The large dark precipitates, shown in Figure 4.14, 4.16 and 4.17 were observed to form individually and as stringers both in the matrix and along grain boundaries. Experimental observations indicated that these large, dark precipitates were present as both elongated and blocky morphologies at sizes up to 30 μm . EDX analysis of these precipitates confirmed them to be Ti rich with small amount of Mo, as shown in Table 4.2 and EDX maps contained in Figures 4.14, 4.15 and 4.17. The precipitates appearing lighter compared to the Ti rich are also present throughout the alloy, although predominantly concentrated along grain boundary positions and especially in the banded regions of smaller grains. Examples of these precipitates can be seen in Figures 4.14 and 4.15. The precipitates were observed to form as elongated precipitates aligned in one direction generally in sizes between 2 and 10 μm . EDX analysis of these precipitates confirmed them to be Ti-Mo rich as shown in Table 4.2 and EDX maps contained in Figure 4.14 and 4.15. The submicron particles were observed to form in bands at close proximity to the lighter precipitates, and EDX analysis showed them to have the similar chemical compositions.

Table 4.2: MX chemical composition (excluding C/N)

Precipitate	Ti rich		Ti-Mo rich*	
	Ti (wt.%)	Mo (wt.%)	Ti (wt.%)	Mo (wt.%)
ST	98.3	1.7	61.7	38.3
PH	97.4	2.6	64.3	35.7
20,000h aged at 700°C	94.7	5.3	63.8	36.3

*Composition for both lighter precipitates and submicron sized spherical precipitates

The chemical compositions displayed in Table 4.2 are typical of MX precipitates: one Ti rich and the other Ti-Mo rich. The Ti rich precipitates appear darker in contrast to the Ti-Mo rich in both SE and backscatter modes making it possible to distinguish between the two without the use of EDX techniques. Imaging carried out in backscatter mode also offers a better contrast between precipitates and the matrix, which proved useful when carrying out any image analysis on the MX precipitates.

Figure 4.14 shows both the large, dark Ti rich and the lighter Ti-Mo rich phases, in addition to the associated EDX maps for elements: Mo, Ti, C and Ni. These maps clearly show that

the dark precipitates are titanium rich and the grey precipitates are rich in both titanium and molybdenum. Figure 4.15 shows an image and the corresponding EDX maps of a Ti-Mo rich precipitate and band of finely dispersed, spherical Ti-Mo rich precipitates. The area around the Ti-Mo rich precipitate can be seen to be denuded of submicron particles.

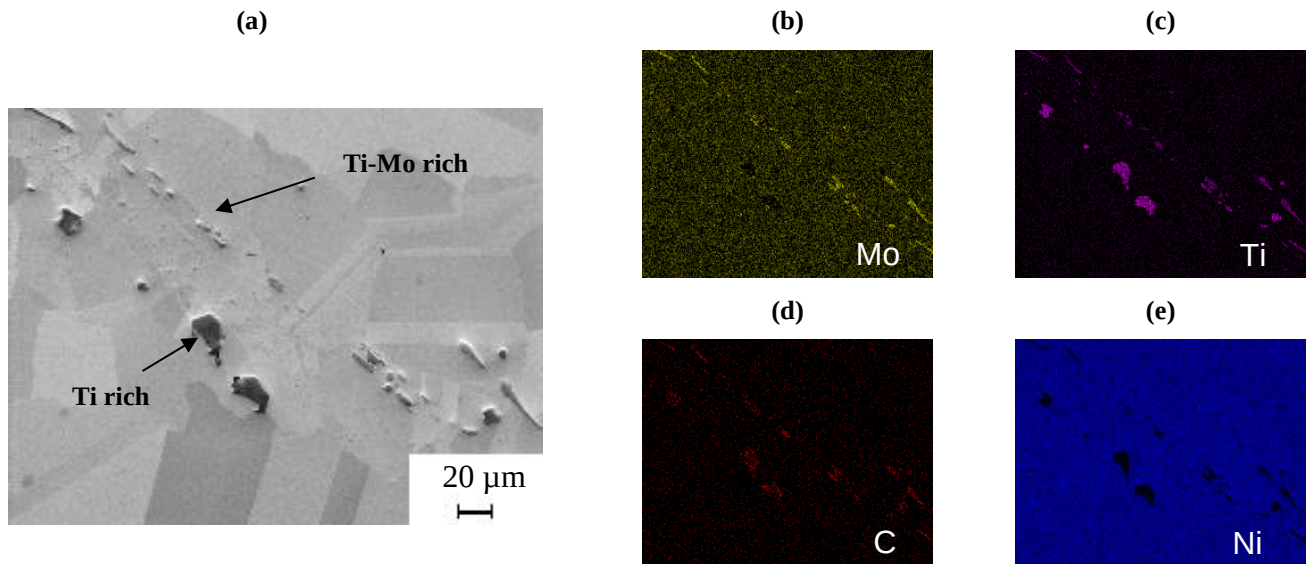


Figure 4.14: (a) An SE image of the solution treated sample showing both Ti rich and Ti-Mo rich MX precipitates, (b) Mo, (c) Ti, (d) C and (e) Ni EDX maps

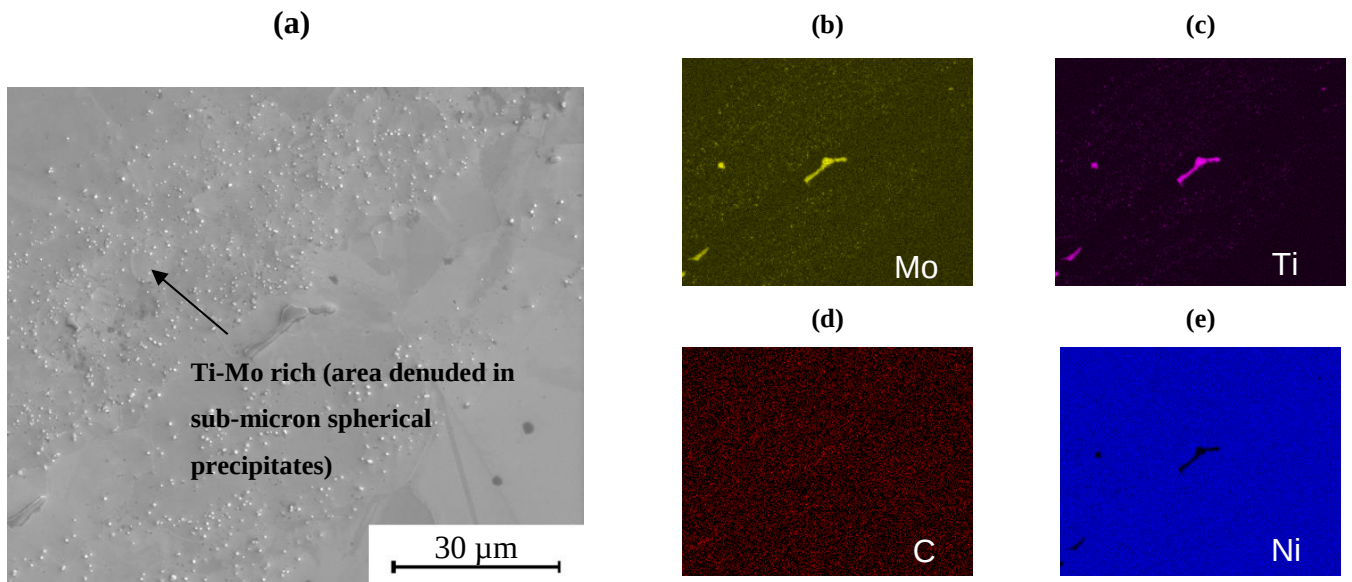


Figure 4.15: (a) A secondary electron image of the precipitation hardened sample showing a large Ti-Mo rich particle and a band of finely dispersed Ti-Mo rich spherical particles, (b) Mo EDS map, (c) Ti EDS map, (d) C EDS map and (e) Ni EDS map

As seen in Table 4.2, the chemical composition of both particle types were studied in samples subjected to different heat treatments. The variation in the Ti rich MX results show a small

increase in Mo content from 1.7 wt.% in the solution treated sample to 5.3 wt.% in the long term aged sample. The Ti-Mo rich MX was found to stay at a relatively constant composition, with very little change observed. It should be noted that only one variant of MX, predominantly TiX, was predicted by the thermodynamic calculations, whereas a stable carbonitride appears to exist containing some Mo substituted for Ti.

It was noted that different compositions could be detected in the same precipitate depending on the placement of the spot. Further analysis showed that many of the larger Ti rich precipitates contained areas rich in molybdenum which exhibited a different contrast, as shown in Figure 4.16.

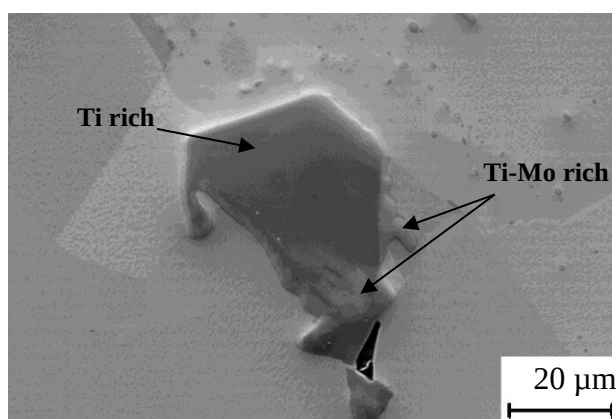


Figure 4.16: SE image of the solution treated sample showing the 'marbled' effect in MX precipitate as a result of Ti-Mo rich regions

The particle size and distribution of the bulk MX precipitates were determined using backscatter micrographs sampled at random from each specimen. The size and distribution of MX precipitates were calculated using image analysis software which determines the size of each precipitate, before grouping each precipitate into a certain size range e.g. 2 – 4 μm. Results indicated that the average MX size increases from 3.9 μm in the solution treated sample to 4.6 μm in the sample aged at 700°C for 20,000 h, a resultant increase of 0.7 μm which is not deemed statistically significant. The bulk MX particle size distribution also indicated that there were an increased number of smaller precipitates in the solution treated sample, however, overall there was very little change between the samples.

At higher ageing temperatures such as 750 and 800°C very little change in terms of chemistry and precipitate size were observed. The analysed EDX spectra showed the chemistry across the 800°C sample to be in line with that recorded in the 700°C ageing temperature. Both the dark Ti rich and the lighter Ti-Mo rich precipitates are still present although the Ti-Mo rich were observed to a lesser degree. The Ti-Mo rich submicron spherical phase was not

observed in the sample aged for 10,000 h at 800°C, however they were present in the shorter ageing temperature of 100 h. It is thought the submicron spherical Ti-Mo dissolve as part of the MX coarsening process. Figure 4.17 shows the two different chemistries of MX precipitates along a grain boundary surrounded by the titanium rich Eta phase in a long term aged sample at 800°C.

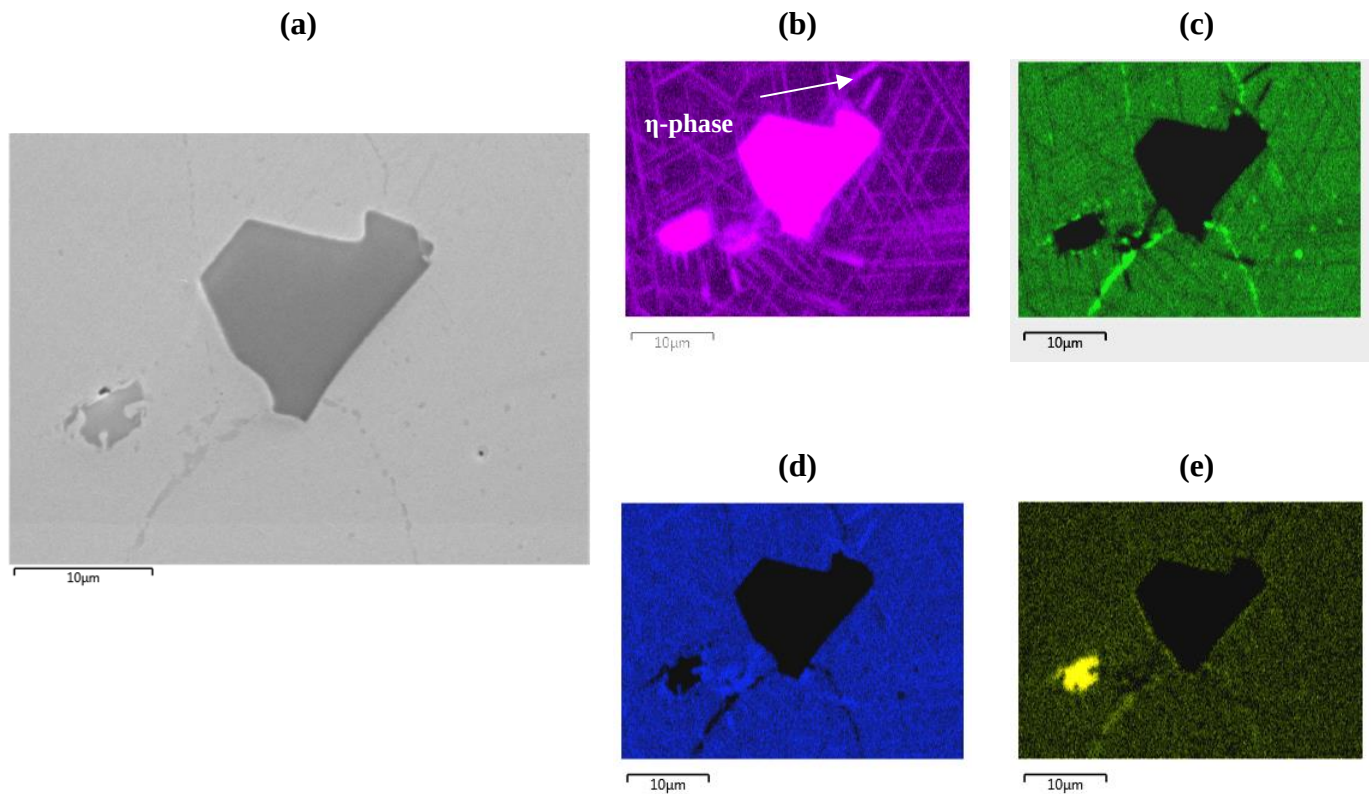


Figure 4.17: (a) An SE image of the sample aged at 800°C aged for 10,000 h showing Ti rich, Ti-Mo rich MX precipitates, $M_{23}C_6$ grain boundary precipitates and the Eta phase (b)Ti, (c) Cr, (d) Ni and (e) Mo EDX maps

4.7 Grain boundary precipitates

To fully characterise the isothermally aged wrought Nimonic 263 it was also important to consider the evolution of the grain boundary precipitates. Grain boundary precipitation was characterised across a number of different samples and ageing temperatures. To do this a combination of electropolished thin foils, carbon extraction replicas and site-specific thin foils were analysed. Site-specific thin foils were produced using the dual beam method, covered in the experimental section 3.9, from the solution treated, precipitation hardened and the long term aged sample of 20,000 h from the 700°C sample set. These preliminary samples were analysed to initially establish the presence of any grain boundary precipitates, and secondly to obtain information on their size and composition.

A number of samples in the solution treated condition were examined in this work, and the majority showed no grain boundary precipitation, as shown in Figure 4.18(a). However, one solution treated sample did present grain boundary precipitates of approximately 100 nm in size, possibly due to differences in cooling rate across the thick section pipe. The precipitation hardened samples contained grain boundary precipitates, at approximately 100 nm in size, as shown in Figure 4.18(b). Analysis of the long term aged sample at 700°C shown in Figure 4.18(c) indicated the presence of larger grain boundary precipitates in the range 200 to 300 nm. Observations from analysis in the TEM therefore indicated that the grain boundary precipitates coarsened during ageing.

Elemental analysis using the EDX technique was carried out on the grain boundary precipitates present in the different samples, and the results are summarised in Figure 4.18(d). The precipitates were extracted using the carbon extraction replica technique and due to this the effect of matrix pick up is reduced. The Cr content of the precipitates was noted to increase slightly when aged at 700°C, with the 8 hour aged sample increasing from 76 wt.% to 79 wt.% after ageing for 20,000 hours. This slight increase is not statistically significant and shows the precipitate to be chemically stable with an increase in thermal exposure. Elemental analysis of the long term aged samples showed the precipitate chemistry to remain relatively stable even after long term ageing at 700°C for 20,000 hours. The average Molybdenum, Cobalt and Nickel contents were detected to be 14.5, 3.6 and 4.4 wt.% respectively. The same analysis was carried out on 750°C sample set with the composition showing little change; containing Chromium, Molybdenum, Cobalt and Nickel at 77.8, 14.6, 4.1 and 3.5 wt.% respectively. Even at the much higher ageing temperature of 800°C the grain boundary $M_{23}C_6$ carbides remained chemically stable. This can be seen from the graph shown in Figure 4.19 (c) showing the change in chemistry against ageing time at 800°C.

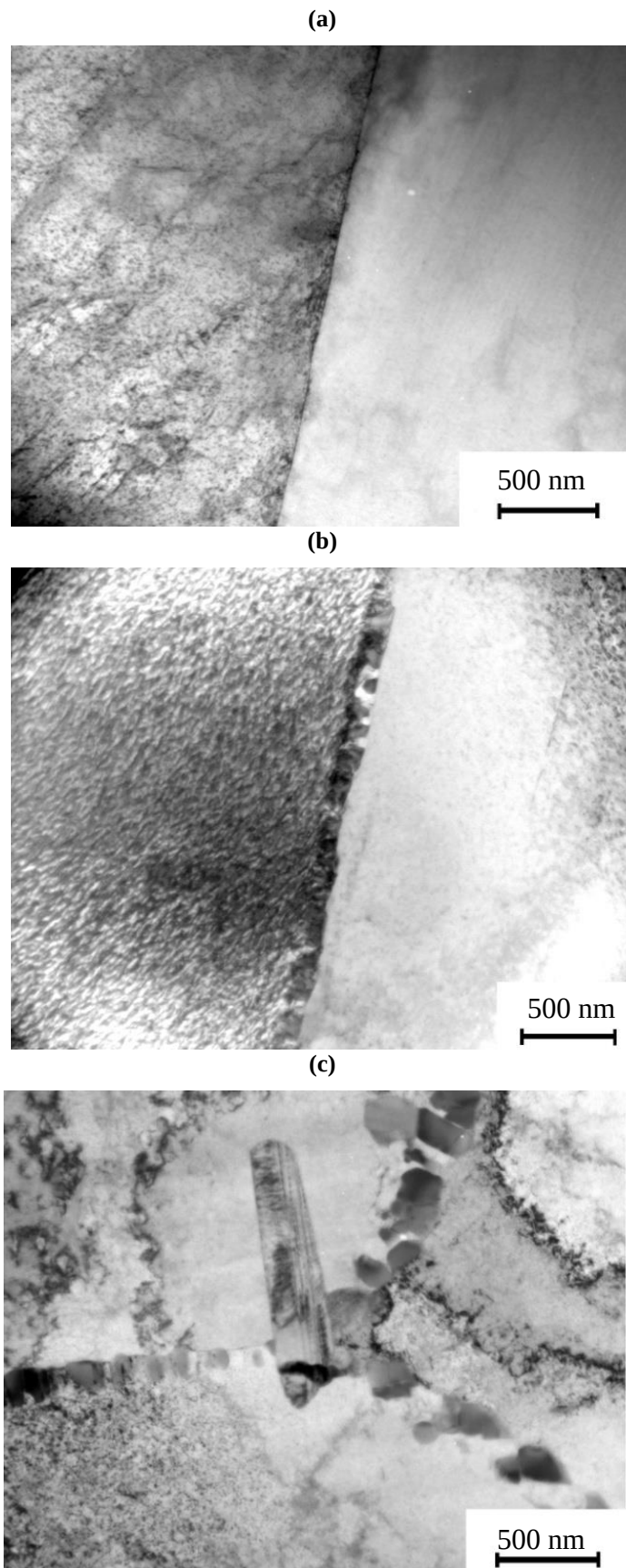


Figure 4.18: Transmission electron micrographs showing (a) Solution treated sample showing no GB precipitation, (b) Precipitation hardened samples showing continuous precipitation of GB particles, (c) Long term aged sample at 700°C showing both GB carbides and a large angular precipitate

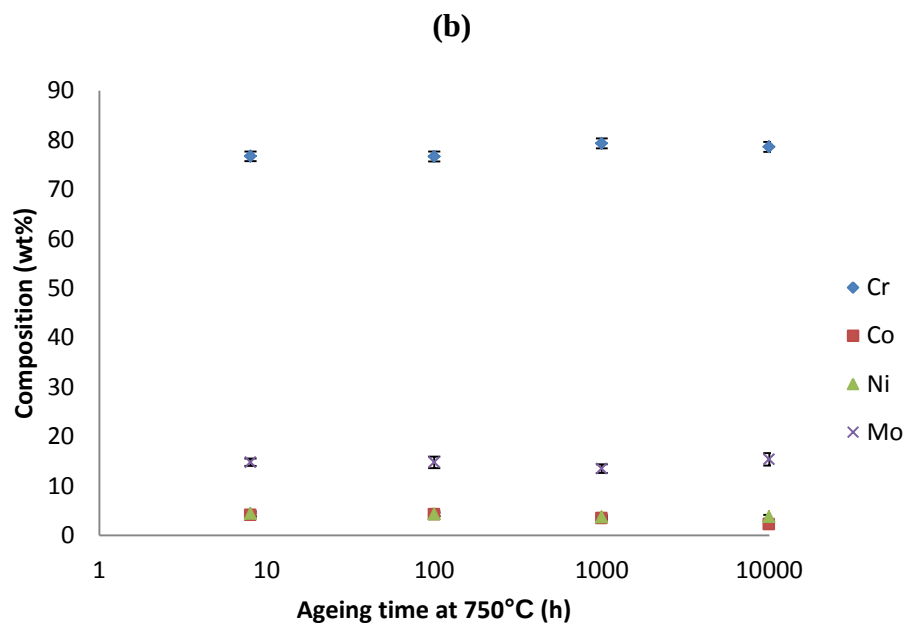
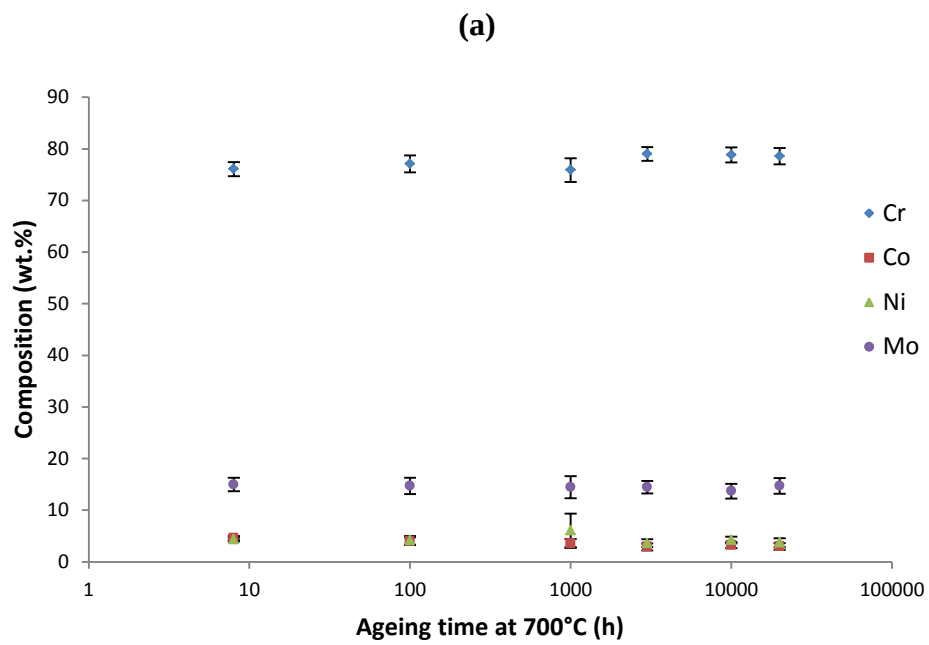


Figure 4.19: Chart showing the compositional change of the GB precipitates in (a) 700°C sample set and (b) 750°C sample set

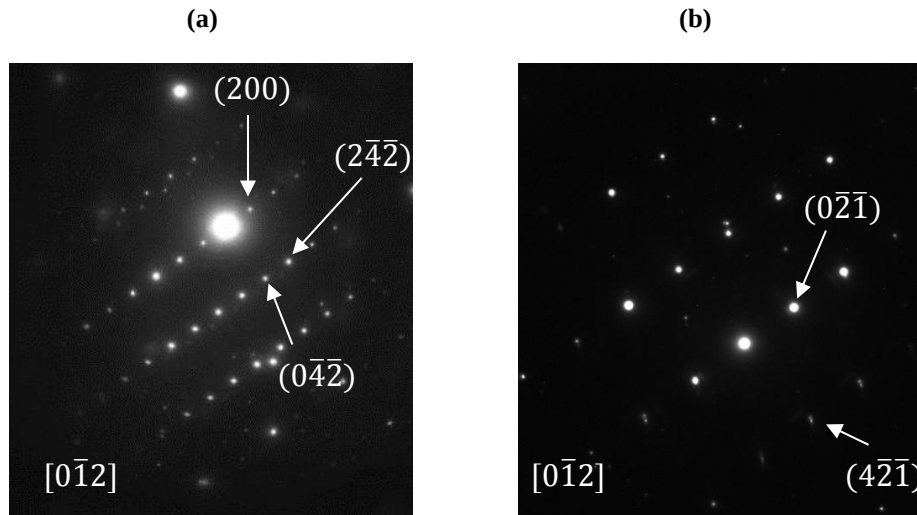


Figure 4.20 Diffraction pattern from (a) grain boundary precipitate in the precipitation hardened sample, (b) larger, elongated angular precipitate in long term aged sample aged for 20,000 h at 700°C

Selected area electron diffraction was carried out in the TEM in order to identify the particles. The diffraction pattern shown in Figure 4.20(a) was consistent with the crystal structure (face centred cubic) and lattice parameter (10.621 Å) of $M_{23}C_6$. Therefore, from the chemical compositions, thermodynamic predictions and electron diffraction, the grain boundary particles were identified as $M_{23}C_6$.

In addition to the grain boundary precipitates, the presence of isolated large, elongated angular precipitates about 1 µm in length, mainly associated with the grain boundaries, was noted in the sample aged for 20,000 h at 700°C. EDX analysis indicated that the composition of these particles was ~69 wt.% Ni and 14 wt.% Ti with small amounts of Al, Cr, Co and Mo substitution. Selected area electron diffraction was also carried out on these particle types, as shown in Figure 4.20(b). The combination of particle chemistry, crystallographic information^[60] and thermodynamic calculations indicated that these particles were the η phase, which was therefore able to form after very long ageing times within the matrix. It has been suggested^[7] that Eta can be detrimental to the mechanical strength of Nimonic 263, and can form at the expense of gamma prime. It was noted that there is a precipitate denuded zone around the η phase particles, consistent with a synergistic relationship between η and gamma prime.

4.8 Gamma prime precipitation and coarsening

The gamma prime phase is the principle strengthening phase present in the majority of superalloys, and this is the case in Nimonic 263. It is therefore important that the presence and evolution of this phase be fully characterised when exposed to a range of different conditions, in the case of this chapter, isothermal ageing. As with the other sections in this chapter the work will focus around four main sample sets, the first being pre heat treatment such as solution treatment and the precipitation hardened sample. The other three are the samples sets aged at the following temperatures 700, 750 and 800°C. As the pre heat treatment for Nimonic 263 does not change between the different isothermal ageing temperatures these results will be discussed along with the 700°C sample set. The gamma prime phase was studied using both thin foils in conjunction with the TEM and solid etched samples using the FEGSEM.

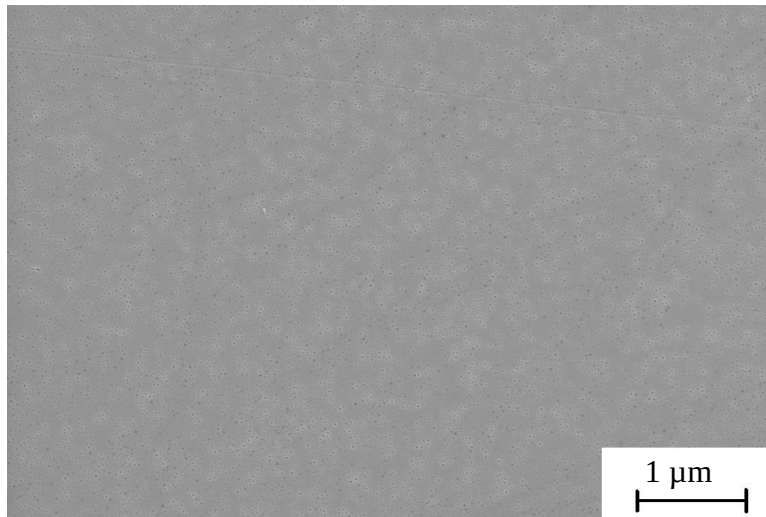
In the thermodynamic calculations covered earlier in this chapter significant work was carried out looking into the precipitation of the strengthening phase gamma prime. The gamma prime phase with a composition from thermodynamic predictions similar to the stoichiometry $\text{Ni}_3(\text{Al,Ti})$ is expected to precipitate out at around 800°C.

The gamma prime phase was initially characterised by etching samples using Fry's reagent, this etchant preferentially dissolves the gamma prime phase leaving holes with which to image. Composition of Fry's reagent is as follows; cuprous chloride, CuCl 200g. Hydrochloric acid conc 1 litre. Water, 1 litre. Once etched it is possible to observe the very fine precipitates within the bulk of the matrix in the different samples. Using the FEGSEM to image these holes enables the microstructural evolution of the gamma prime phase to be characterised in terms of both its size and distribution. Representative micrographs showing fine scale precipitation are shown in Figures 4.21(a – e). No gamma prime precipitates were observed in the solution treated sample, or if present they were too small to be detected. However, fine precipitates, assumed to be gamma prime, were detected in the precipitation hardened sample and samples aged at 700°C. The micrographs presented in Figure 4.21 show that there is significant coarsening of these particles with increasing ageing time.

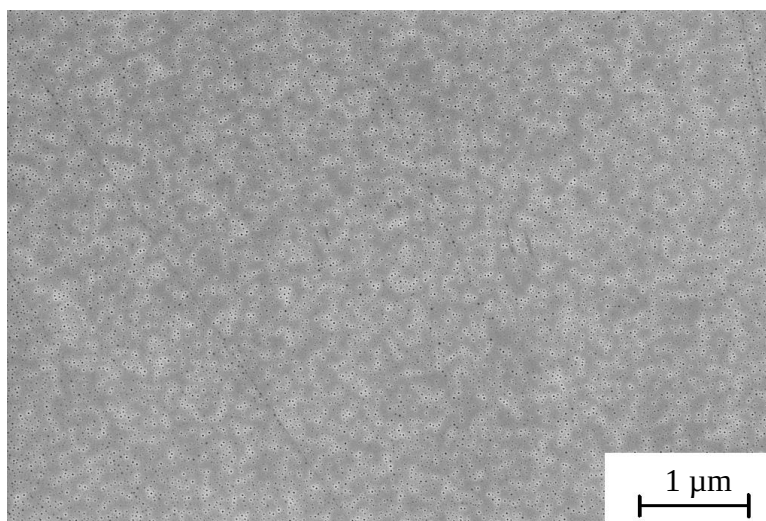
The coarsening behaviour of the fine particle distribution has been quantified by investigating the average size and distribution of the gamma prime precipitates in each sample. Image analysis software was used to analyse ~10 micrographs from each sample condition. A significant number of particles were considered in each sample condition, typically over 10,000, ensuring good statistical significance in the measurements. The results for the short

term aged samples, displayed in Figure 4.22(a) as the number of particles within a particular size range, show a relatively narrow distribution, as would be expected for newly formed precipitates. The average particle sizes in the short term aged samples were: 9.8 nm in the precipitation hardened sample, 11.4 nm after 8 h, 11.5 nm after 100 h and 15.2 nm after ageing for 1000 hours.

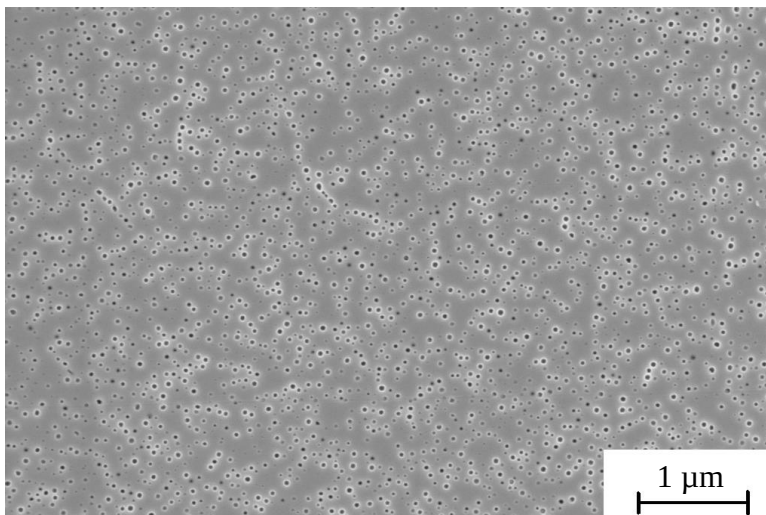
(a)



(b)



(c)



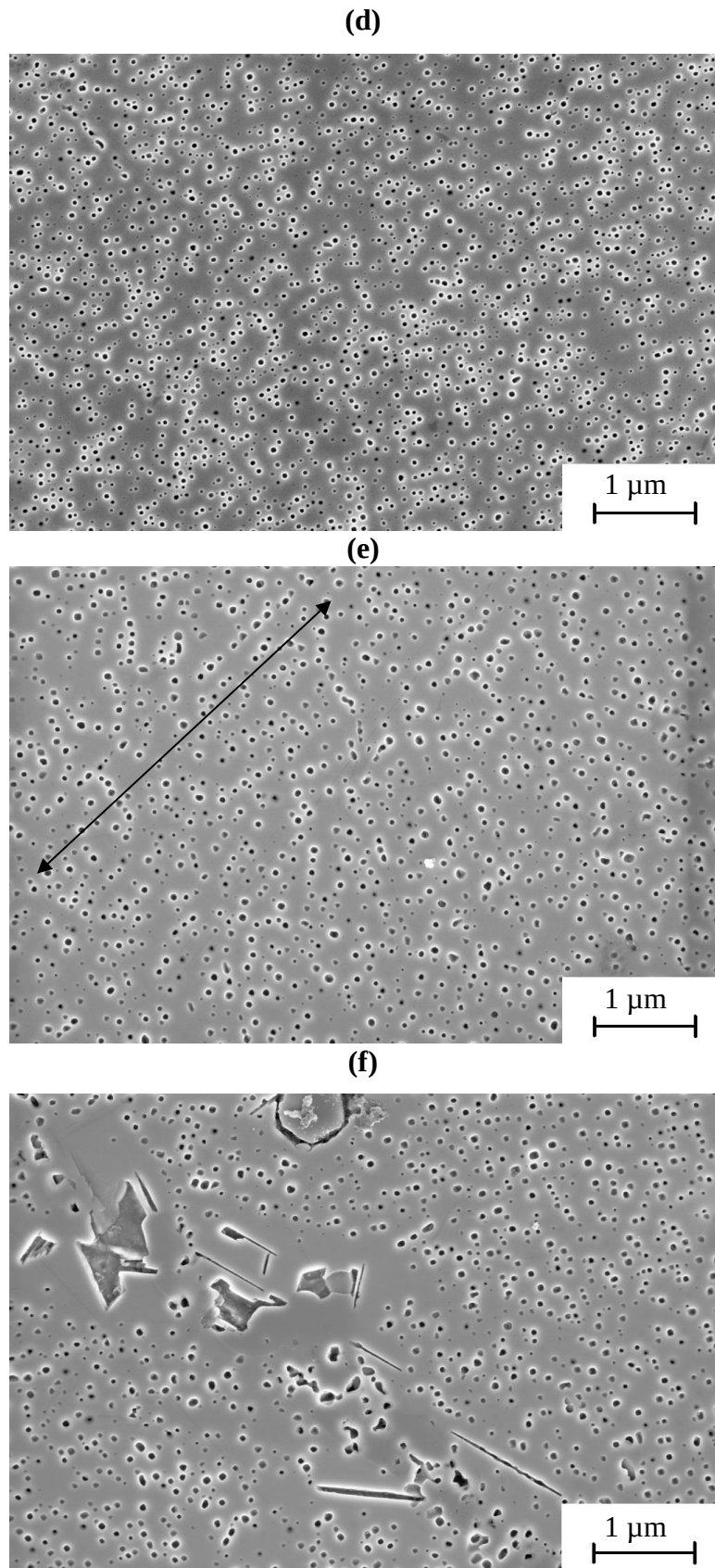


Figure 4.21: Micrographs showing gamma prime taken at the same magnification in (a) Precipitation hardened sample, (b) Aged at 700°C for 100 h, (c) Aged at 700°C for 3000 h (d) Aged at 700°C for 10000 h, (e) Aged at 700°C for 20000 h and (f) Aged at 700°C for 20000 h showing extensive precipitation along the grain boundaries, in addition to the gamma prime particles within the matrix

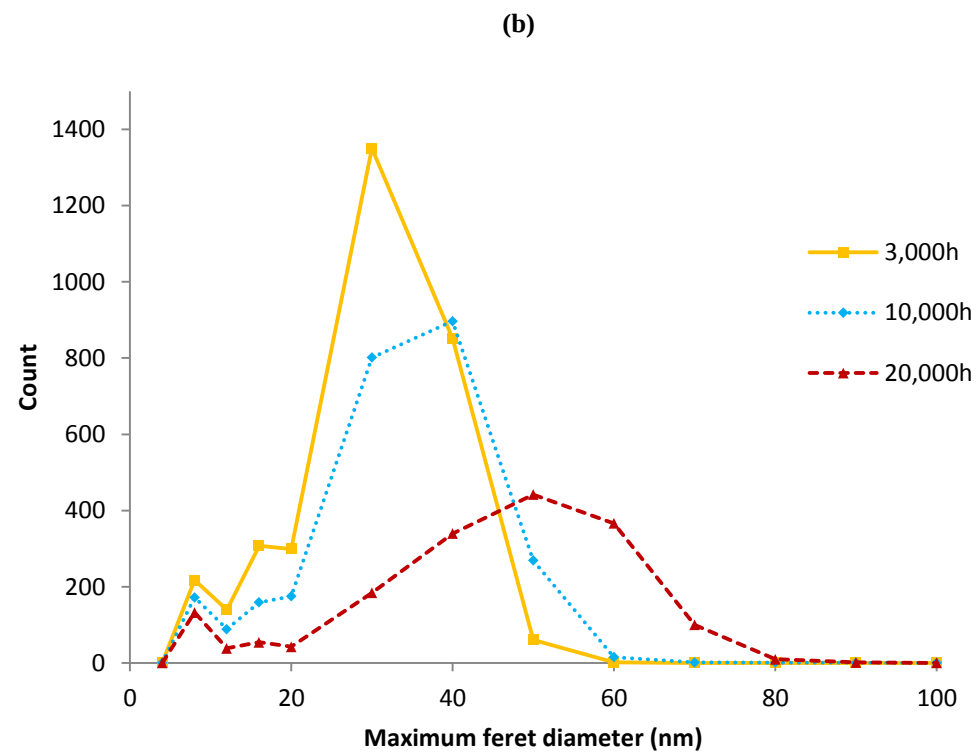
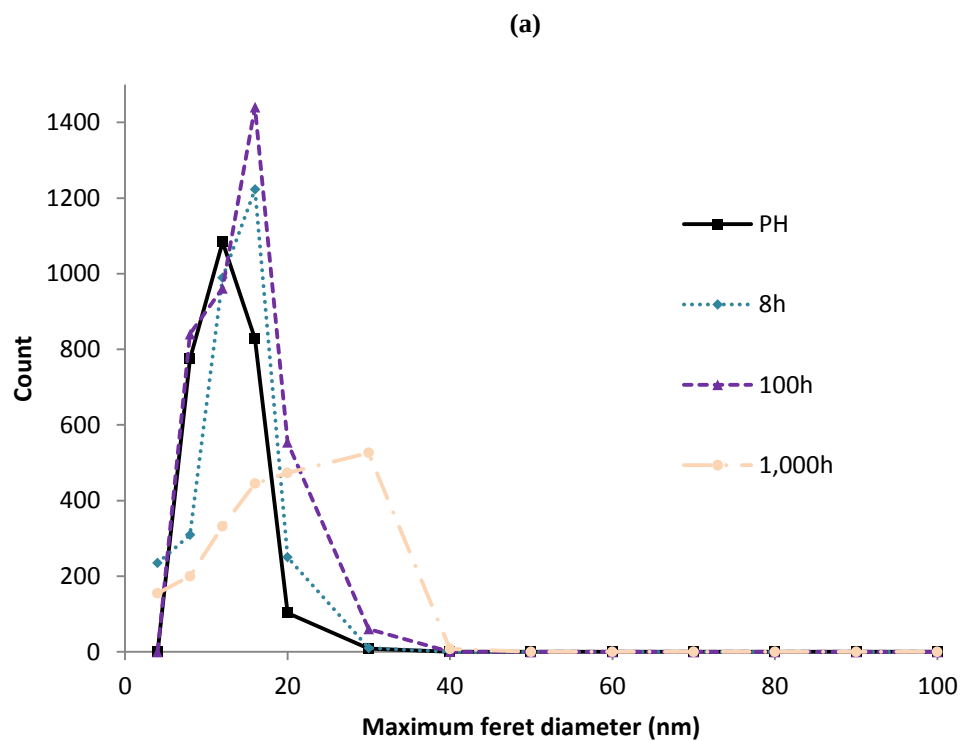


Figure 4.22: Particle size distribution of (a) short term aged samples (b) Long term aged samples

Figure 4.22(b) shows the particle size distribution of the long term aged samples. As expected, these distributions are much broader than the short term ageing heat treatments. The average particle sizes in the long term aged samples are: 24.6 nm in the 3000 hour aged, 28.2 nm in the 10000 hour aged and 39.2 nm in the 20000 hour aged. The average particle size was based 5 – 10 images depending on the number of precipitates in each image. The average particle sizes for all samples are plotted in Figure 4.23(a) as a function of ageing time at 700°C. Figure 4.23(b) further plots the average particle size as a function of the cubic root of time for comparison with standard particle coarsening theory. It can be seen that an approximately linear fit is indeed observed, and the steeper gradient in the 750 and 800°C sample sets indicate a faster rate of coarsening at higher temperatures.

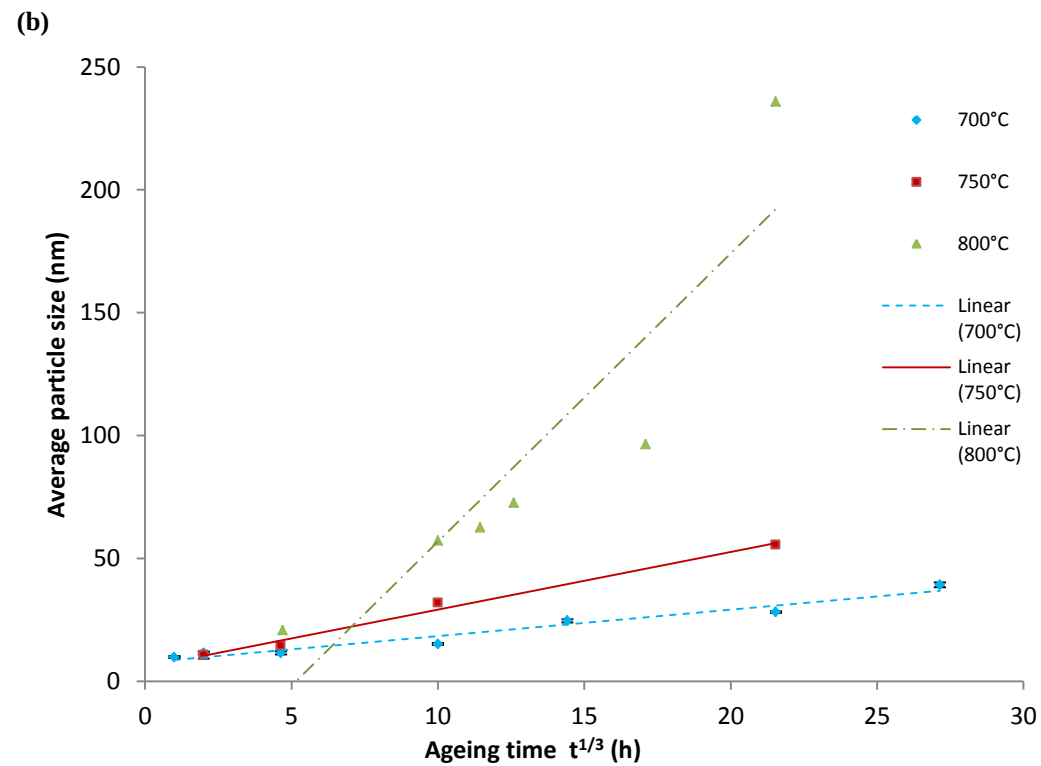
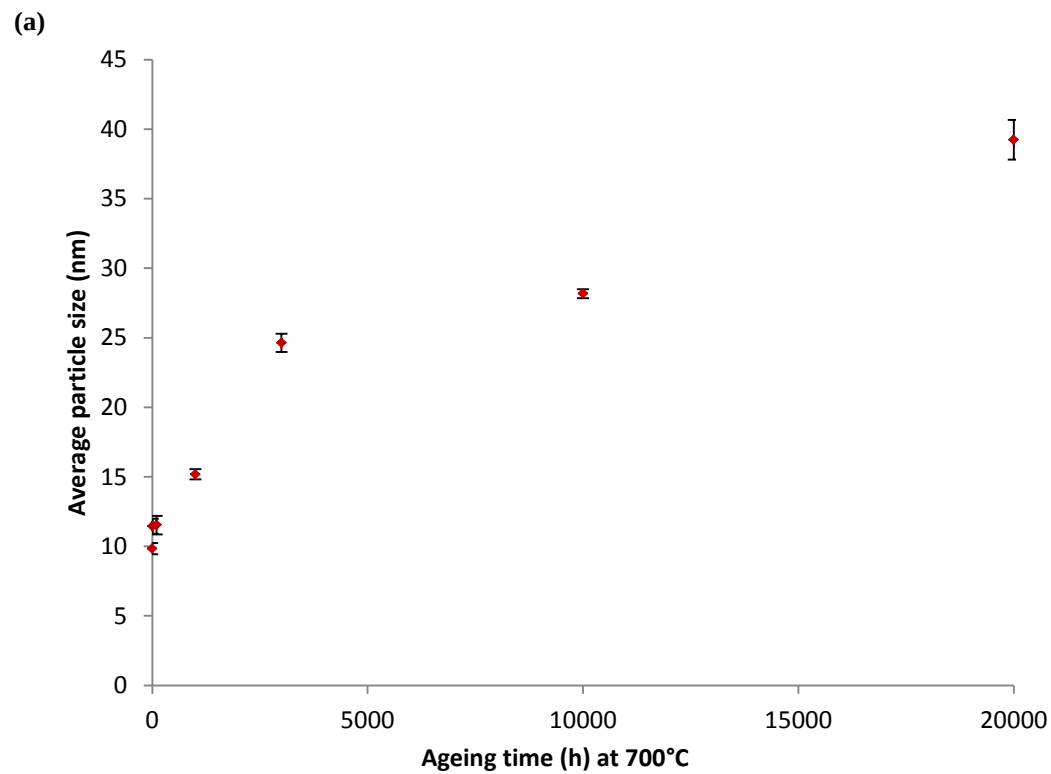


Figure 4.23: (a) Average particle size against ageing time for 700°C sample set, (b) average particle size against ageing time^{1/3} for 700, 750°C and 800°C sample set

The gamma prime phase was also studied in the TEM looking at electropolished thin foils, an example of this work is shown below in Figure 4.24

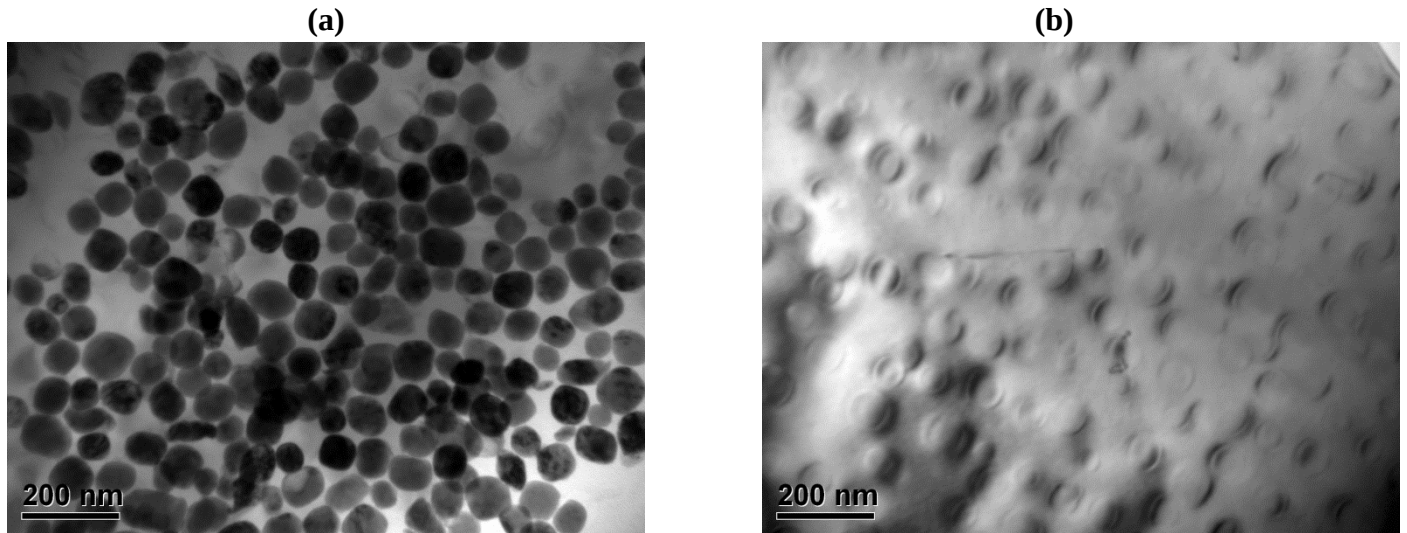


Figure 4.24: TEM micrograph of long term aged 700°C for 20,000 h showing (a) γ' precipitates in an electron transparent area and (b) γ' precipitates and their associated strain field in a thicker region of an electropolished sample

Figure 4.24 (a) clearly shows the presence and morphology of the gamma prime phase when aged for 20,000 h at 700°C, however due to precipitate overlap it is very difficult to carry out any meaningful analysis in terms of area fraction measurements. Figure 4.24 (b) is from a thicker region in the sample which does not have the same degree of electron transparency.

4.9 Eta transformation and evolution

After long term ageing Eta phase was found to be present in Nimonic 263, as results from the sample isothermally aged at 700°C for 20,000 h indicated. After 20,000 h at 700°C only a small amount of grain boundary Eta phase was observed. As Figure 4.25 shows long term exposure at 750°C showed an increase in the amount of Eta phase present when compared to the corresponding 700°C sample which contained little to no Eta phase. To study the effect of higher ageing temperatures on Nimonic 263 a set of samples were isothermally aged at 800°C. The 800°C ageing set renders information on the precipitate stability of precipitates such as $M_{23}C_6$ and the MX phase in terms of both their coarsening and chemical evolution. Results will also help to inform the effect of higher ageing temperatures on the alloys hardness properties and coarsening rate of γ' . Most significantly to this part of the results section it will allow the evolution of the Eta phase to be observed at an accelerated rate.

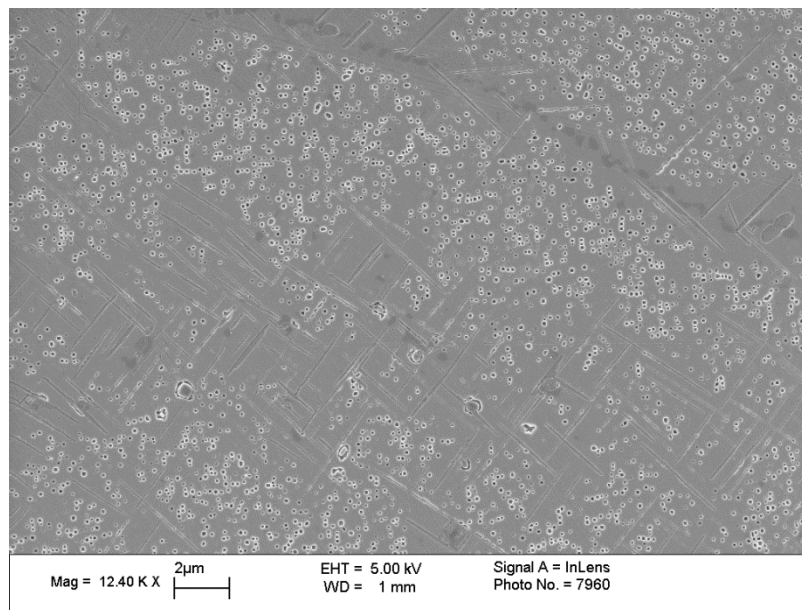
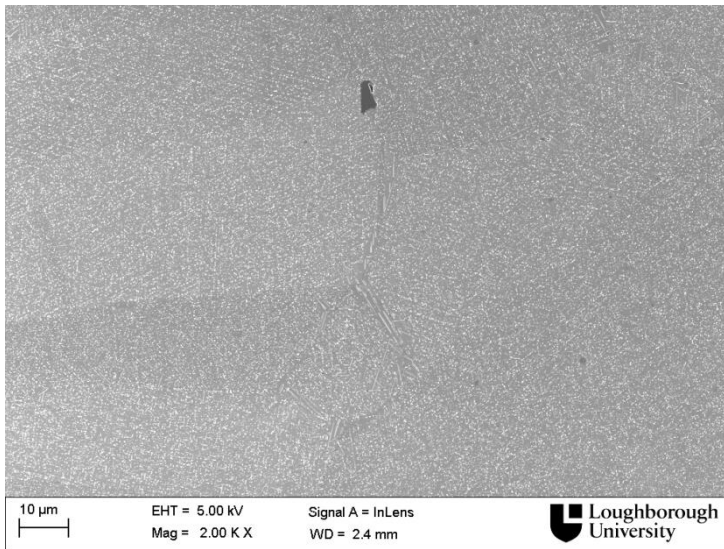


Figure 4.25: Electron micrograph show Eta phase present in the sample aged at 750°C for 10,000 h

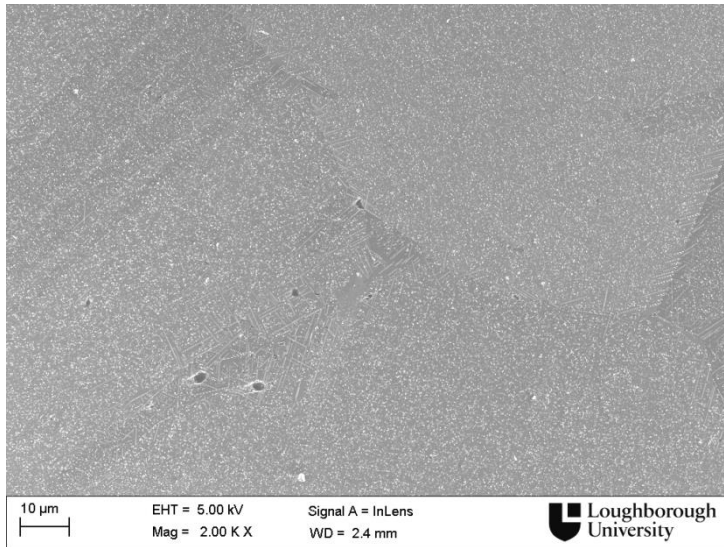
(a)



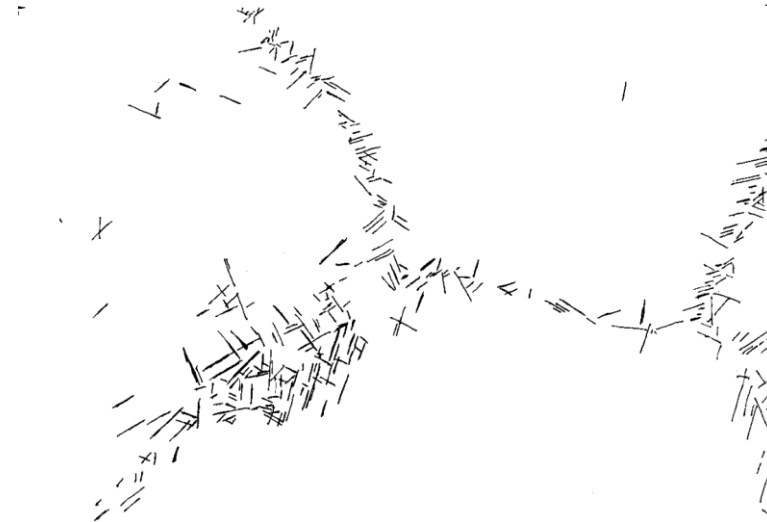
(b)



(c)



(d)



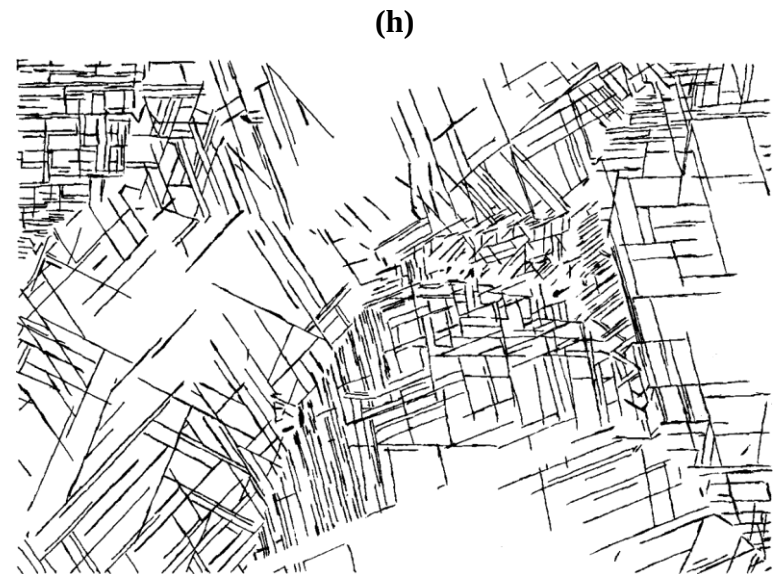
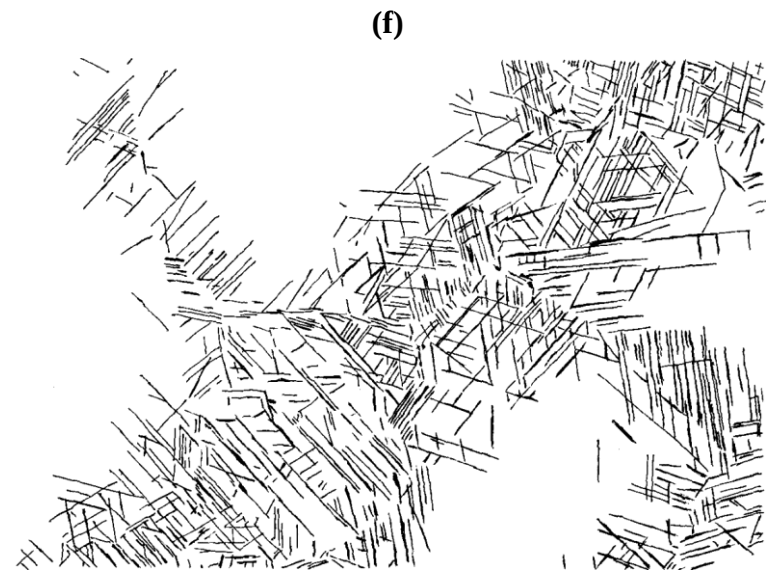
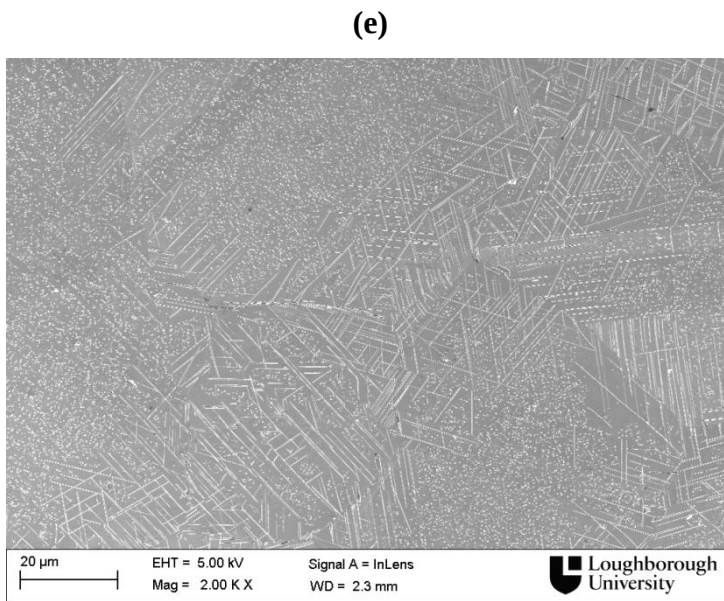


Figure 4.26: Electron micrographs and associated traces of Eta (η) precipitation in samples aged at 800°C for (a, b) 1500 h, (c, d) 2000 h, (d, e) 5000 h and (g, h) 10,000 h

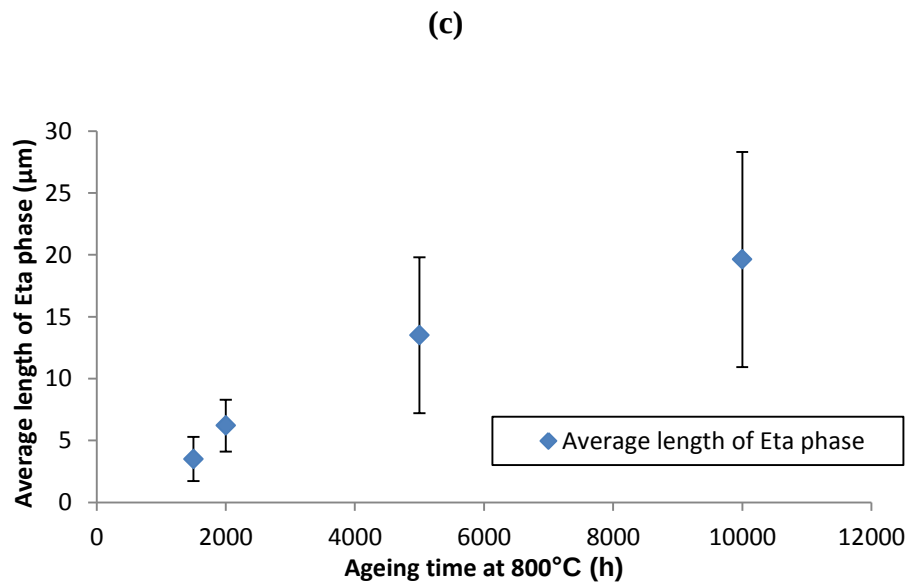
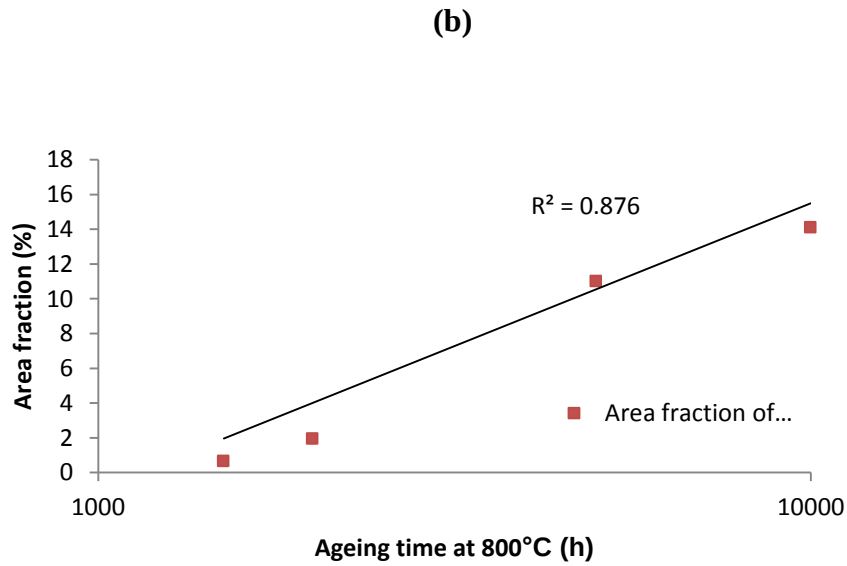
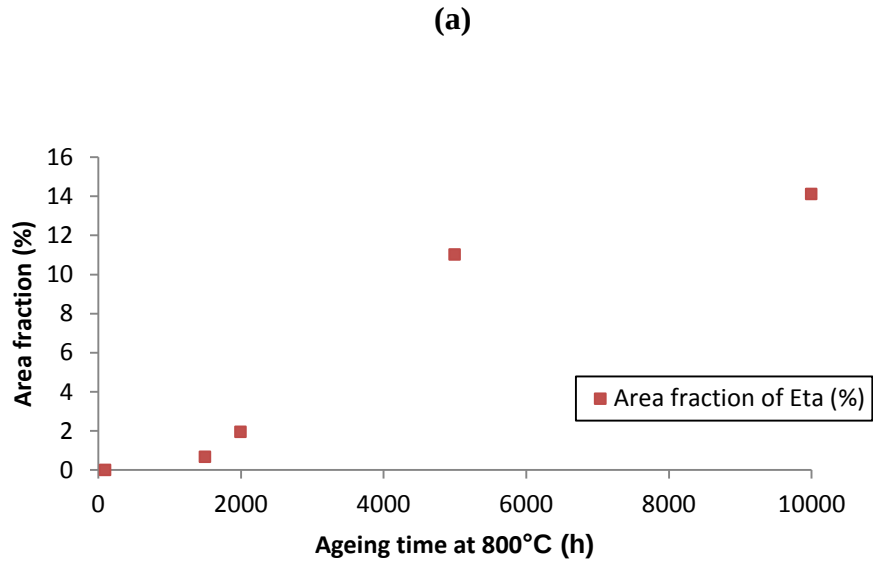


Figure 4.27: (a) Area fraction of Eta phase against ageing time at 800°C, (b) Area fraction of Eta phase against log of the ageing time at 800°C and (c) the average length of Eta phase with ageing at 800°C

Figure 4.26 shows images taken of samples in the 800°C isothermally aged sample set at a series of different ageing times. The Eta phase present in each sample has been traced in an aim to highlight their presence. The images are in order of ageing time from 1500 to 10,000 h and show the evolution of the Eta phase with exposure time. This evolution is clearly observed, although work has also been carried out to quantify this change. Once the images were traced the area fraction of the Eta phase in each image was calculated using image analysis software, the result is shown in Figure 4.27 (a). The result clearly shows that as ageing time increases so does the area fraction of the Eta phase. Work was also carried out in an attempt to measure the average length of the Eta phase. Observations clearly showed another positive correlation with the average length of the Eta phase increasing with ageing time, this, however proved very difficult to quantify due to the crossing of Eta phase precipitates and the subsequent definition of an individual 'object' by the software. To work round this limitation in the software the lengths of a random sample of Eta laths from each image were measured. The results from this work are shown in Figure 4.27 (b), although an overall increase in average size is noted with increased ageing time the error also increase. This indicates that precipitation or transformation of the Eta phase is still occurring at long exposures times and that lengthening of the existing Eta phase is still occurring concurrently. Graphs in Figures 4.27 (a) and (b) appear to show the amount of Eta phase and it's length of are beginning to plateau. After thermal exposure of 800°C for 10,000 hours the Eta phase is thought to be reaching its maximum volume fraction. One of the reasons for this plateau is thought to be to do with the congestion of the Eta network, so far observations have shown lengthening of the Eta precipitates stops once they come into contact with other Eta precipitates.

In the section studying the evolution of the gamma prime phase an alignment of the gamma prime is observed after long term ageing at 700°C in Figure 4.21 (e), this has been highlighted on the image with an arrow. Other example of this gamma prime alignment were seen throughout samples in both the 750°C and 800°C sample set. Figure 4.28 (a) below is further evidence of this transformation. In this image the Eta phase appears to be cutting through existing gamma prime precipitates. This phenomenon has also been observed in etched samples like that in Figure 4.29 (b) which shows the 10,000 h sample aged at 750°C.

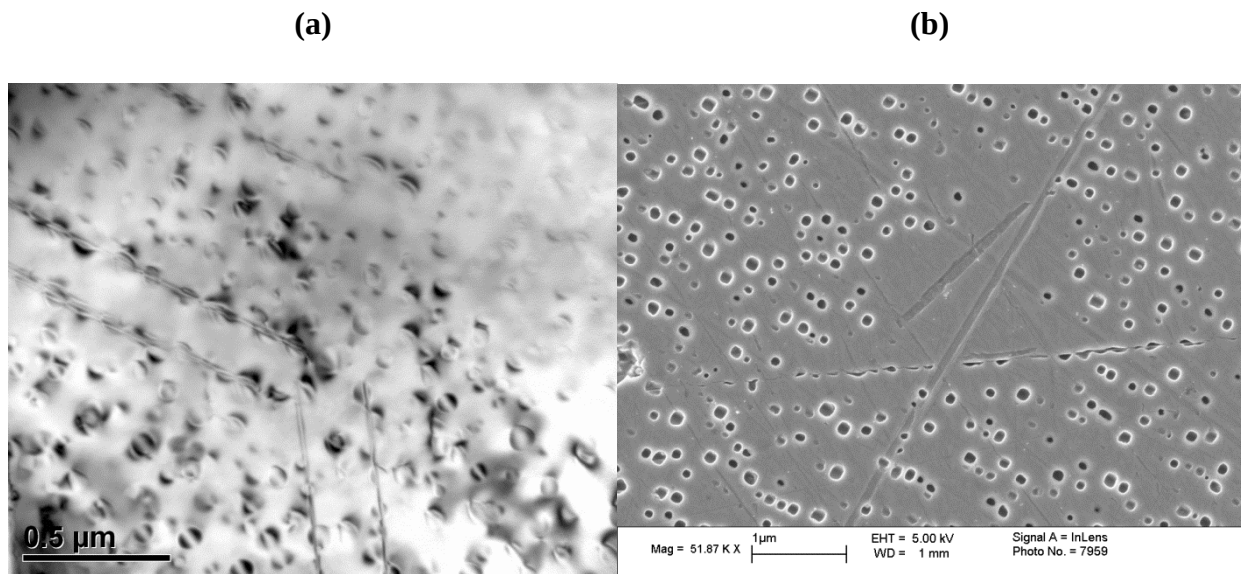


Figure 4.28: (a) TEM micrograph of suspected Eta transformation and (b) electron micrograph from etched sample again showing suspected Eta transformation

4.10 Rejuvenation of Nimonic 263

Results from this chapter demonstrate that Nimonic 263 has a stable microstructure below 750°C, meaning, it is of great interest for operators considering the manufacture of next generation plant. The harmful Eta phase has been observed after both long term ageing at 700°C or shorter ageing times at 800°C. One of the advantages of using Nickel base superalloys is that there is the potential to rejuvenate aged samples to their near virgin states. The practicalities of carrying out a near solution heat treatment on what would effectively be highly complex and stressed areas of the plant are for the moment ignored. This investigation is focusing first on whether it can be done and the effects on both the microstructure and mechanical properties afterwards.

The rejuvenation work was carried out on what was seen as the most extreme, in terms of softening of the alloy, and significant Eta precipitation. The sample used was aged at 800°C for 10,000 h. After such exposure there is a high volume fraction of the Eta phase and any untransformed γ' has been seen to significantly coarsen. The microstructure of the aged alloy is shown below in Figure 4.29

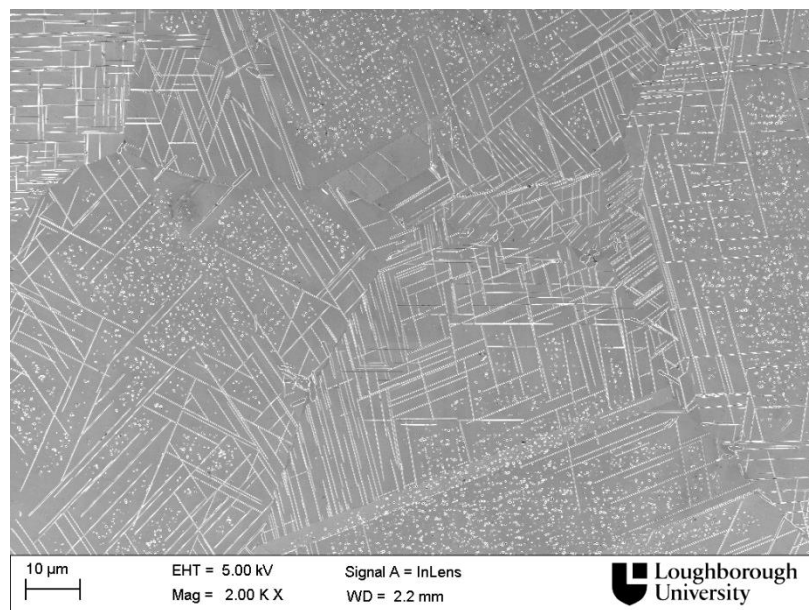


Figure 4.29: Electron micrograph showing Nimonic 263 isothermally aged at 800°C for 10,000 h

Two different rejuvenation heat treatments were chosen based on two different heat treatments already used in this research.

- The standard solution treatment used in Nimonic 263 → 1150°C for 2 h
- The stress relief heat treatment used in a later results chapter concerning welded Nimonic 263 samples → 980°C for 3 h

The long term aged samples were given the heat treatments in a high temperatures furnace before being quenched after exposure. The heat treatment at 1150°C was found to fully dissolve both the Eta and γ' phase in addition to grain boundary $M_{23}C_6$. Large irregular shaped MX phases were present throughout the alloy, an example of which can be seen in Figure 4.30, and are thought to be present due to the breakdown of the Ti rich Eta phase (Ni_3Ti).

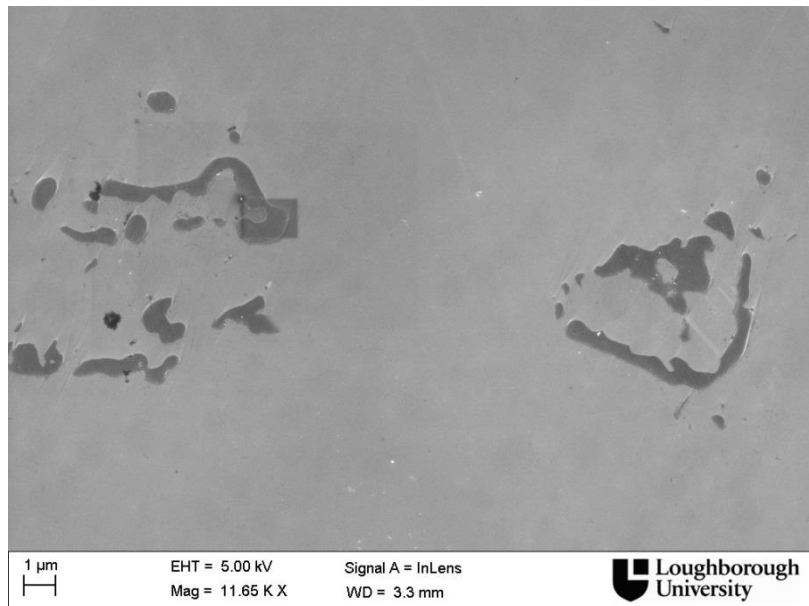


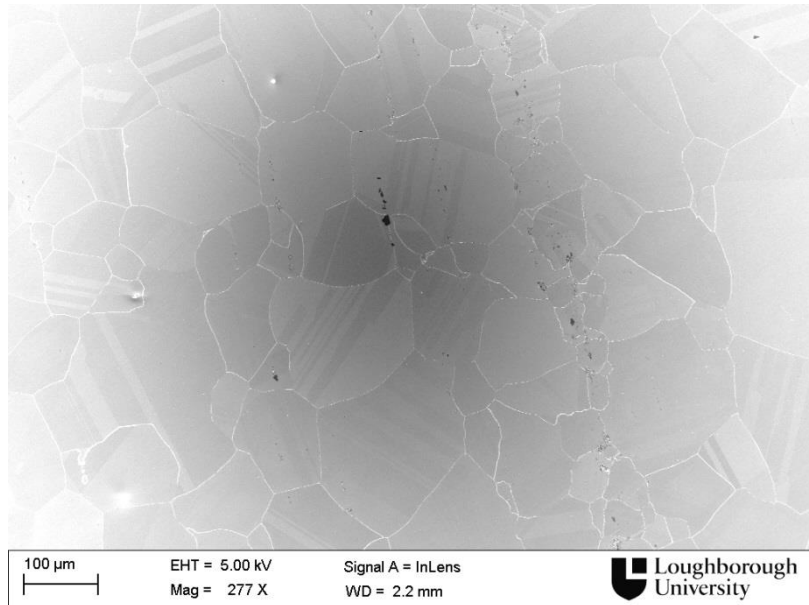
Figure 4.30: Electron micrograph showing long term aged nimonic 263 subjected to standard solution heat treatment of 1150°C for 2 h

The hardness of the alloy before the rejuvenation heat treatment was 250 HV, after the rejuvenation heat treatment it softened to 168HV. The softening is attributed to the dissolution of the γ' and Eta phases. The standard precipitation hardening heat treatment of 800°C for 4 hours was then applied to provide a controlled precipitation of γ' and grain boundary strengthening $M_{23}C_6$.

After this precipitation heat treatment the hardness of the alloy increased to 273HV¹⁰ (a recovery of 23HV¹⁰ from the long term aged condition). The resultant microstructure

appeared to be similar to virgin materials in the PH condition. The γ' precipitates were found to be present at approximately 9.7 nm and at an area fraction of about 0.05. An example of the rejuvenated microstructure can be seen in Figure 4.31 (a) and (b).

(a)



(b)

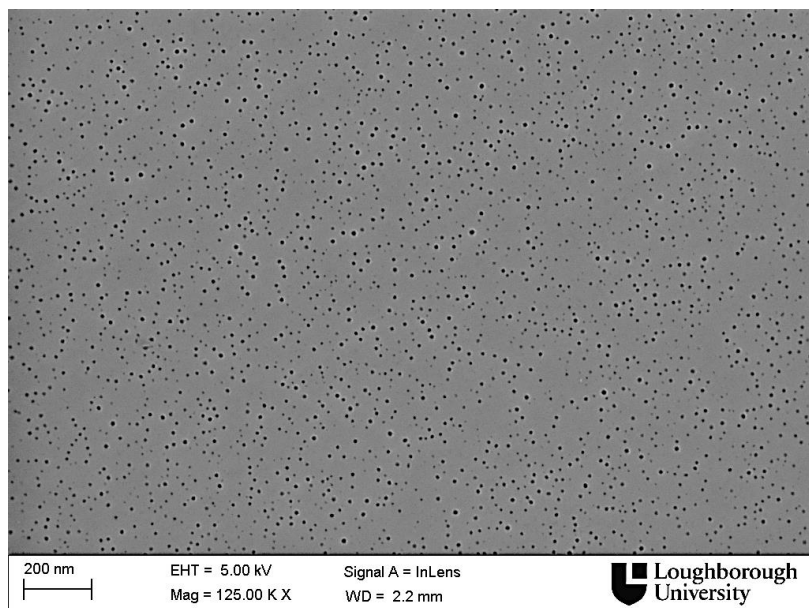


Figure 4.31: Electron micrograph showing (a) microstructure of Nimonic 263 after it has been subjected to both rejuvenation and precipitation heat treatment and (b) γ' precipitates in the same condition

The second rejuvenation heat treatment of 980°C for 3 hours was found to only partially dissolve precipitates contained in the long term aged sample. Whilst the gamma prime was fully dissolved the Eta phase only experienced partial dissolution. The grain boundary carbides which had experienced significant coarsening during long term ageing were also still present after this heat treatment. An example of this microstructure is shown below in Figure 4.32.

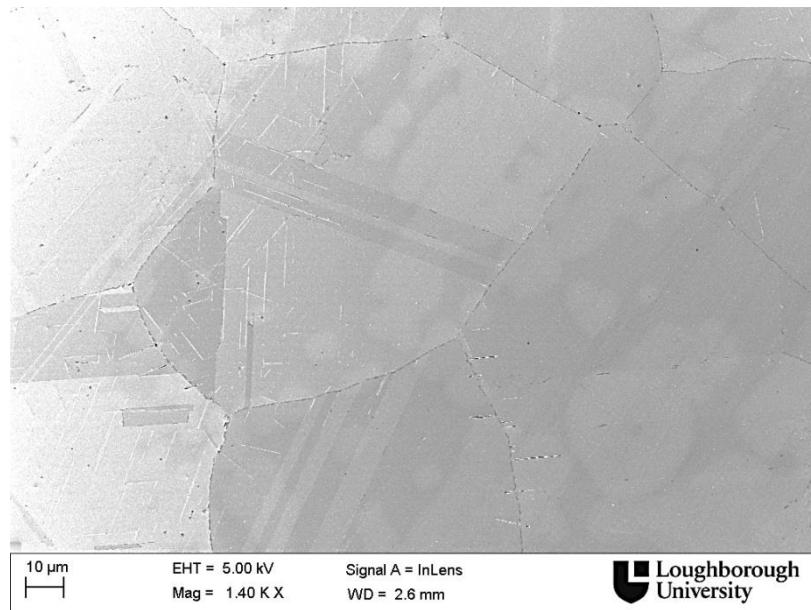


Figure 4.32: Electron micrograph showing long term aged nimonic 263 subjected to the stress relief heat treatment of 980°C for 3 h

The hardness was found to decrease from 250 HV¹⁰ to 181HV¹⁰ after the 980°C stress relief heat treatment indicating significant softening had occurred. After ‘rejuvenation’ the precipitation heat treatment of 800°C for 4 hours was again performed as before. After the precipitation hardening heat treatment the γ' phase re-precipitated out at an average particle size of 9.9 nm, the area fraction was not calculated in this instance. The hardness of the alloy was found to increase to 288HV¹⁰, although the Eta phase was still present.

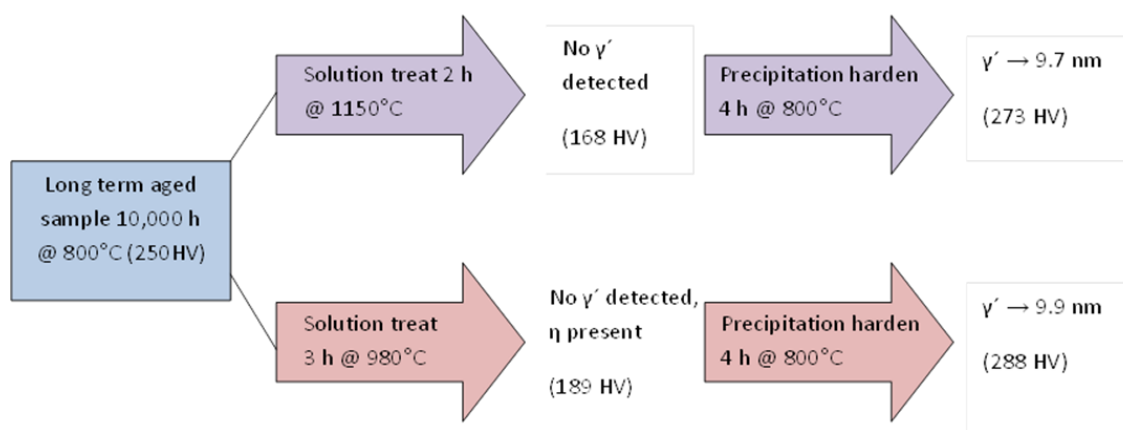


Figure 4.33: Diagram summarising the rejuvenation investigation and the effect of each heat treatment on the alloys hardness and γ' precipitate size

The results from this investigation are summarised in Figure 4.33 above. This investigation shows that rejuvenation of the alloy is possible with both rejuvenation heat treatments increasing both the hardness of the alloy and reducing the size of the re-precipitated γ' , as would be preferable. The effect of reintroducing the rejuvenated alloy back into service is unknown, in terms of whether its creep strength would degrade more quickly or the γ' precipitates would coarsen at an increased rate. Work by Yao and Thomson^[61] has looked at the effect of rejuvenation on the tensile strength of a γ' strengthened nickel base alloy. The work found that the mechanical properties of alloy were restored to that of the alloy in the as-received condition. After the rejuvenated alloy re-entered simulated service it was found to experience a more rapid decline in mechanical properties when compared to virgin material. The practicalities of such a heat treatment would certainly restrict its use for long length of complex pipework but such a heat treatment may find some use in larger cast components such as valves which can be heat treated in isolation.

4.11 Summary

Microstructural evolution in thick section Nimonic 263 has been studied using a number of analytical techniques, with particular focus on pre heat treatments and long term ageing at 700°C, 750°C and 800°C.

Hardness measurements showed a large increase of approximately 100 HV after solution treatment in the precipitation hardening heat treatment, primarily attributable to the precipitation of fine γ' . Further changes in hardness on long term ageing at temperatures

ranging from 700°C to 800°C were relatively small, although there was some apparent softening with increasing thermal exposure. The γ' precipitates were observed to coarsen as a function of thermal exposure, and quantification of the evolution of the particle size distribution showed good agreement with standard particle coarsening theory.

Significant banding was present in the microstructure with a bimodal grain size distribution comprising fine grains within the banded regions. There was little overall change in the bulk grain size, although the banded regions were noted to coarsen after long term ageing.

The alloy contained two different types of larger MX precipitates; one Ti rich and the other Ti-Mo rich. These precipitates were observed to coarsen very slowly when aged at 700°C, only increasing by 0.7 μm after 20,000 hours. Some individual particles were found to contain distinct regions which were rich in each of the two compositions observed.

The grain boundaries in the samples after solution treatment only remained particle-free, with precipitation occurring during the initial precipitation hardening heat treatment. Grain boundary precipitates were identified as the Cr-rich M_{23}C_6 phase, and were also observed to coarsen with long term ageing. The grain boundary precipitates were found to be chemically stable with little change observed even at long exposure and higher ageing temperatures. As a result of long term ageing for 20,000 hours at 700°C, large, angular, individual particles were detected in the vicinity of the grain boundaries, which were identified as the η phase. This needle like Eta phase was found to be present at higher area fraction at lower exposure times when aged at higher temperatures. Results and literature point to this phase forming through the transformation and alignment of the gamma prime phase after ageing. The influence of the precipitation of this phase on the long term creep properties of the material requires further investigation.

A specimen subjected to long term ageing at 800°C was later given rejuvenation heat treatment; the investigation studied the effects of two different rejuvenation heat treatments. The investigation successfully demonstrated the alloys ability to undergo rejuvenation. It was found that higher temperature fully dissolving both γ' and η precipitates before the second stage precipitation heat treatment enabled the controlled precipitation or a near virgin microstructure.

Chapter 5

Microstructural characterisation of Nimonic 263 welds

5.1 Introduction

Predicting and observing the microstructure of Nimonic 263 in its wrought form is an important part of this research, and the results from the last chapter will go a long way in assessing its suitability as a candidate alloy in respect of ageing at high temperature. However, in addition to the suitability of wrought materials other considerations, such as the materials ability to be welded have to be taken into account. Due to the shape and size of some assemblies it is impractical to produce a single complex component, and instead several components are joined together to produce such assemblies. The usual method for joining together components that experience high temperature and pressure conditions is welding. Other drivers for welding include: component repair, retrofitting and the joining of higher temperature components to those that operate at lower temperatures, usually made from different materials. The latter case, connecting high temperature parts of the plant to those at a lower temperature is often referred to as dissimilar metal welding, which will not be covered in this research which focusses on similar metal welds.

Traditionally alloys have been developed for their high temperature strength, stress rupture, and oxidation properties with little thought towards their later fabrication. Due to this factor, industry has been hit with exaggerated fabrication costs for some alloys due to the unpredictable and uncontrollable metallurgical variations causing problems such as cracking during welding. Nimonic 263's place as a candidate alloy is partly due to its ability to be welded.

In this chapter the weld microstructure is initially predicted using thermodynamic calculations. These predictions are then validated by studying a series of welded samples and investigating them in terms of both the microstructural and mechanical property evolution. The results are then discussed and related to the underlying science discussed in the literature review before conclusions are drawn.

5.2 Sample Conditions

To study the effect of welding Nimonic 263 on an industrial scale, full scale Nimonic 263 forgings were welded. Two different sets of welded samples were analysed in this research IP (I) and IP (II). The IP (I) samples were sourced from project sponsor E.On Engineering and the IP (II) samples were provided by another sponsor, Doosan Babcock. Production of the IP (I) welded samples involved milling a 15 mm channel into the circumference of a forged pipe of dimensions; 360 mm external diameter, 240 mm internal diameter and 5 m in length. The channel was then filled back up with a Nimonic 263 filler material, as shown in Figure 5.1 (a). The resultant weld is made up of 20 passes put down at a heat input of 5.9 kJ.cm^{-1} and a feed rate of 21 cm/min. The weld passes are approximately arranged 5 high and 4 wide, although this varies slightly between each weld. A macro overview of one of the welded samples can be seen below in Figure 5.1 (b)

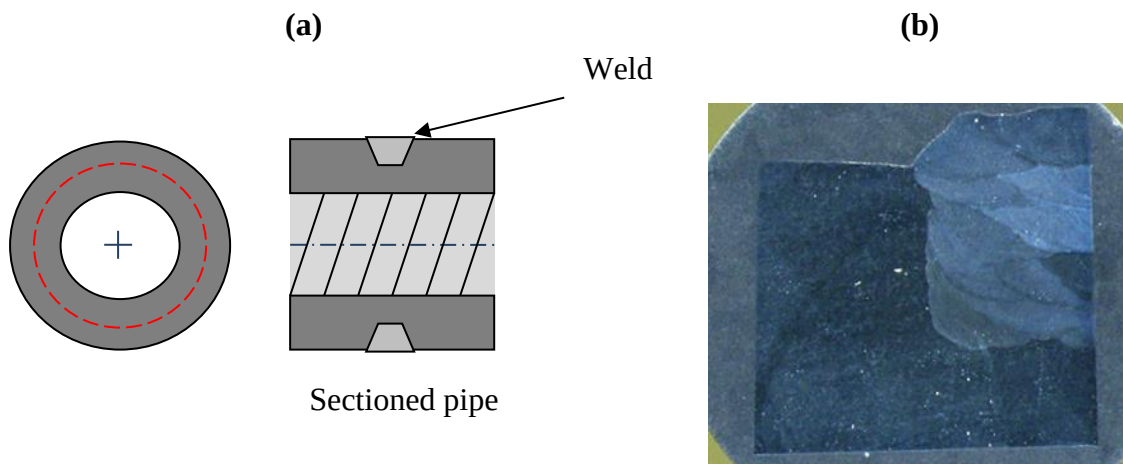


Figure 5.1 – (a) Diagram showing a section view of the welded samples and (b) a macrograph of the stress relief welded sample highlighting the multipass weld structure

The parent material, or pipe, used to produce the welded samples was well within the alloy's nominal composition, set by Special Metals. This parent pipe does show a slight variation in chemical composition to that of the samples studied in previous work, although this is not thought to be significant. The weld filler material, however, showed large variances from the Special Metals nominal composition. Both compositions are shown in Table 5.1 in addition to the nominal composition set by special metals. Any elemental compositions above specification have been highlighted in red, those below in blue and those that fall within the limits have been coloured green. The weld metal compositions shown are as-deposited weld metal chemical composition.

Table 5.1 – Composition of welded samples

Elemental composition (wt.%)	C	Si	Mn	Cr	Co	Mo	Ti	Al	Fe	N
Nominal composition (set by Special Metals)	0.04 – 0.08	0.4 max	0.6 max	19.00 – 21.00	19.00 – 21.00	5.6 – 6.1	1.9 – 2.4	0.6 max	0.7 max	-
Weld material IP (I)	0.075	0.71	0.073	18.62	18.31	5.39	2.71	0.64	0.75	-
New 263 pipe material IP (I)	0.051	0.1	0.15	19.5	19.93	5.76	2.28	0.52	0.31	-
Weld material IP (II)	0.067	0.24	0.35	20.02	19.7	5.78	2.24	0.51	0.43	-

This section will consider the effects of three different post weld heat treatments: A stress relief heat treatment that aims to reduce the amount of thermo-mechanical stresses in the weld remaining from the welding process. It is also intended as a re-solution heat treatment in which to dissolve any phases formed during welding. The treatment is carried out at 980°C for 3 hours. The hardening heat treatment is designed to strengthen the weld and its surrounding parent through the controlled precipitation of the γ' phase. Finally, the third sample combines both heat treatments through carrying out the stress relief followed by the hardening heat treatment. To thoroughly characterise the microstructural behaviour of the welded samples it was necessary to carry out further heat treatments to the as-received samples. These heat treatments are detailed in Table 5.2 along with the as received weld samples. It is not confirmed by either industrial partner whether the welding of either sample set were carried out in the solution treated or precipitation hardened condition. Both sample sets are thought to have been welded in precipitation hardened condition due to hardness values and the presence of γ' in areas of the parent material well away from the HAZ.

Table 5.2 – Weld samples and the corresponding heat treatments

Sample ID	Description	Heat treatment	Method of heat treatment and cooling	Notes
57	As welded	None (E.On)	Air cooled	As received from E.On
58	Stress relieved	3 h @ 980°C (E.On)	Air cooled	As received from E.On
59	Hardened	4 h @ 810°C (E.On)	Air cooled	As received from E.On
66	Stress relieved produced from as welded	3 h @ 980°C	Air cooled – thin section	-
67	Hardened produced from as welded	4 h @ 810°C (Loughborough)	Air cooled – thin section	-
68	Re solution as welded parent	2 h @ 1150°C	Air cooled – thin section	-
70	Stress relief trial (SM)	0.5 h @ 1150°C, 4h @ 800°C, 3 h @ 980°C	Dilatometer quench 100°C S ⁻¹	Fast cool
71	Stress relief trial (SM)	0.5 h @ 1150°C, 4h @ 800°C, 3 h @ 980°C	Dilatometer cooling rate 100°C per hour till 500 °C then quench	Slow cool. Differences observed between edge and centre of dilatometer sample
72	Stress relief trial on weld metal from as welded	3 h @ 1000°C	Dilatometer quench 100°C S ⁻¹	Fast cool
73	Stress relief on weld metal from as welded	3 h @ 980°C	Dilatometer quench 100°C S ⁻¹	Fast cool
74	Stress relief on weld metal from as welded	3 h @ 980°C	Dilatometer cooling rate 100°C per hour till 500 °C then quench	Slow cool (produced from 1000°C sample)

A number of samples have been used in this research chapter, a brief summary of the samples and there inclusion follows. Samples 57- 59 originate from the as received sample from IP (I). One of the first steps in the research was to repeat the heat treatments carried out in industry. For this purpose the as-welded sample was sectioned and samples 66 – 68 were produced. Samples 70 and 71 were produced from a piece of Nimonic 263 cylindrical bar to study the effectiveness of the 980°C stress relief heat treatment. Samples 72 – 73 were sourced from the weld metal of the as-welded sample with the intention to investigate the effect of cooling rates on the weld metal microstructure.

5.3 Thermodynamic predictions

The precipitation trends of the welded samples were extensively modelled, as in Chapter 4, before carrying out any metallographic analyses. The composition of the parent material is different from that of the samples previously analysed in the isothermally aged chapter, and this variation is highlighted in Table 5.1. The new different parent composition has been thermodynamically modelled to see how the phase stability varies with temperature. The composition of the weld parent material shown in Table 5.1 has been thermodynamically modelled to see which phases are predicted to exist and how the phase stability varies with temperature. Figure 5.2 shows the predicted phase evolution of the weld parent alloys microstructure with (a) all phases and (b) with the Eta phase suspended. The Eta phase has been suspended from the second calculation to give a more representative prediction of the alloy's early microstructure.

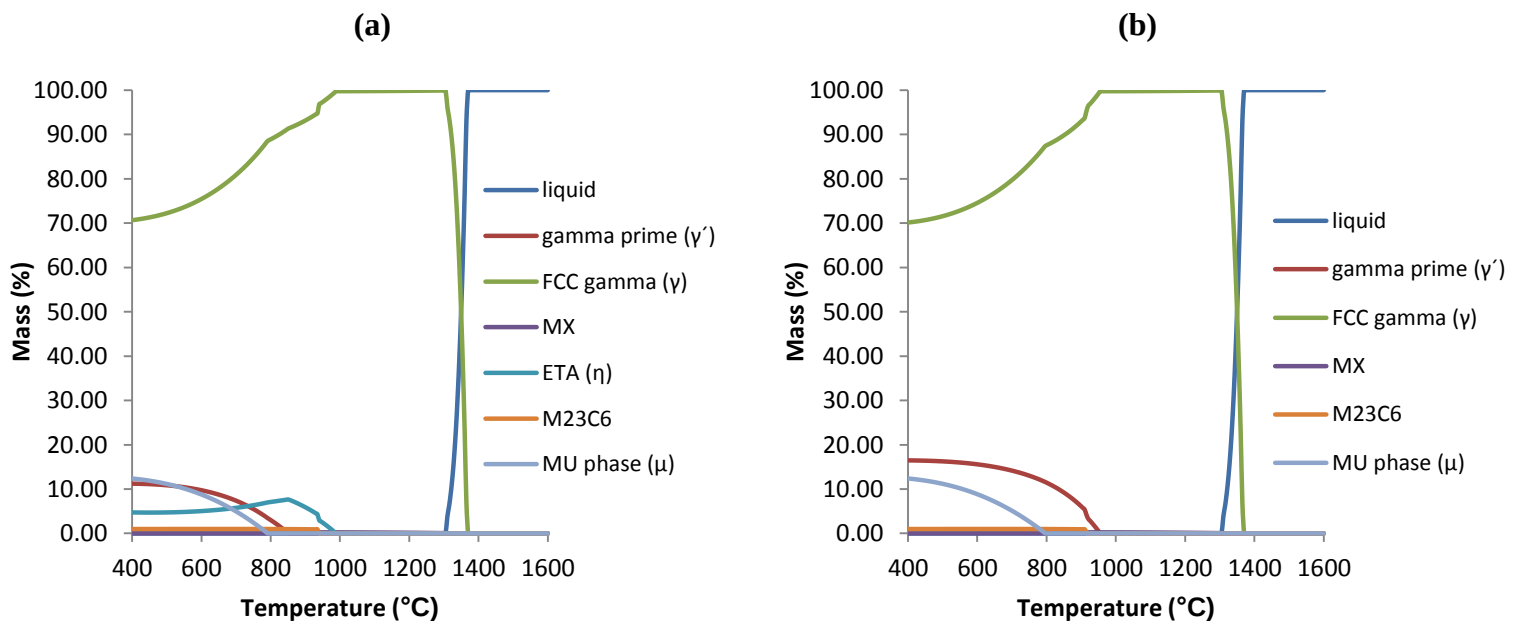


Figure 5.2 – Predicted phases against temperature in equilibrium conditions for weld parent material (a) all phases and (b) with Eta suspended

The thermodynamic predictions for the weld parent material showed there to be more γ' present in both the calculations than in the original pipe material studied in Chapter 4. With all phases enabled for calculation, 11.2 wt.% of γ' was predicted to exist for the weld parent material compared to 6.8 wt.% in the corresponding calculation for the parent pipe from the isothermally aged chapter. With the Eta phase suspended, 16.5 wt.% γ' is predicted to be present compared with 13.9 wt.% in the corresponding calculation for the parent pipe

examined in Chapter 4. Whilst it is already accepted that the γ' dissolution temperature is higher when the Eta phase is suspended for calculation, the effect of composition has been previously unstudied. In the weld parent, γ' was predicted to dissolve at 850°C compared to 745°C in the original parent pipe. There is predicted to be less Eta phase present at equilibrium in the weld parent pipe (4.7 wt.%) than in the original pipe (6.4 wt.%). This is probably due to the lower Ti-Al ratio in the weld parent (3.93:1) when compared to the higher Ti-Al ratio in the original pipe (6.39:1). The calculation does show that the fraction of Eta phase varies with 4.7 wt.% predicted at 400°C, which increase to a peak of 7.7 wt.% at 850°C. The predicted amounts of both the Mu phase and $M_{23}C_6$ precipitates are similar between the two parent materials. The predicted amounts of both the $M_{23}C_6$ and Mu phase are identical in both parent calculations at 1 wt.% and 12.4 wt.% respectively. MX phase is predicted to 0.25 wt.% and begins to form at 1300°C, again in both calculations.

The filler material, designated 'weld metal', is again of a different composition that lies significantly outside the composition limits set by Special Metals. It should be noted that the term 'weld metal' refers to the as deposited weld metal chemistry not that of the filler material pre-welding. Using the analysed composition of the weld metal, equilibrium calculations were again carried out to predict the phase stability with change in temperature.

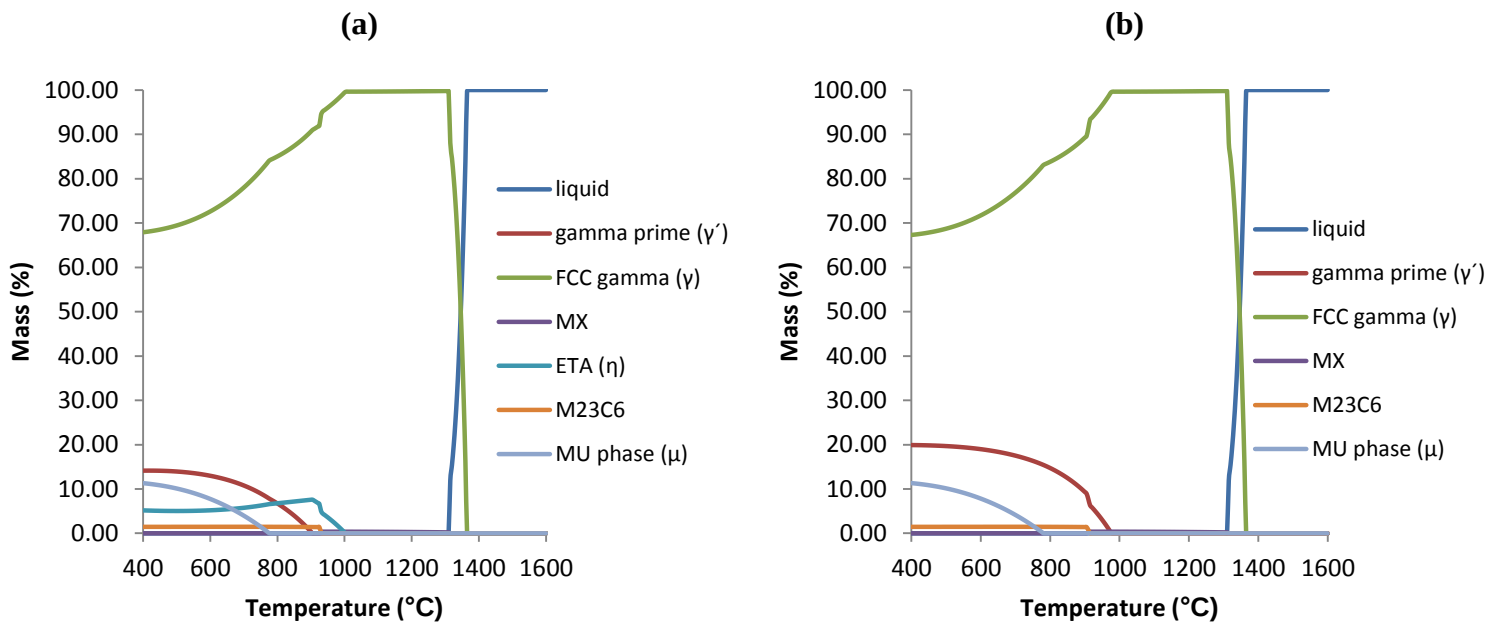


Figure 5.3 – Predicted phases against temperature in equilibrium conditions for weld metal (a) all phases and (b) with Eta suspended

The thermodynamic predictions for the weld metal showed there to be more γ' present in both the calculations than in the parent. With all phases enabled for calculation, 14.1 wt.% of

γ' was predicted to exist in the weld metal compared to 11.2 wt.% predicted in the corresponding calculation for the parent. With the Eta phase suspended, 19.9 wt.% γ' is predicted to be present compared with 16.5 wt.% predicted in the corresponding calculation for the parent. A variation was noticed in the γ' dissolution temperatures for calculations allowing for all phases. In the weld metal, γ' was predicted to dissolve at 900°C compared to 850°C in the parent, which suggests γ' is stable at higher temperatures in the weld metal.

Initial observations of the welded samples using optical microscopy showed the weld metal to contain a dendritic microstructure throughout. This dendritic microstructure indicated that the weld is likely to contain chemically segregated regions, and therefore non-equilibrium calculations were carried out to predict how the composition of the weld metal changes during cooling. Figure 5.4 shows how the weld metal solidifies by calculating first how the mass percent of the liquid phase changes with temperature.

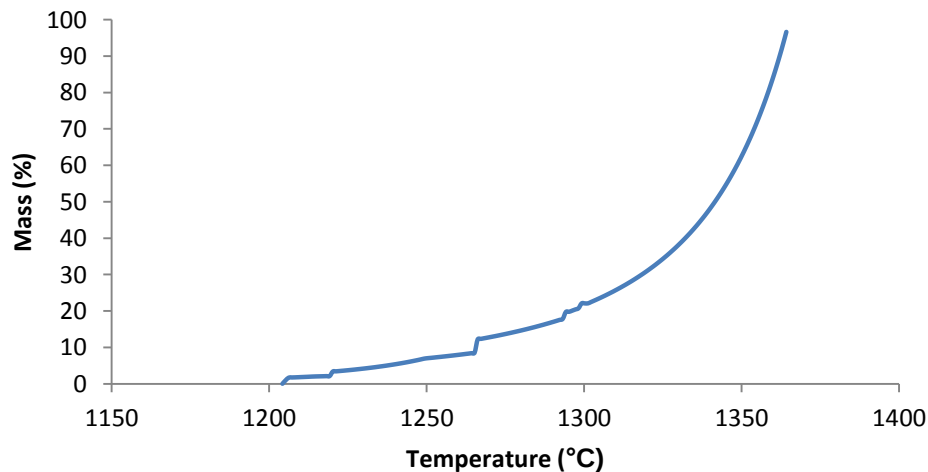


Figure 5.4 – Predicted mass fraction of the liquid phase with change in temperature

Solidification of the liquid phase begins at 1364°C forming FCC γ , and the phase has fully solidified at 1204°C giving a solidification range of 160°C. The Scheil method can also be used to further model chemical segregation by calculating any compositional change in the liquid phase during solidification.

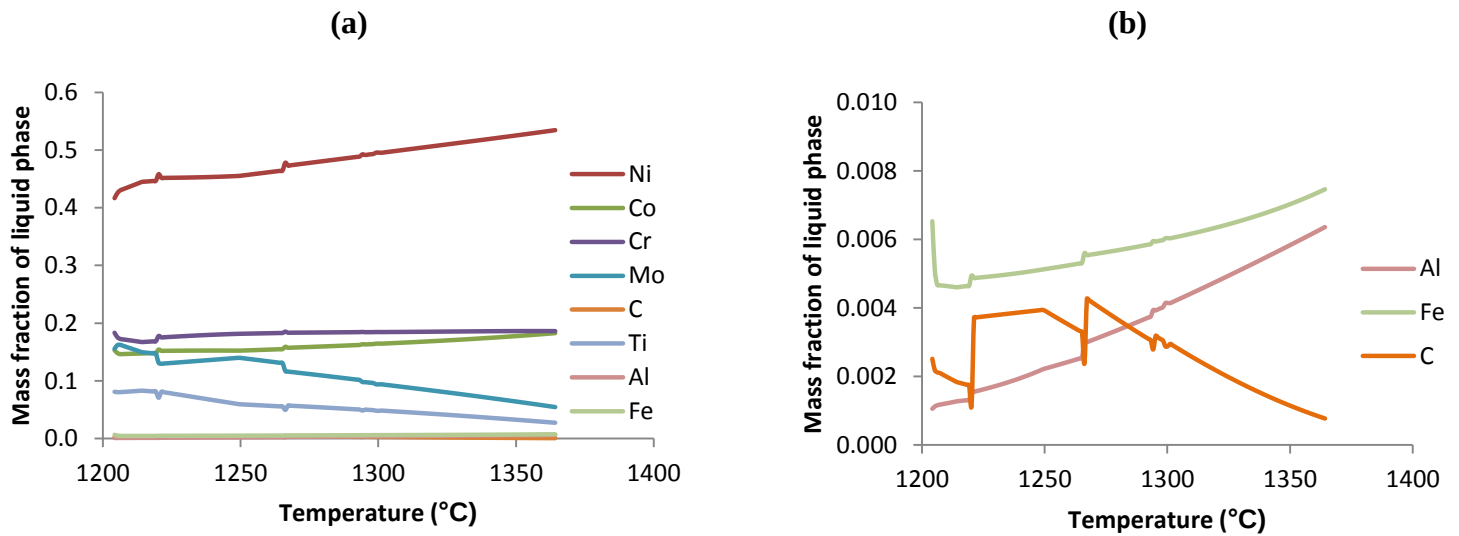


Figure 5.5 – Predicted change in chemical composition of liquid phase against temperature focusing on (a) Ni, Co, Cr, Mo, Ti and (b) Al, Fe and C

Figures 5.5 (a) and (b) display the change in chemical composition with temperature. In Figure 5.5 (a) the nickel content of the liquid can be seen to decrease from 0.53 at the start of solidification to 0.42 at the end of solidification. The same is true of cobalt, decreasing from 0.18 at the start of solidification to 0.15 at the end. The chromium content remained relatively stable at approximately 0.18 throughout solidification. The titanium content increased three fold from 0.027 at the start of solidification to 0.081 at the end. The molybdenum content also showed significant change, 0.055 at the start of solidification with the composition of the final liquid found to contain a fraction of 0.156. This result indicates that Ti and Mo do not solidify at the same rate as other elements in the alloy, causing elevated levels in some of the last liquid phase to solidify. Figure 5.5 (b) is an expanded version of Figure 5.5 (a) displaying mass fraction values up to 0.010, enabling the meaningful display of changes in aluminium, iron and carbon. The graph shows that iron preferentially solidifies due to the decrease in iron content during solidification from 0.0075 to 0.0051. The same is true of aluminium, decreasing from 0.0064 to 0.0011 throughout solidification; this decrease could prove significant due to the importance of aluminium when forming γ' .

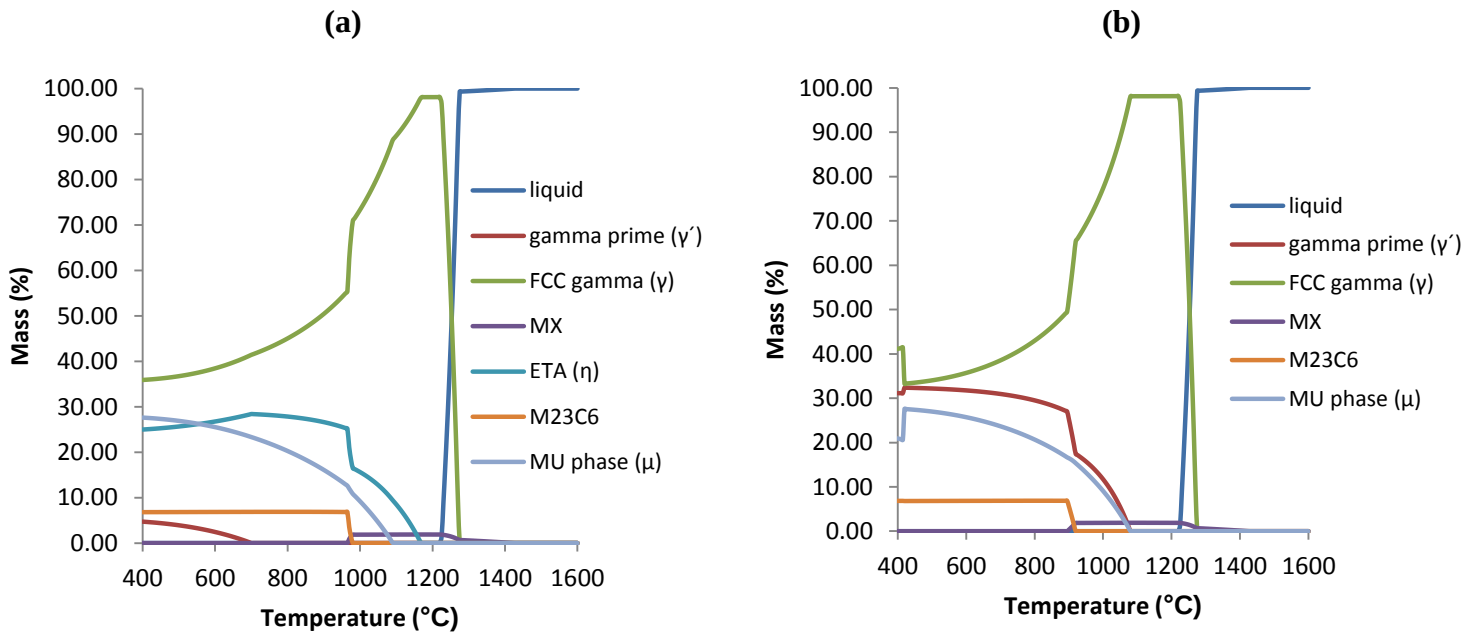


Figure 5.6 – Predicted phases against temperature in equilibrium conditions for segregated weld metal (a) all phases and (b) with Eta suspended

In order to model the effect of the chemical segregation in the liquid phase, further calculations were carried out using the equilibrium method. The composition of the last liquid to form was deemed not useful or representative, due to the small amount of liquid predicted to solidify at this composition. Instead, the bulk composition at 1260°C with 8% liquid left to form was used. The segregated composition at this temperature was: 46.15 wt.% Ni, 15.42 wt.% Co, 18.26 wt.% Cr, 13.38 wt.% Mo, 0.35 wt.% C, 5.69 wt.% Ti, 0.24 wt.% Al and 0.53 wt.% Fe. Calculations were carried out as before with the listed composition for both all phases and the Eta suspended calculation, and the results are shown in Figure 5.6 (a) and (b). The calculation allowing for all phases shows a large amount of Eta precipitation, with the segregated regions at a peak level of 28.4 wt.% at around 700°C. Attention should also be drawn to the relatively small amount of γ' predicted to form at 4.7 wt.% in comparison. Large amounts of the Mu phase are also calculated to form with 27.6 wt.% predicted to exist. The increase in Mu phase is likely to be due to the increase in Mo content within the segregated regions. With the Eta phase suspended, an increase in the amount of γ' is predicted to be present at 32.4 wt.%. The increased amount of Mu phase is also still predicted. Both calculations also showed an increase in the amount of MX and $M_{23}C_6$ predicted to occur at 1.9 and 6.8 wt.% respectively. It is again thought that banding of the MX phase will be

observed throughout the sample microstructure due to their concentrated formation in segregated areas. A similar phenomenon was commented upon in Chapter 4 in relation to the isothermally aged samples. The banded precipitation is thought to be present as a result of chemical segregation and processing.

5.4 Hardness evolution through welded samples

An initial investigation was carried out to assess how both production and the subsequent heat treatments had affected the mechanical properties. To carry out this assessment a series of hardness tests were carried out through both the parent and the welded areas of each sample. Testing each part of the weld indicates how the hardness of both the weld and parent materials vary, tracking the change through the section also highlights any evolution in hardness present in the areas close to the join between weld and parent material. Hardness results for the as welded and both laboratory and industrially heat treated samples are shown in Figure 5.7.

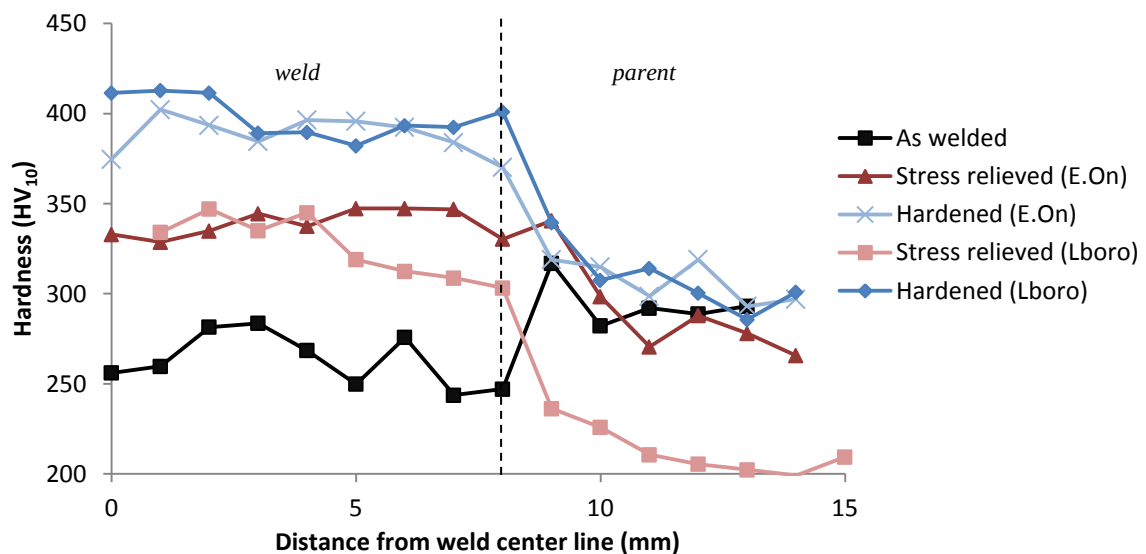


Figure 5.7 – Hardness evolution across the welded samples

In the ‘as welded’ sample, the average hardness of the parent material was calculated to be 295 HV₁₀ compared to the slightly lower value of 264 HV₁₀ for the weld area. The effect of the stress relief heat treatment varies between those provided from industry and those produced in the laboratory furnaces. With the industrial heat treated sample the hardness of the parent showed a decrease in hardness to 280 HV₁₀. In the weld metal however the hardness is significantly increased after heat treatment to 339 HV₁₀. The same heat treatment

carried out on a section of the ‘as welded’ sample produced different results. The parent material decreased in hardness from the as welded value down to 213 HV₁₀, with the weld metal increasing to 326 HV₁₀. After the hardening heat treatment, increases in hardness were recorded for both the parent and weld materials in both the industrial and laboratory heat treatments. The industrially heat treated sample had a parent hardness of 307 HV₁₀ and a weld hardness of 388 HV₁₀. The Loughborough heat treatment showed a similar trend with 308 HV₁₀ recorded in the parent and 398 HV₁₀ for the weld. It can be seen that there is a marked change in hardness from the weld material to that of the parent in all heat treated samples. The data contained in Figure 5.7 were acquired by taking a hardness measurement every 1 mm, this spacing may have been too large to fully evaluate the evolution of properties and the possible effect of a heat affected zone in the weld. A second investigation was carried out across all conditions along a traverse line 2 mm either side of the weld line. In this investigation the load was reduced from 10 kg to 1 kg and the indent spacing to approximately 200 µm. Results showed a small variation between indents in the weld material of 10 – 20 HV₁, such variation was previously observed in the earlier testing and can be accounted for by both experimental and small changes in the weld. Importantly, no significant location specific variations were observed e.g. large reduction or increase in the hardness at the fusion line which is not accountable to material changes. The differences between the industrial and Loughborough heat treatments is most likely to be due to different cooling rates brought about by the section size. A fourth post weld heat treatment sample was also produced by carrying out the hardening heat treatment on a stress relieved piece of weld material. The hardness traverse from the centre of the weld towards the parent material can be seen in Figure 5.8.

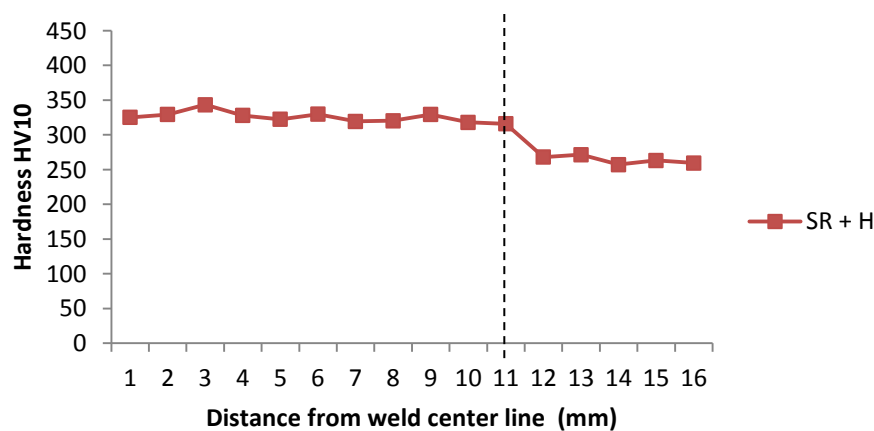


Figure 5.8 – Hardness evolution through the stress relieved + hardened sample

5.5 Optical microscopy of welds

An assessment of the grain structure was carried out, not only to study the welds at lower magnification, but also to help formulate a research plan with which to characterise the various samples. To prepare for observation under optical microscopy the sample was etched in Kalling's No. 2 reagent for 20 seconds, revealing the microstructure through preferential attack.

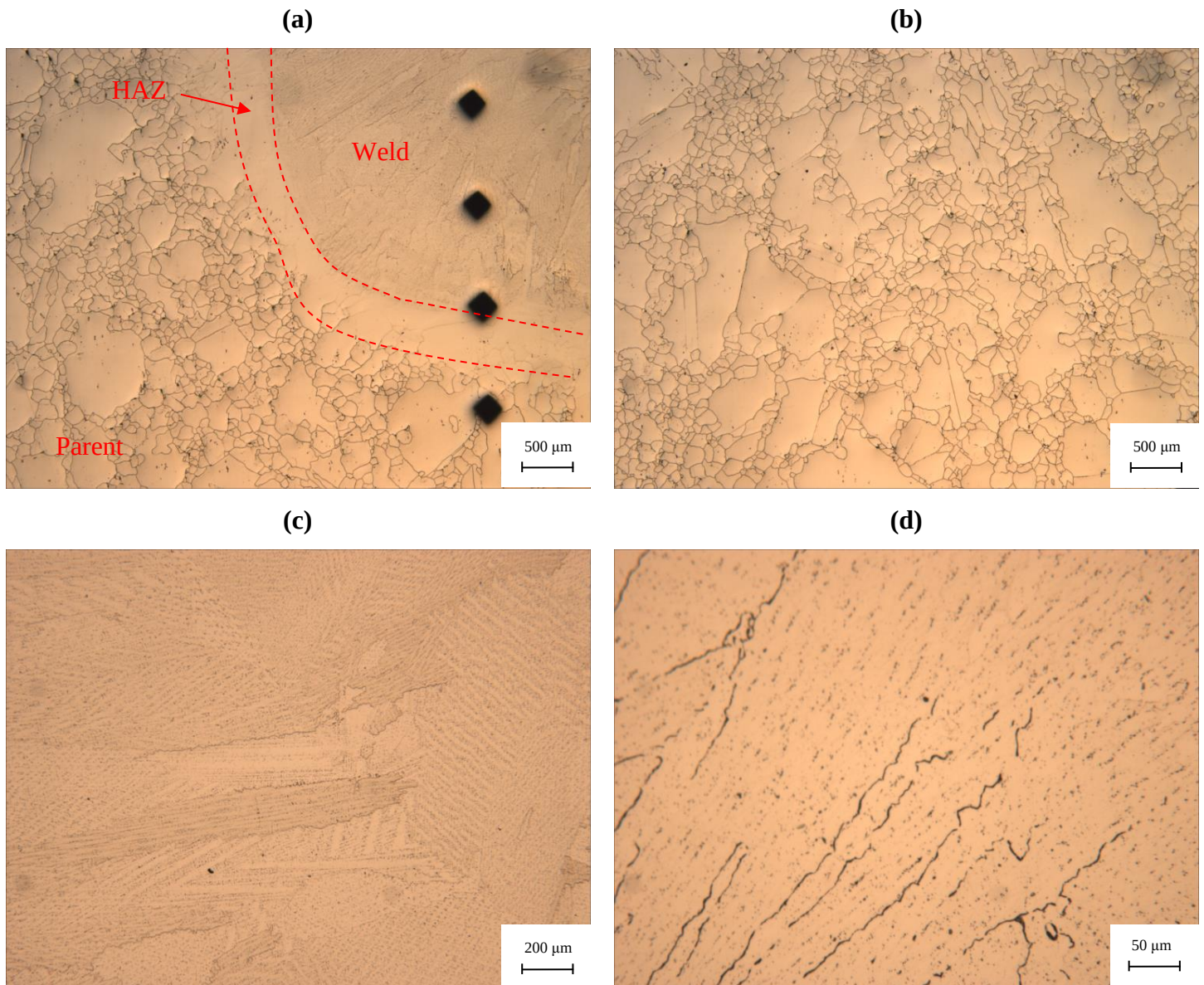


Figure 5.9 – Optical micrographs for the ‘as welded’ sample showing (a) three zones of welded sample, weld metal, HAZ and parent 2 x, (b) grain structure of parent material 2 x, (c) weld microstructure 5 x (d) 20 x

Figure 5.9 (a) shows the grain structure of the parent material in the as welded sample to be polycrystalline, at approximately 100 μm , similar to that observed in previous work. A number of very large grains up to 1 mm in size were observed throughout the parent material.

In order to establish whether this was an effect of the welding procedure, a piece of parent material was resolutioned at 1150°C and then re-examined, and it was found that the large grains were still present. Welded samples are typically made up of three distinct areas or zones; Parent, Heat Affected Zone (HAZ) and weld. These areas can be seen in Figure 5.9 (a) and have been labelled appropriately. Interestingly, only the ‘as welded’ sample was observed to have a significant heat affected zone. The heat affected zone in the as welded sample was measured to be approximately 200 µm. The weld grain structure is observed to vary throughout the sample, this is thought to be due to its position within the weld and each individual weld pool. Figure 5.9 (c) and (d) shows grain boundaries of the weld region to be serrated in nature. In the weld area there is evidence of dendrite formation; dendrites are not usually observed due to the high solution temperature and subsequent quench carried out as the standard heat treatment for Nimonic 263.

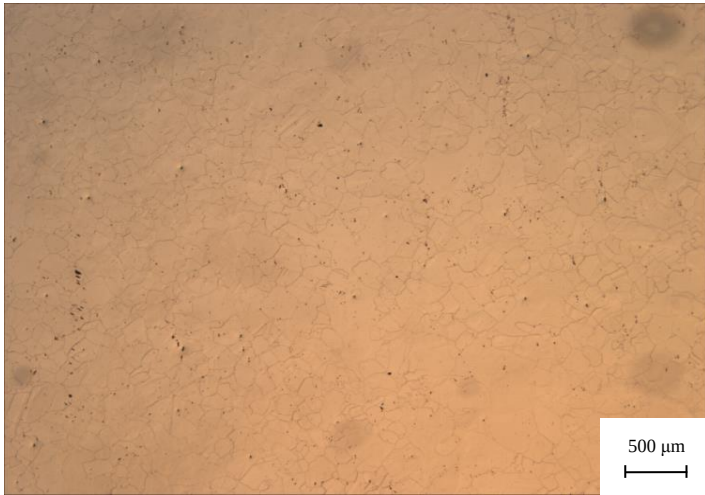
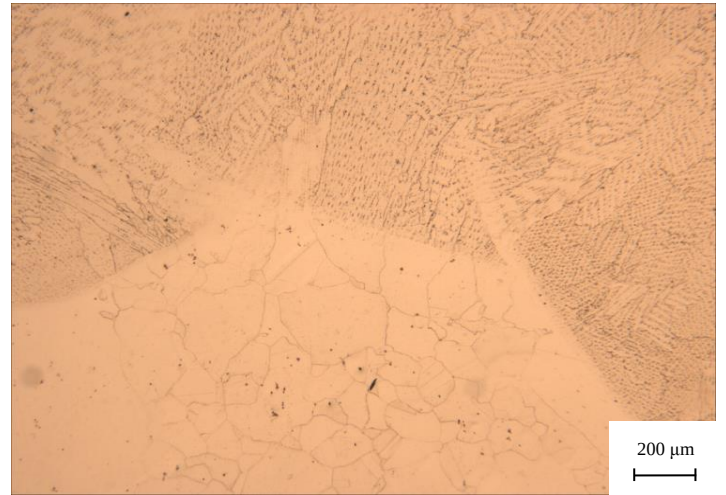
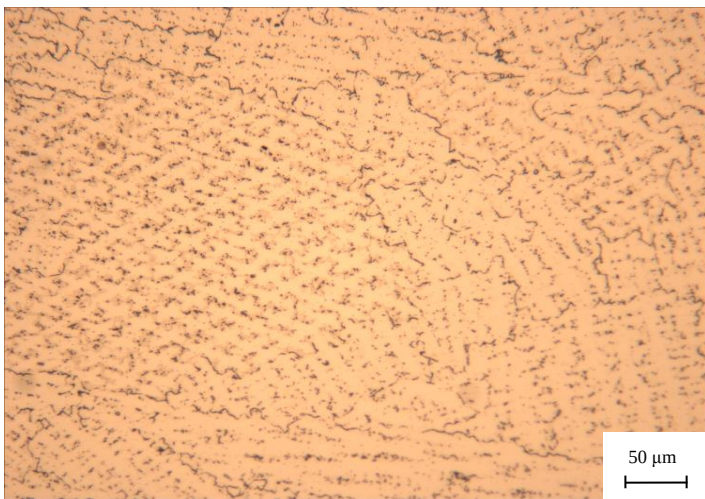
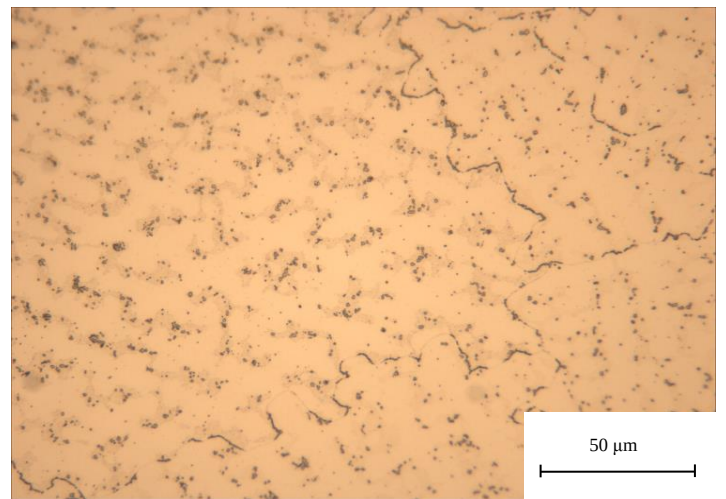
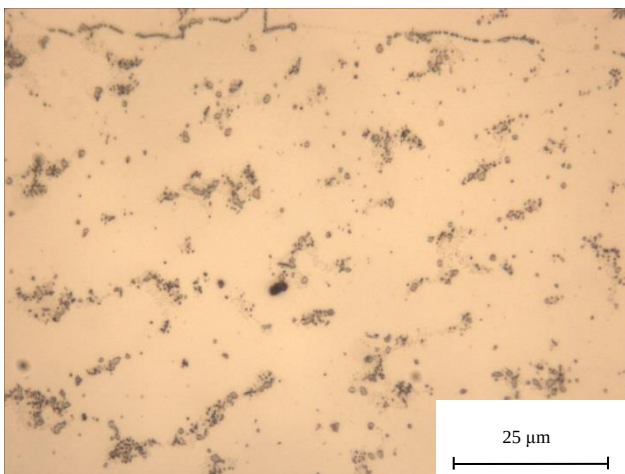
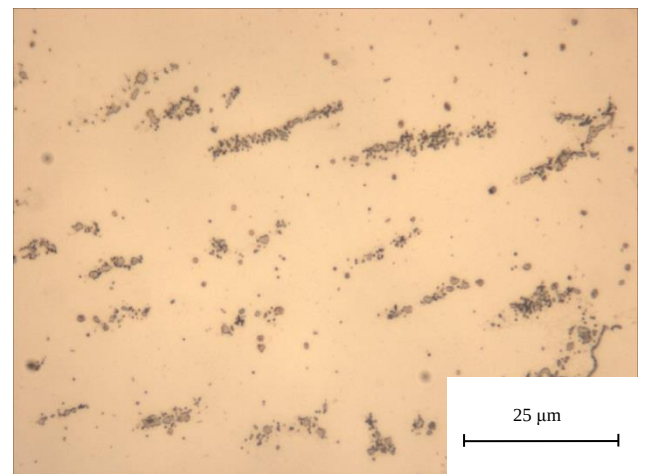
(a)**(b)****(c)****(d)****(e)****(f)**

Figure 5.10 – Optical micrographs for the stress relieved E.On sample showing (a) grain structure of parent material 2 x, (b) join between weld metal and parent 5 x, (c) Higher magnification of weld structure 20 x, (d) high magnification image showing the formation of equiaxed dendrites 50 x, (e) micrograph showing precipitation within the interdendritic zone 100 x and (f) micrograph showing precipitation concentrated within the interdendritic zone of an area containing more elongated dendrites 100 x.

Figures 5.10 (a – f) show a series of micrographs highlighting the microstructure of the stress relieved welded sample produced by IP (I). Figure 5.10 (a) shows that the grain size is similar to that in the ‘as welded’ sample, the presence of the large grains were again observed. The HAZ in the stress relieved sample shown in Figure 5.10 (b) is very small compared to the 200 μm one present in the ‘as welded’. The grain structure in the weld areas again seem to be serrated, this can be observed in Figure 5.10 (c) and (d). Although both elongated and equiaxed dendrites were observed in the weld areas Figure 5.10 (d) and (e) is an example of an area containing the equiaxed dendrites. The interdendritic zones of the dendrite areas contain significant precipitation of what in optical microscopy looks to be the copper colour MX phase surrounded by some small precipitates, this can be seen in Figure 5.10 (e) and (f).

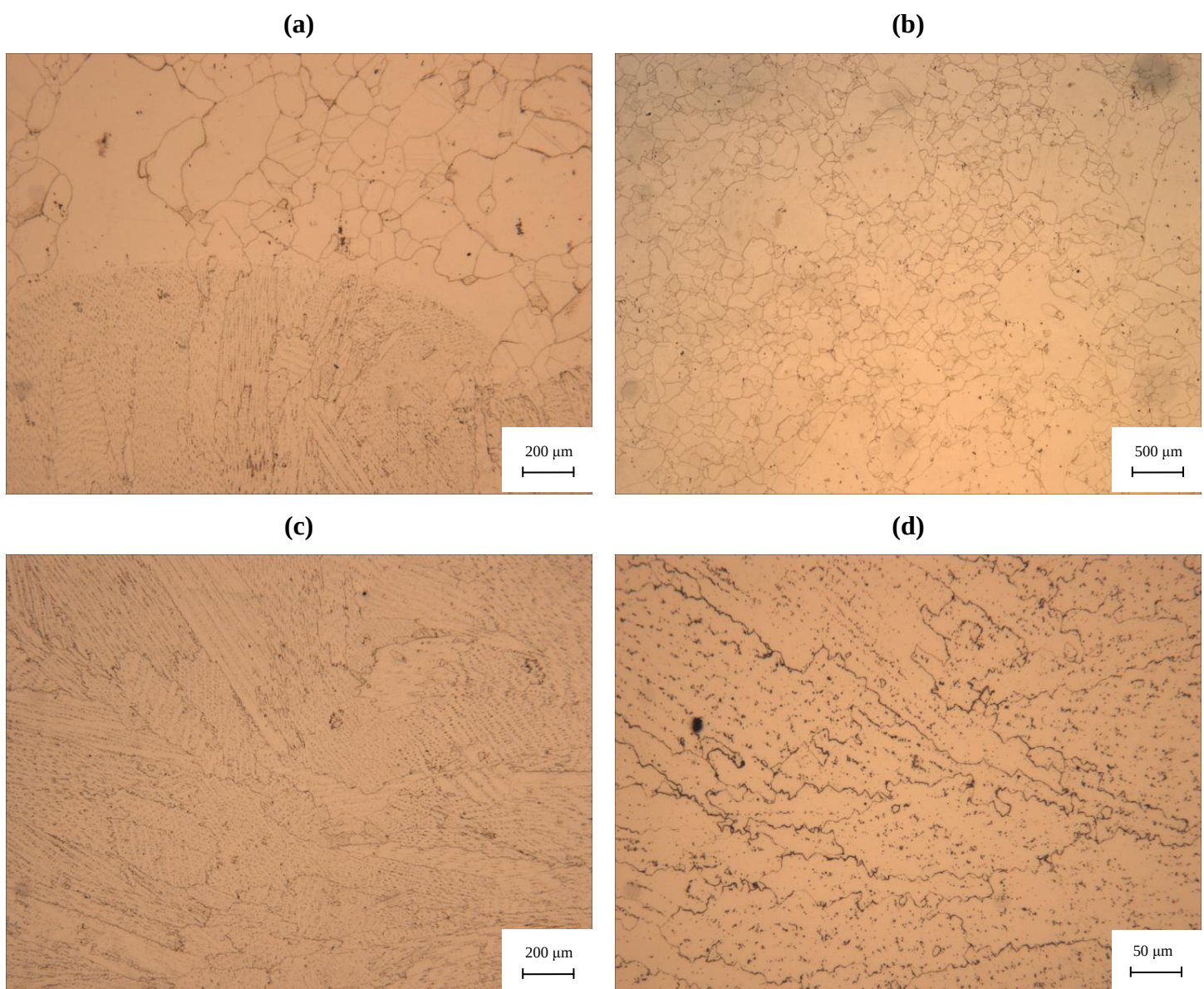
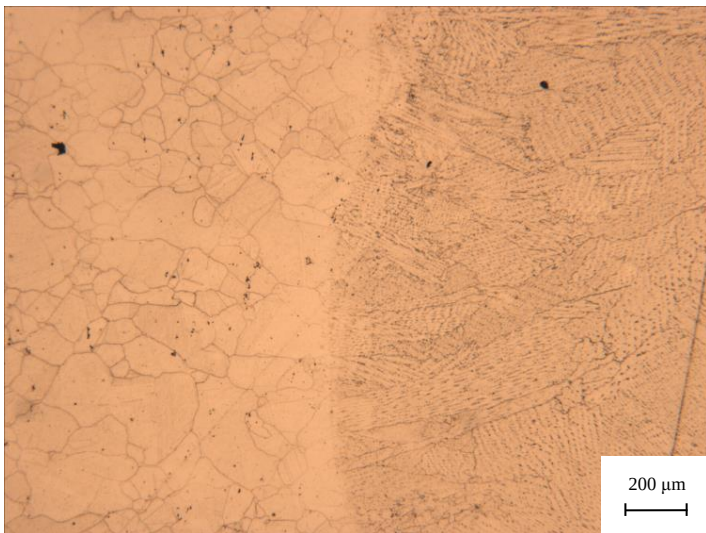


Figure 5.11 – Optical micrographs for the hardened E.On samples showing (a) join between weld metal and parent 5 x, (b) grain structure of parent material 2 x, (c) weld microstructure 5 x (d) weld microstructure 20 x

Figures 5.11 (a – d) show a series of micrographs highlighting the microstructure of the hardened welded sample produced by E.On. Again, in contrast to the ‘as welded’ sample the HAZ is seen to be non-existent with a clear interface between the welded and parent regions, this is shown in Figure 5.11 (a). The grain structure of the parent material observed in Figure 5.11 (b) and is typical of what has been previously observed with an average grain size of about 100 μm and the presence of the larger grains. Figure 5.11 (c) and (d) show that the weld grain structure is serrated with their size and shapes varying depending on the particular region of the weld metal looked at. MX precipitates are observed to form in an ordered fashion along a certain direction again depending on the particular region of the weld. Higher magnification images did not show any detectable precipitation in the interdendritic regions, as was observed in the stress relieved sample.

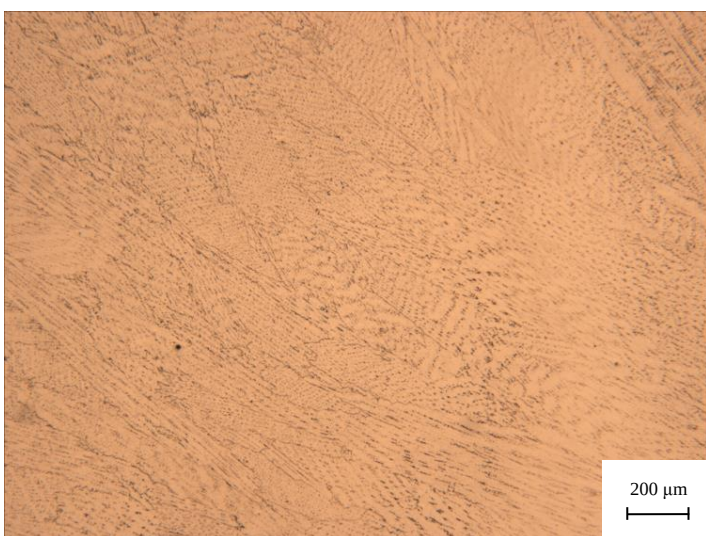
(a)



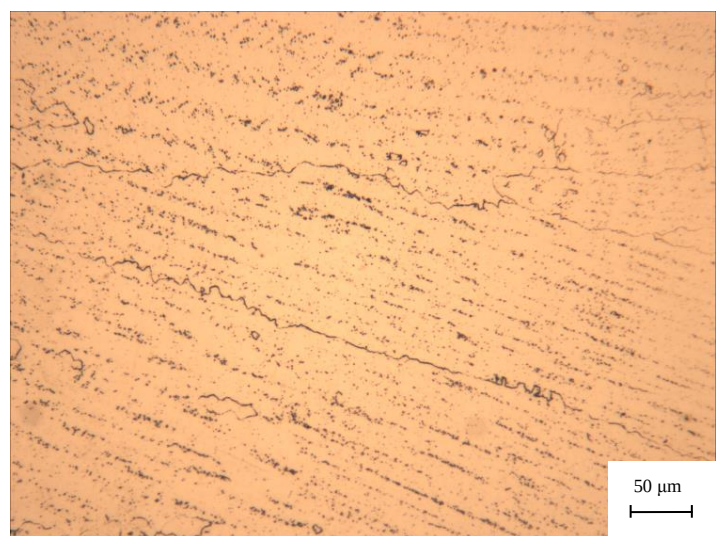
(b)



(c)



(d)



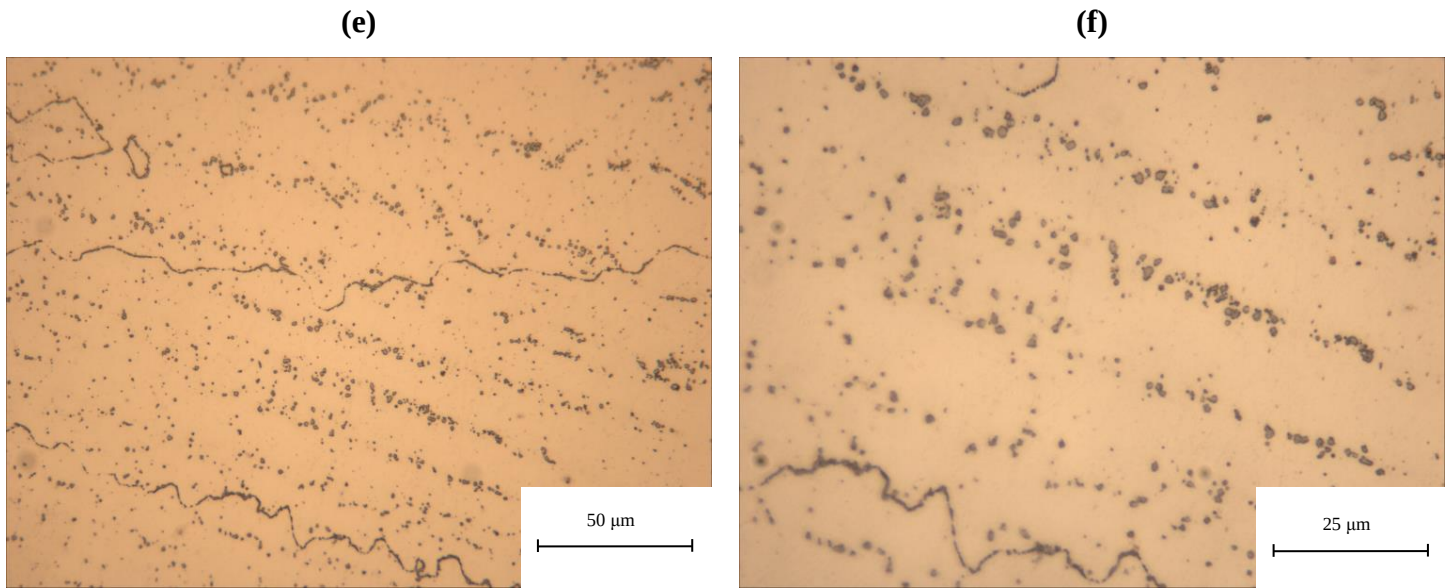


Figure 5.12 – Optical micrographs for the stress relieved Loughborough sample showing (a) join between weld metal and parent 5 x, (b) grain structure of parent material 2 x, (c) weld microstructure 5 x (d) weld microstructure 20 x, (e) weld microstructure 50 x, (f) weld microstructure 100 x

Figure 5.12 (a – f) show a series of micrographs highlighting the microstructure of the stress relieved welded sample produced at Loughborough. Results were typical of the stress relief heat treatment produced by IP(I), with the only change observed at high magnification showing less precipitation in and around the interdendritic areas.

Figure 5.13 (a – d) a series of micrographs highlighting the microstructure of the hardened welded sample produced by Loughborough. Results were typical of the hardening heat treatment produced by IP(I).

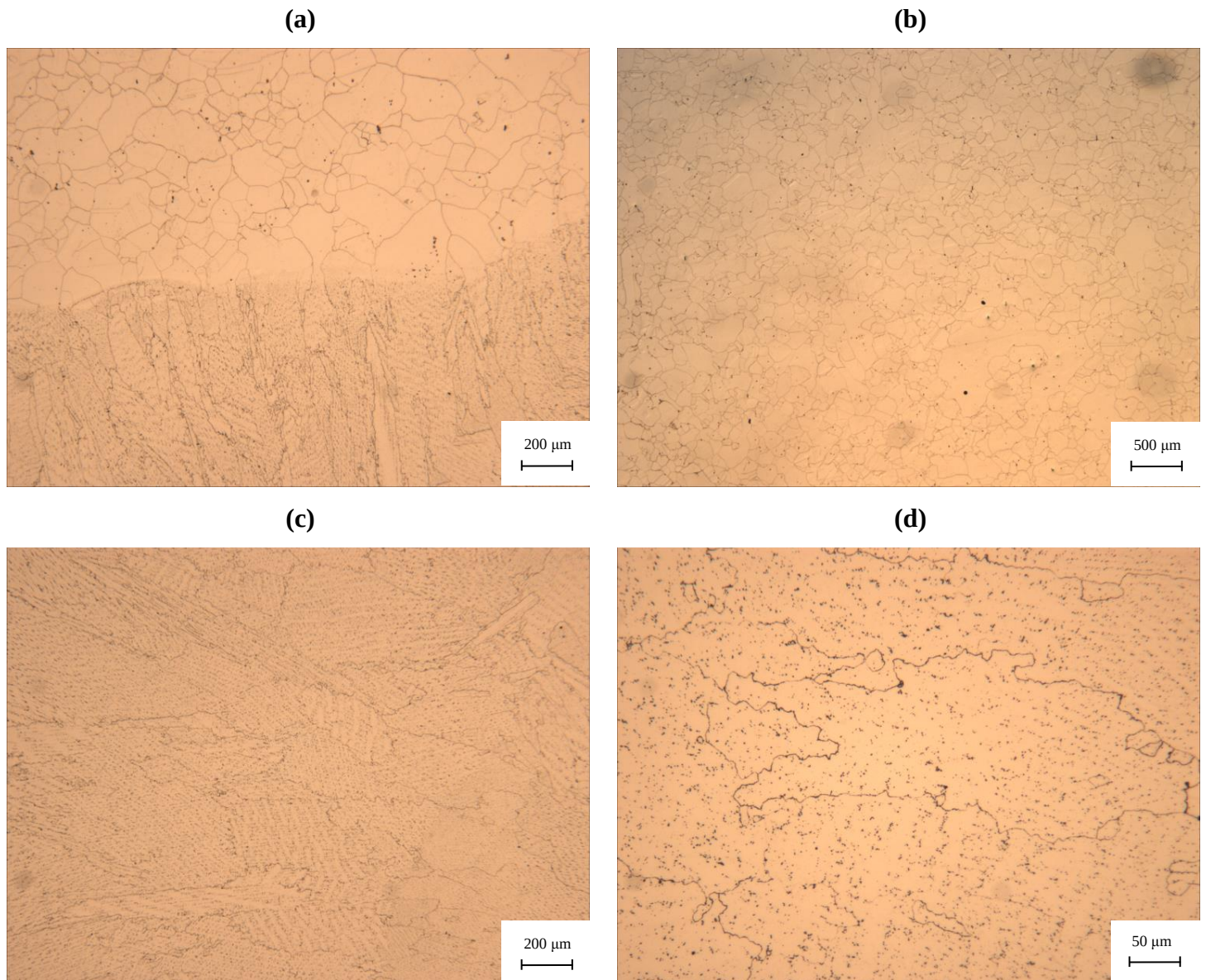


Figure 5.13 – Optical micrographs for the hardened Loughborough sample showing (a) join between weld metal and parent 5 x, (b) grain structure of parent material 2 x, (c) weld microstructure 5 x (d) weld microstructure 20 x

After conducting significant optical microscopy on the welds, it became clear that the microstructure of the welded samples was more complex than previously seen when looking at the isothermally aged forged samples. A significant programme of electron microscopy was therefore planned to study the precipitation trends in both the parent and the weld.

The inverse pole figure map shown in Figure 5.14 was produced using the EBSD technique and shows further evidence of serrated boundaries but also some misorientation within the welded grains. The IPF map shows how the crystallographic orientation of the weld metal changes from grain to grain with no preferred orientation observed.

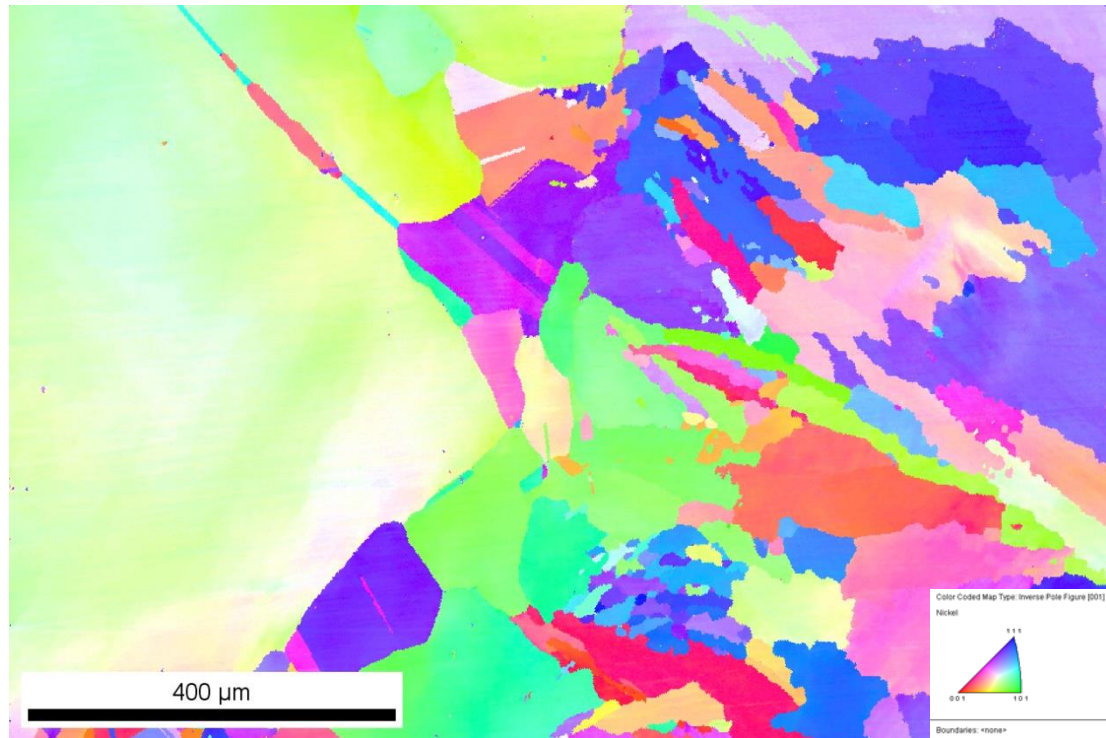
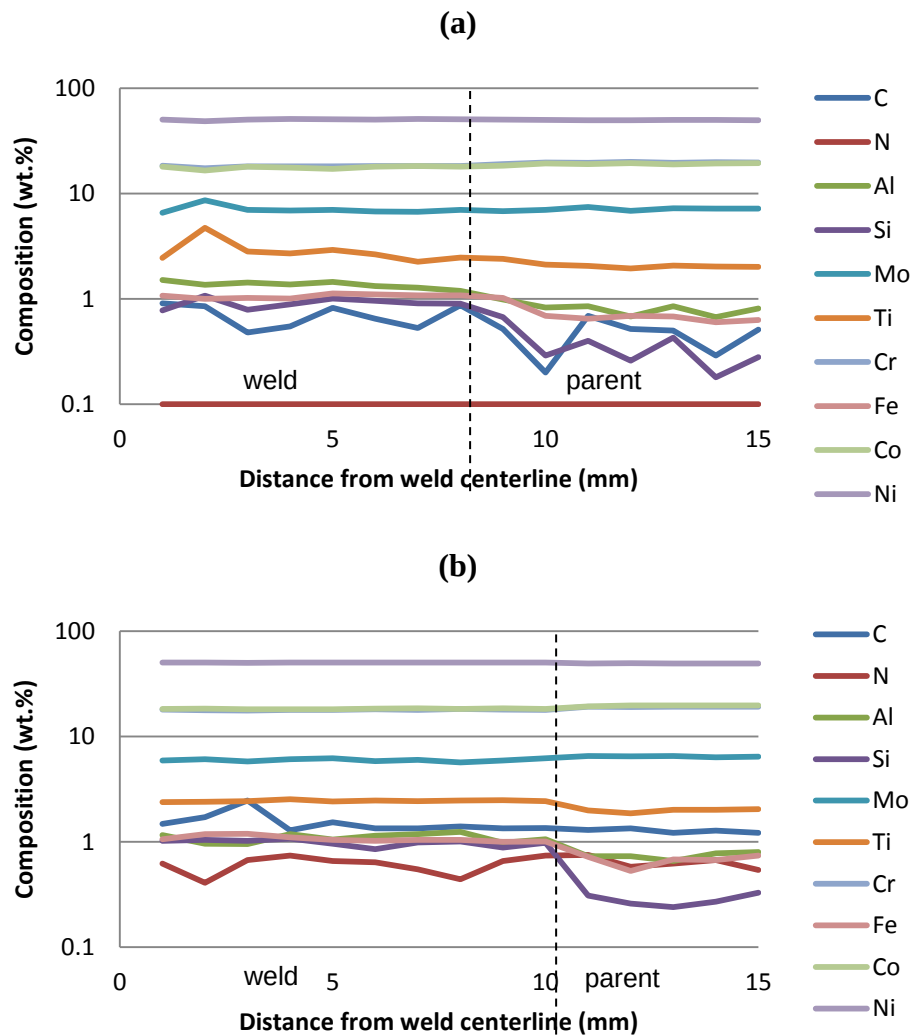


Figure 5.14 – IPF map show the crystallographic orientation within each grain

5.6 Chemical variation through the sample

The chemistry of each area, in addition to the thermal exposure dictates the precipitation behaviour of the particular area or region. To fully understand how the welded samples are behaving, the chemical evolution of each sample should be investigated. To assess this, the EDX technique was implemented in the form of a line scan, with an individual EDX spectra recorded every 1 mm.



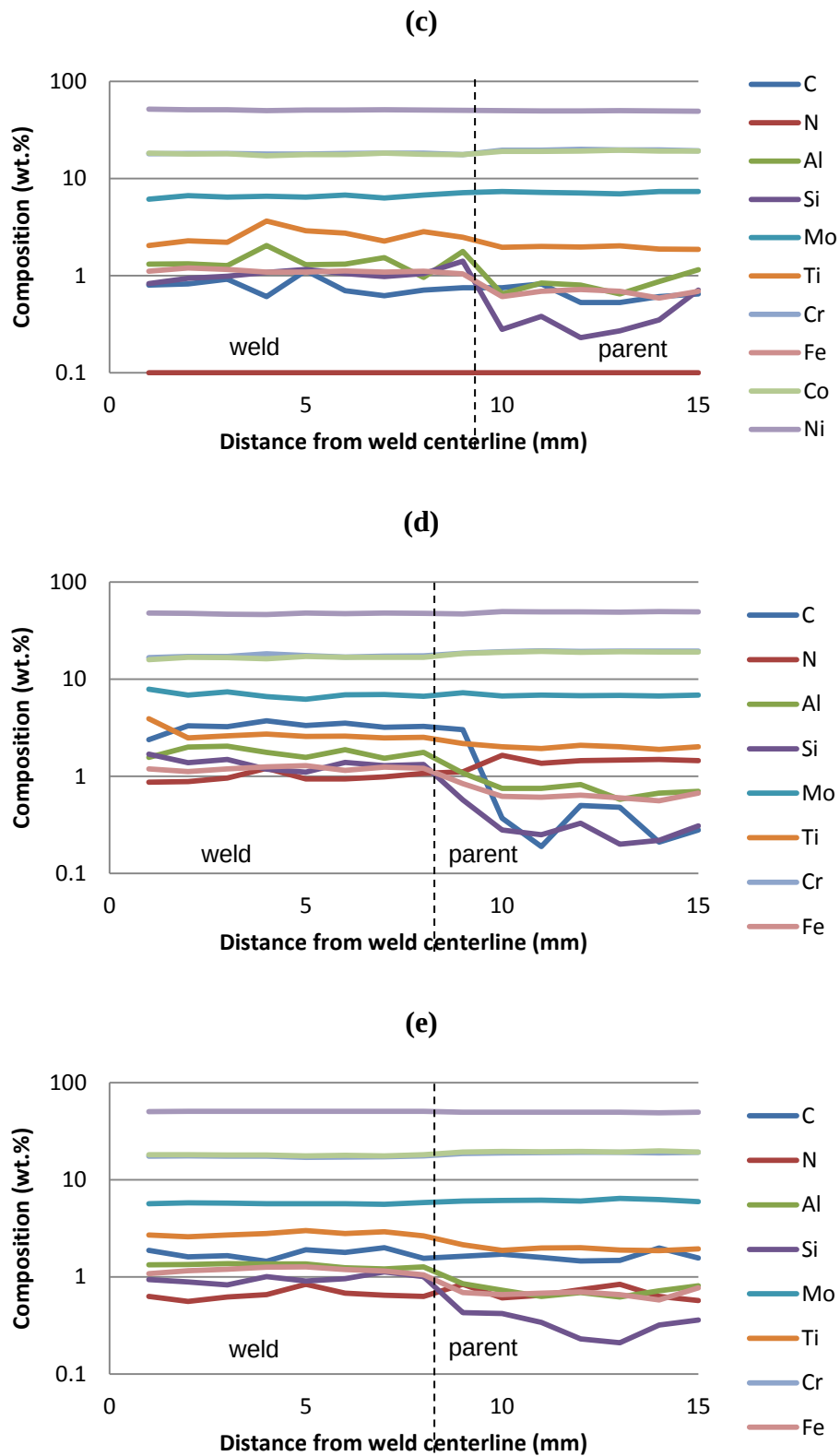


Figure 5.15 – Series of graphs showing the change in composition between weld and parent material for (a) as welded, (b) stress relieved E.On, (c) hardened E.On, (d) stress relieved Loughborough and (e) hardened Loughborough

The composition evolution of the welded samples shown in Figure 5.15 (a – e) show an expected change in the elements: C, Al, Si, Ti and Fe. There were small compositional differences between the different welded samples but the same overall trends were observed. A decrease in the level of C between the weld and parent material was detected in each of the welded samples changing on average from 1.59 wt.% in the weld metal to 0.87 wt.% in the parent. The detected change in C between weld and parent can only be viewed as an indicator of a difference in content between the two, as quantification of small atomic number elements is very limited using the EDX technique. In the case of the stress relieved sample shown in Figure 5.15 (d) there was a significant decrease in the amount of carbon detected between the weld and parent with the composition recorded to be 3.22 wt.% and 0.34 wt.% respectively. On average the Al content was seen to decrease from 1.37 wt.% in the weld metal to 0.76 wt.% in the parent. The Si content was seen to decrease from 1.03 wt.% in the weld metal to 0.31 wt.% in the parent. The Ti content was seen to decrease from 2.66 wt.% in the weld metal to 1.99 wt.% in the parent. Finally the Fe content was seen to decrease from 1.11 wt.% in the weld metal to 0.66 wt.% in the parent. The remaining elements included in the graphs showed little or no change. The variations can be accounted for by the difference in composition between the weld and parent material.

Optical work in section 5.5 indicated that the precipitation trends of the alloy varied within the dendritic and interdendritic areas. Due to this observation, thermodynamic calculations were carried out which predicted that the last liquid to solidify would be of a significantly different composition to that first formed. This composition was then used to model the precipitation in the last regions containing the last liquid to form. To see how this prediction compares it was decided to carry out some box EDS measurements on the dendritic and interdendritic area of the welds. It was decided to use the ‘as welded’ sample as that would contain the most severe segregation, as the samples subjected to post weld heat treatment would have experienced further diffusion. The results showed very little difference between the dendritic and inter dendritic areas. Although chemical segregation was observed after producing EDX maps of the weld microstructure.

5.7 Precipitate evolution

5.7.1 MX evolution

The MX phase is predicted to form throughout Nimonic 263 according to equilibrium calculations. Previous work carried out on Nimonic 263 found the MX phase to be present in three different forms: large Ti rich precipitates, and smaller Ti-Mo rich precipitates in two different morphologies, elongated and sub micron spherical precipitates. Research into the welded samples has not focused on MX precipitation, although the interactions between the MX and the γ' phase have been observed and commented on later in this chapter. Both the Ti rich and the Ti-Mo rich MX have been observed across all four conditions, however, the sub micron spherical were absent. The MX precipitates although observed throughout the weld material tended to precipitate out within the interdendritic regions as can be seen labelled in Figure 5.16 and Figure 5.17.

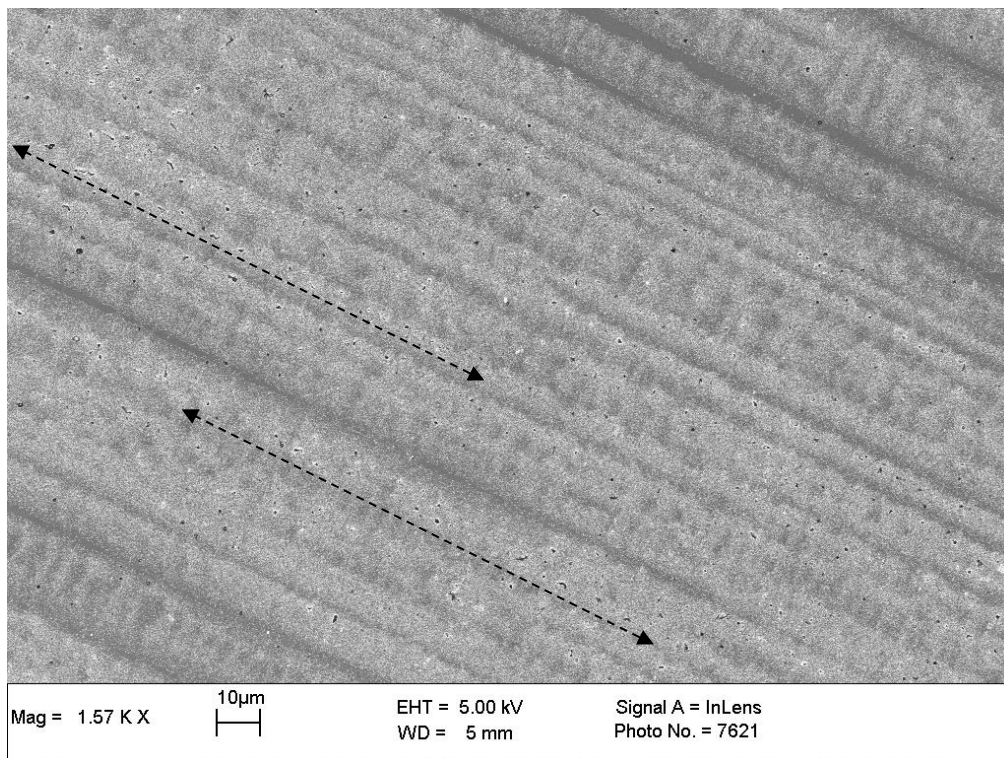


Figure 5.16 – Alignment of MX phase along the direction of dendrite growth in the interdendritic regions of the weld metal (stress relieved laboratory produced sample)

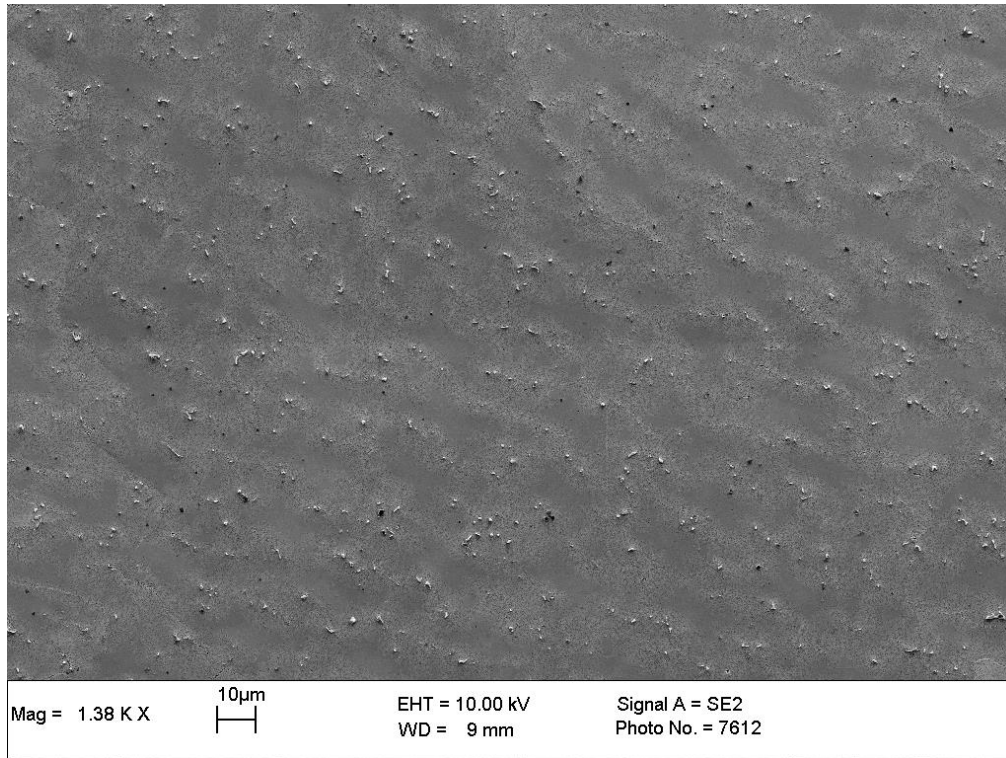


Figure 5.17 – Concentration of MX in the interdendritic regions of the weld metal (stress relieved laboratory produced sample)

5.7.2 Grain boundary precipitates

Carbon extraction replicas were produced to assess the grain boundary precipitates for the three post weld heat treatment conditions; As-welded, Stress relieved and hardened. Several extraction replicas were made for each condition. The replicas were taken only from the weld metal using the method discussed in the Experimental section. Analysis of the as-welded replicas showed little to no precipitates present in the weld metal.

Replicas from the stress relieved and hardened samples did show the presence of grain boundary precipitation as seen in Figure 5.18. Although not extracted the impression of the γ' phase has been imprinted on the carbon film and is observed throughout the replicas.

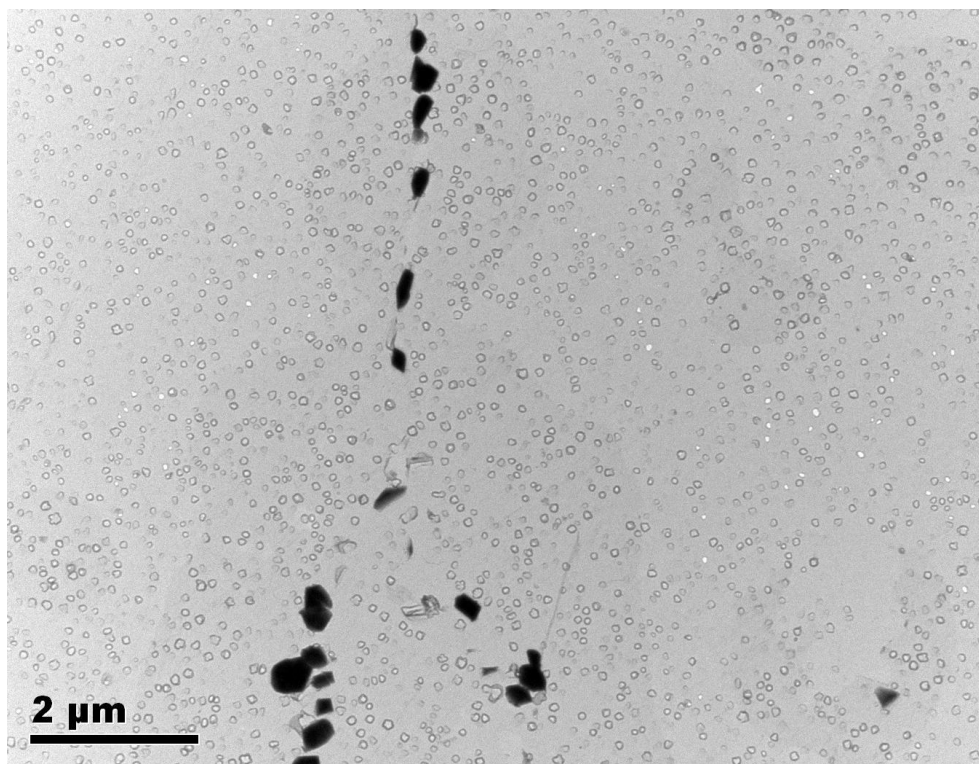


Figure 5.18 – TEM micrograph of a carbon extraction replica showing precipitation along a grain boundary (industrially produced stress relieved sample)

EDX analysis was carried out on the precipitates present in both the stress relieved and hardened samples, the results are shown in the form of a graph in Figures 5.19 (a) and (b).

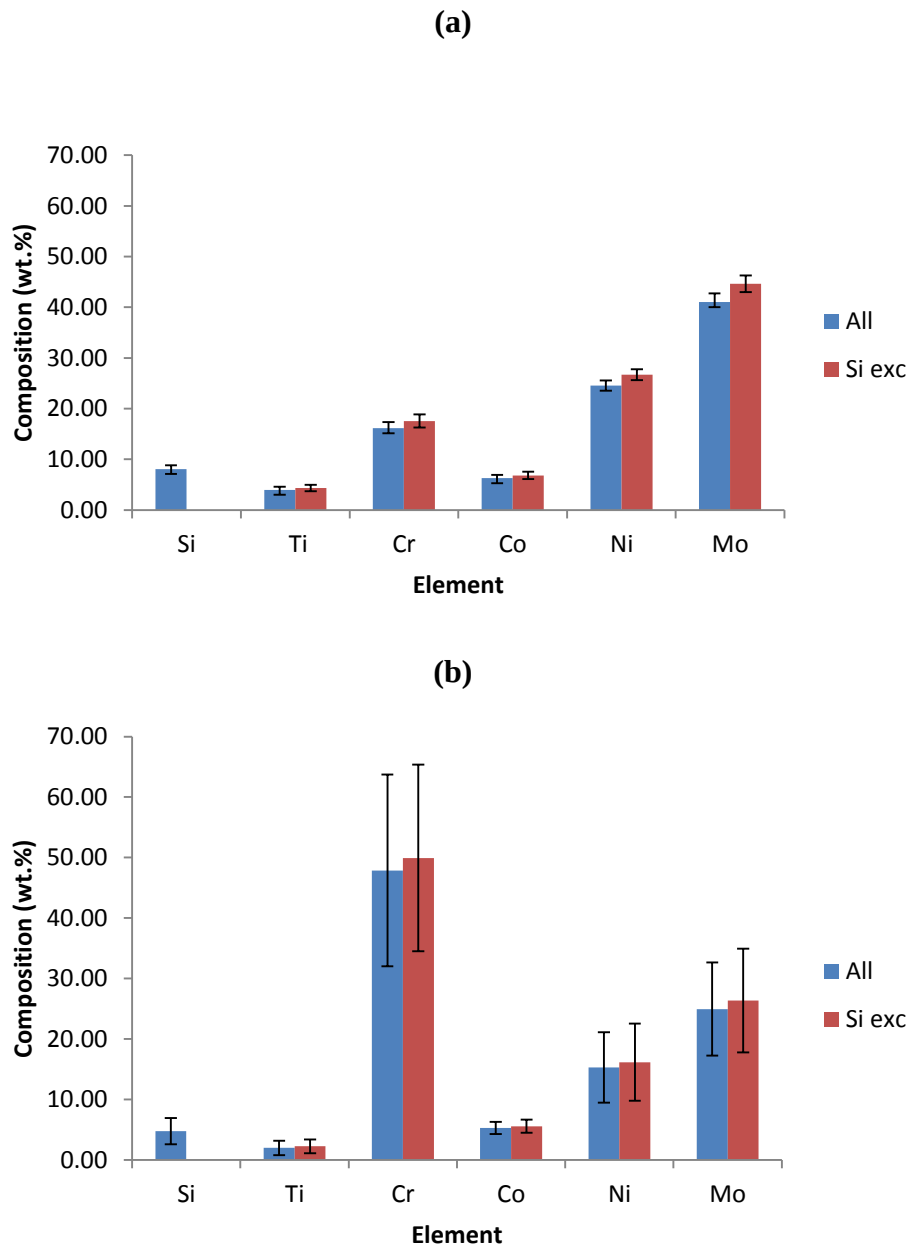


Figure 5.19 – (a) average EDX results from grain boundary precipitates in (a) stress relieved weld sample and (b) hardened weld sample

Results from both samples showed the grain boundary precipitates to be Mo-Ni-Cr rich with small amounts of Co, Ti and Si also detected. Although the analysed weld metal composition in Table 3.3 in the experimental section showed 0.71 wt.% Si to be present the amount detected in the grain boundary precipitates is high so an individual quantification was also produced with Si suspended, this is also shown in Figures 5.19 (a) and (b). The composition detected in the stress relieved sample is unlike the Cr rich $M_{23}C_6$ phase usually observed along grain boundaries or any other phase predicted to be present in the alloy. Using the

segregated composition listed earlier in the work another thermodynamic equilibrium calculation was produced allowing for further possible phases. The resulting calculation shown in Figure 5.20 predicts the presence of the high temperature carbide M_6C , at a peak of approximately 13 wt.% and stable between 835 and 1145°C. The M_6C phase has been highlighted on the graph.

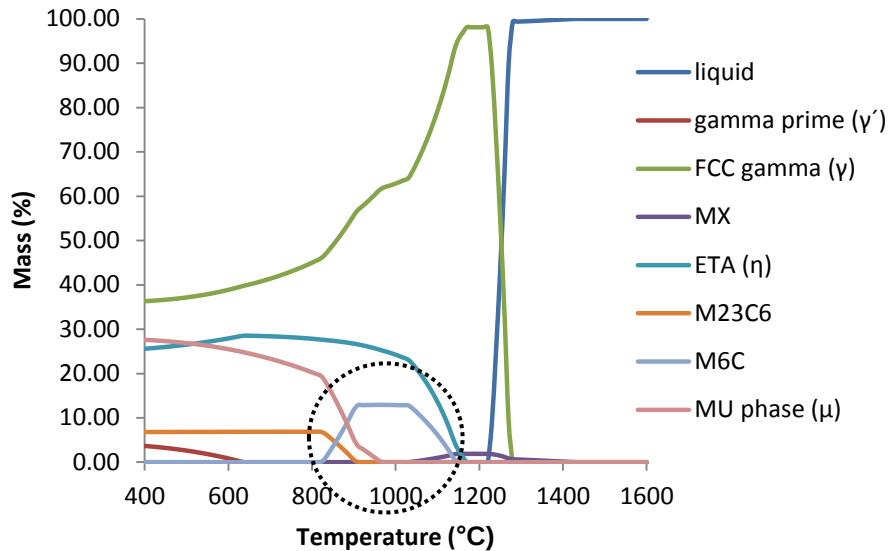


Figure 5.20 – Thermodynamic equilibrium calculation of the segregated composition showing the prediction of the M_6C phase

The chemistry of this predicted phase is similar to that detected using EDX analysis. The predicted composition of the M_6C is shown in Figure 5.21.

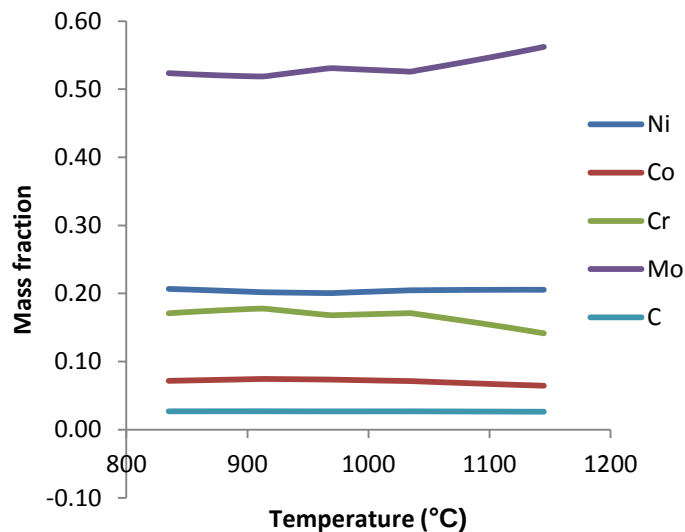


Figure 5.21 – Predicted phase composition of the segregated M_6C phase

The average composition of the M_6C carbide is predicted to be 53 wt.% Mo, 20 wt.% Ni, 17 wt.% Cr, 7 wt.% Co and 3 wt.% C. If this is compared to the EDX determined composition shown in Figure 5.18 (a) from the stress relieved sample a close match can be seen. The detected composition was 45 wt.% Mo, 27 wt.% Ni, 18 wt.% Cr, 7 wt.% Co and 4 wt.% Ti, carbon although detected was not quantified due to the inference of the carbon film. EDX results from the hardened weld sample showed a large standard deviation in the elements Cr, Mo and Ni. The large standard deviation suggests a lot of variation in the chemistry of the precipitates in this sample. The raw data shows the presence of two main compositions, a Cr rich and Mo rich phase. The Cr rich phase has a composition similar to that of the Cr rich $M_{23}C_6$ previously observed in Chapter 4 in relation to the isothermally aged samples.

5.7.3 γ' evolution

As mentioned in the literature review, the γ' phase is the principal strengthening mechanism in Nimonic 263, strengthening it through precipitation hardening. Understanding the precipitation and evolution of the γ' phase is important when predicting how the alloys will behave mechanically. Table 5.3 summarises information from Figure 5.22 (a) and (b), which are graphs displaying only the precipitation of the γ' phase. The table contains information on the mass fraction of γ' predicted to be stable and the dissolution temperature for both the calculations allowing for all phases and that with the Eta phase suspended for both parent and weld materials at equilibrium and that of the last liquid to form.

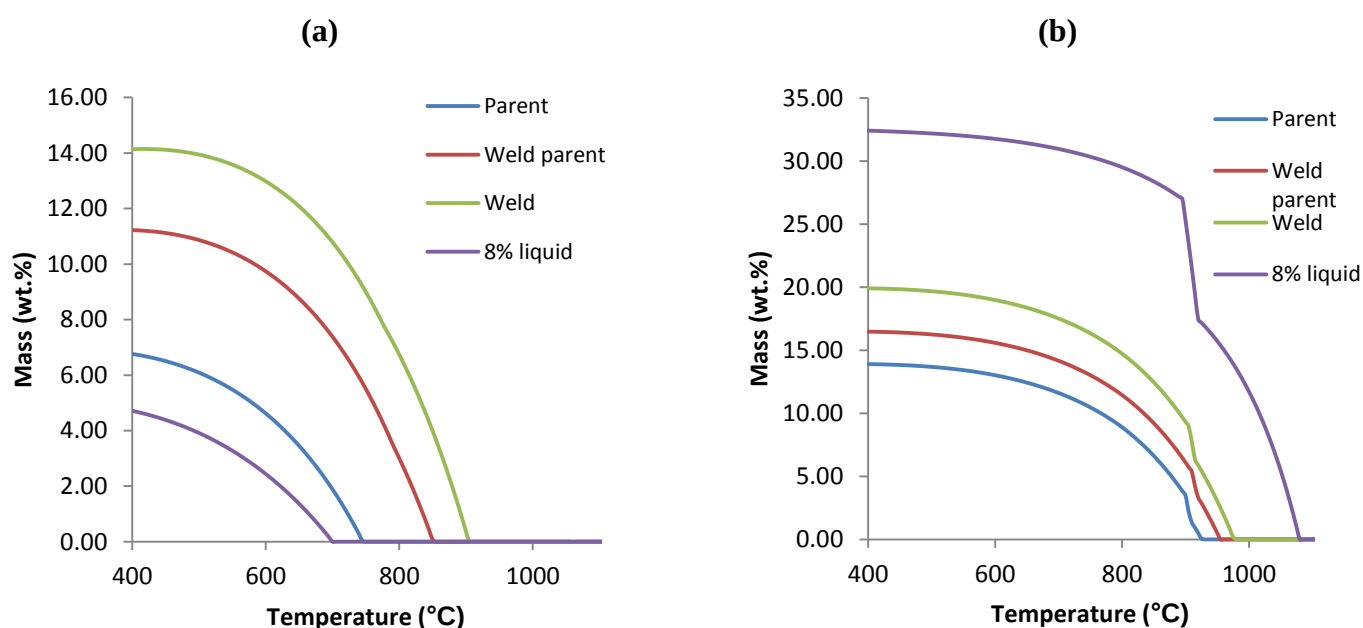


Figure 5.22 – Graph showing the γ' precipitation trends for (a) calculations allowing for all phases and (b) Eta suspended

Table 5.3 – Summarising the predicted γ' precipitation in the welded samples

	Parent		Weld Parent		Weld		8% liquid	
	Mass fraction (wt.%)	Dissolution temperature (°C)	Mass fraction (wt.%)	Dissolution temperature (°C)	Mass fraction (wt.%)	Dissolution temperature (°C)	Mass fraction (wt.%)	Dissolution temperature (°C)
All phases	6.76	745	11.22	870	14.14	900	4.71	730
Eta suspended	13.90	925	16.47	950	19.91	975	32.42	1075

As welded IP(I)

The γ' phase was observed after etching the welded samples with Fry's reagent for 50 seconds, exposure to this etch dissolves the γ' leaving holes that can be imaged using electron microscopy. For each sample both the average particle size and area fraction was calculated using image analysis software.

After preparation and analysis of the 'as welded' sample, imaging was carried out using the in-lens mode of the FEGSEM. Micrographs from this analysis are shown below in Figure 5.23 (a) and (b).

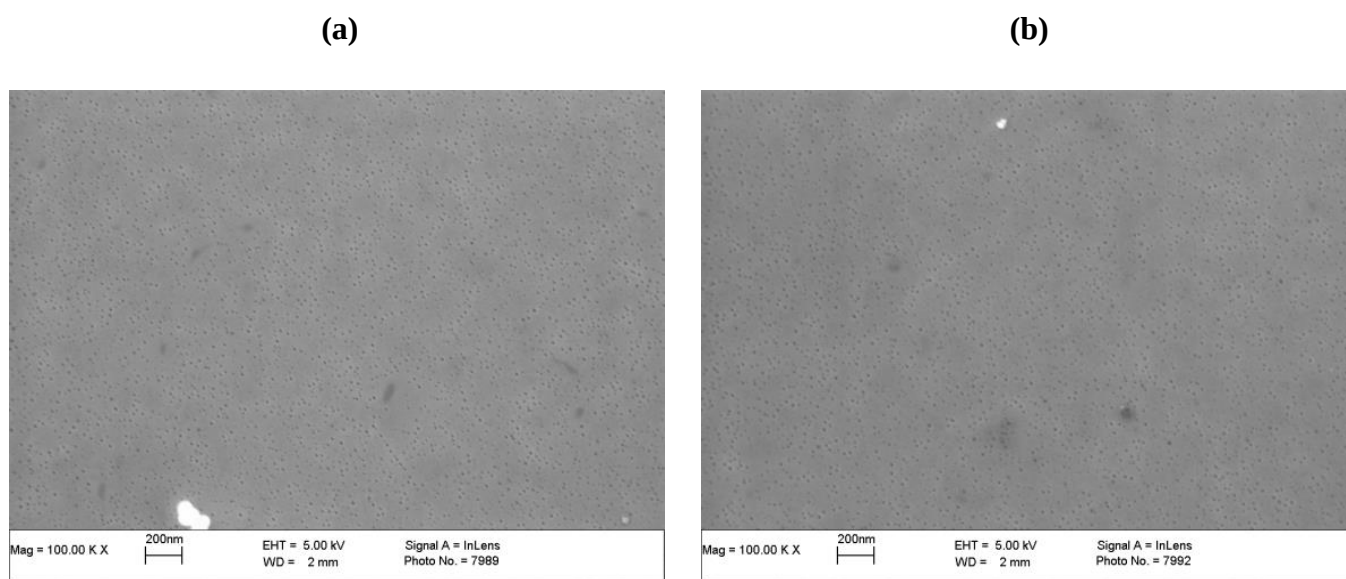


Figure 5.23 – Electron micrographs showing the presence of γ' in two areas of parent material (a) 10 mm from weld centreline and (b) 14 mm from weld centreline

Characterisation of the 'as welded' sample showed no γ' to be present in the weld metal, it was, however, present throughout in the parent material as shown in Figure 5.23 (a) and (b). In the parent material the average γ' size was calculated to be 12.8 nm. The exclusive presence of the γ' phase in the parent material may explain the higher hardness value in this region $\approx 30 \text{ HV}_{10}$ higher than in the weld.

EDX mapping was carried out to establish if there was any evidence of segregation between the dendritic and interdendritic regions of the weld. Figure 5.24 (a – e) shows one such map. It is clear that Mo, Si and Ti have segregated in the interdendritic regions of the weld.

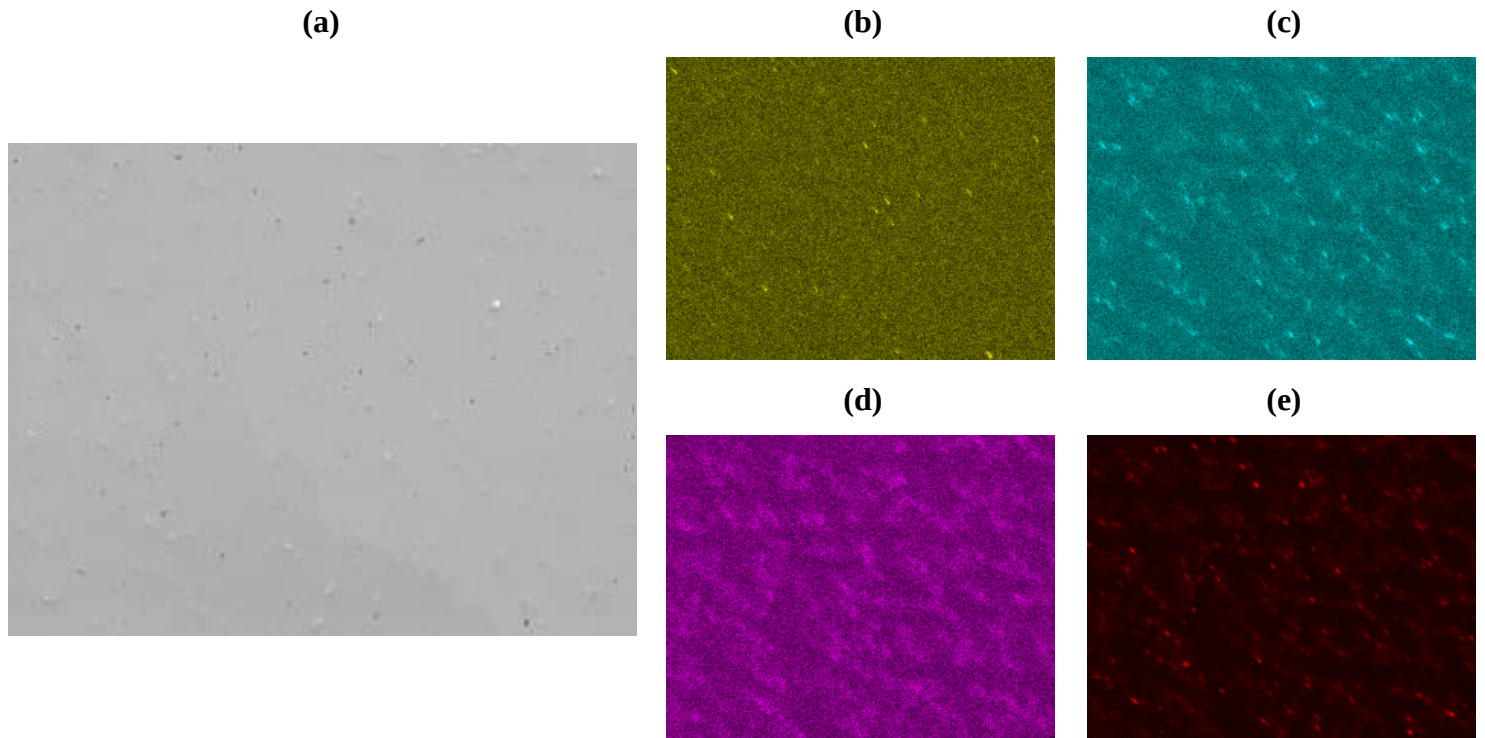


Figure 5.24 – EDS map showing (a) SE image (b) Al, (c) Mo, (d) Si and (e) Ti

Stress relieved sample - IP(I)

Analysis of the weld sample given the industrial stress relief heat treatment is shown in the micrographs in Figures 5.25 (a – f). Figure 5.25 (a) and (b) again show that γ' is observed in the parent material and calculated to be 12.5 nm in diameter. In the weld metal two distinct groups of precipitates are observed. The distribution of what is thought to be γ' is observed at two different sizes in the dendritic and interdendritic regions of the weld. The majority of the weld microstructure is made up of the dendrite area, in which the γ' was calculated on average to be 41.9 nm, see Figure 5.25 (d). In addition to these there is also the precipitation of some large spherical precipitates between 200 – 300 nm in diameter, concentrated within the interdendritic regions. Both regions can be seen in Figures 5.25 (c), (e) and (f).

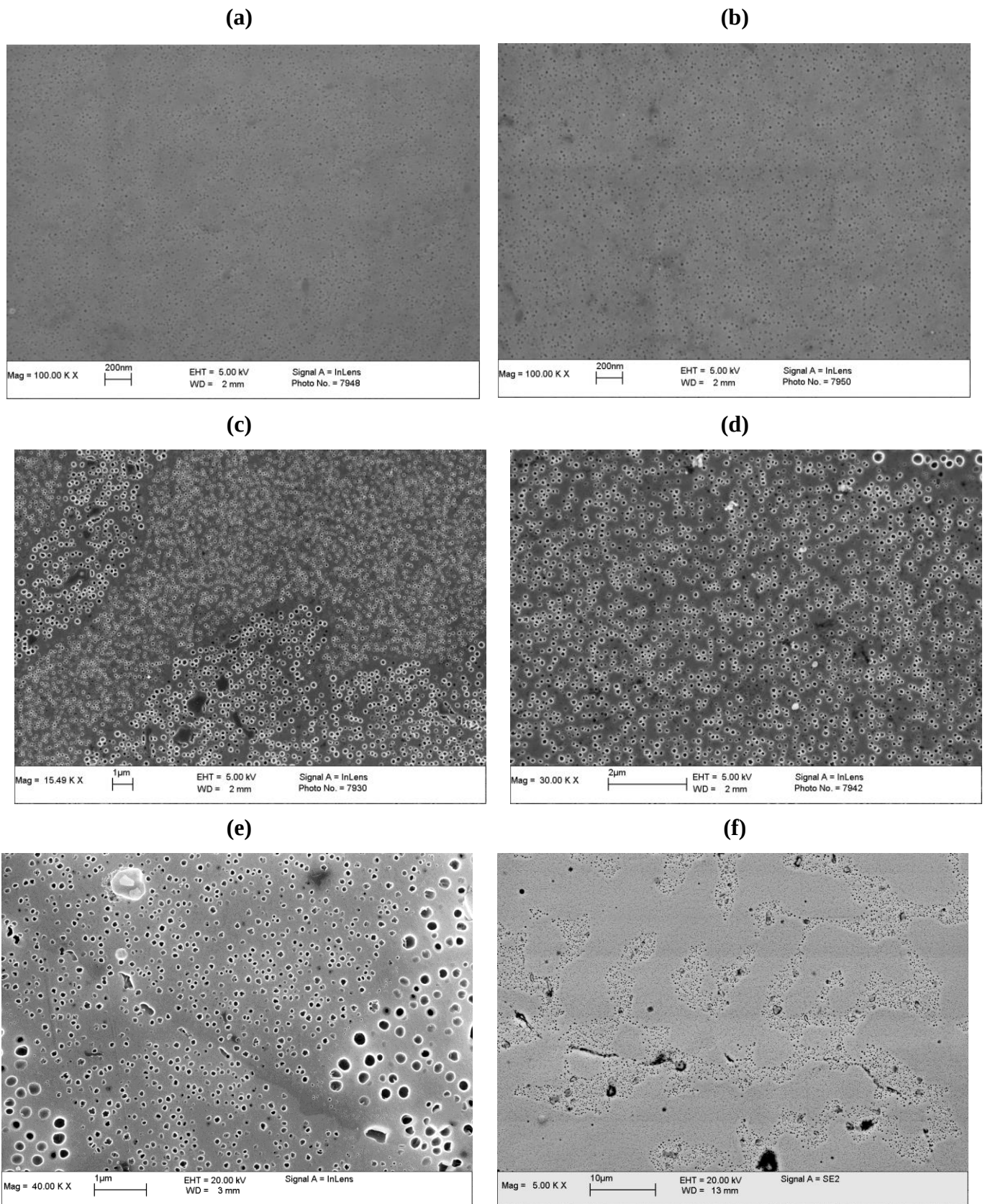


Figure 5.25 – Electron micrographs showings (a) and (b) presence of γ' in parent material, (c) presence of two regions of γ' precipitates of differing size, (d) γ' present in the dendritic regions of weld metal, (e) high magnification image of both regions containing the γ' phase and (f) micrograph clearly showing the different types of precipitation in both the dendritic and interdendritic structures.

Figure 5.25 (f) clearly shows the difference in the precipitation trends between each area. The image has been reproduced in Figure 5.26 to more clearly indicate the dendritic and interdendritic regions and outline the segregated microstructure.

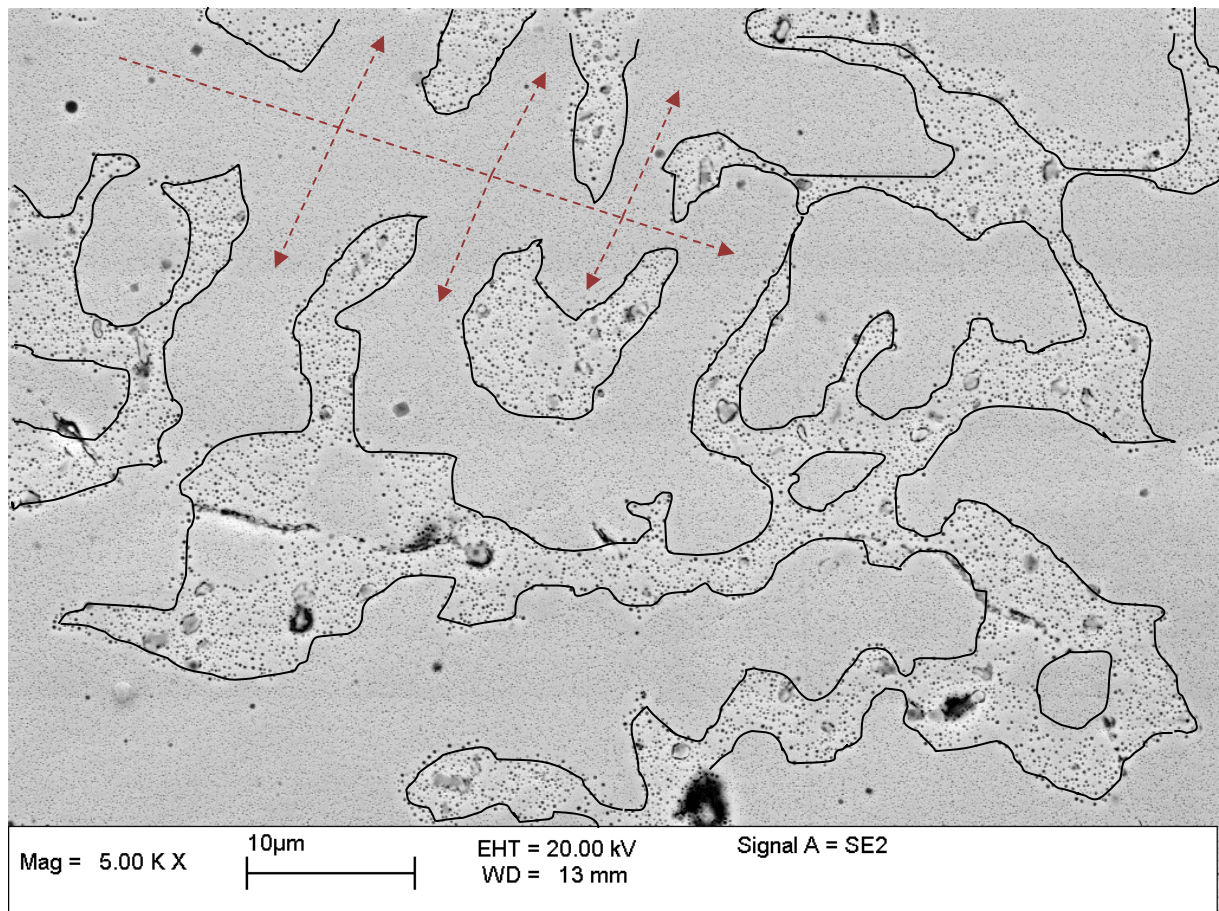


Figure 5.26 – SE micrograph of stress relieved weld metal with the interface between dendritic and interdendritic regions traced

After observation of the large spherical precipitates present in the interdendritic regions a thin foil was produce using the FIB in-situ lift out technique. The foil enabled a more detailed study into both the chemistry and crystallography of the precipitates to be carried out.

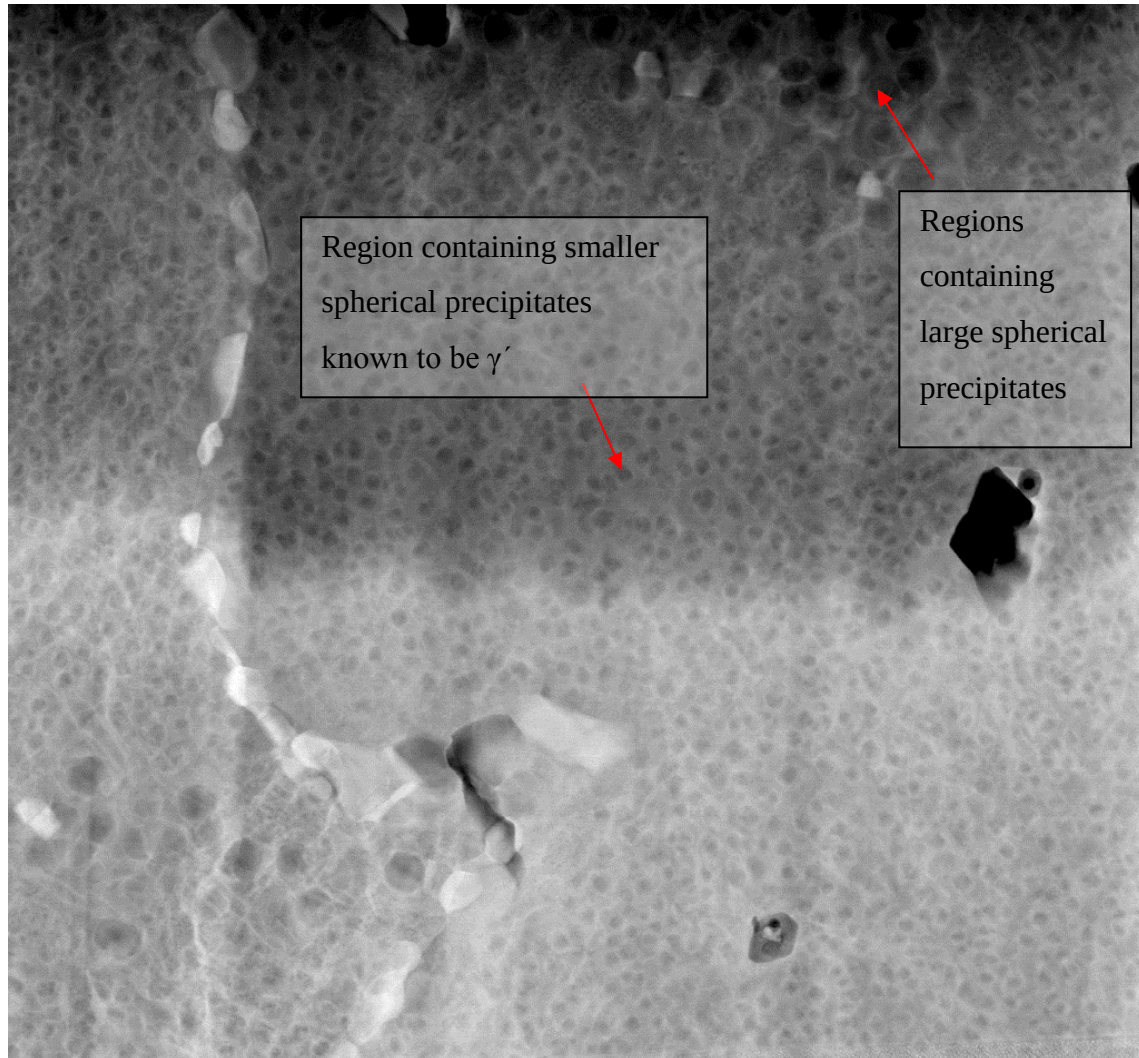


Figure 5.27 – High magnification STEM image showing both distributions of γ' in the stress relieved sample
Figure 5.27 shows the presence of both the smaller dendritic γ' and the larger interdendritic spherical phase thought to be γ' , these have been highlighted on the Figure. In addition to the bright field imaging, EDX maps of this area were also collected and are shown below in Figure 5.28 (a – g) and Figure 5.29 (a – g).

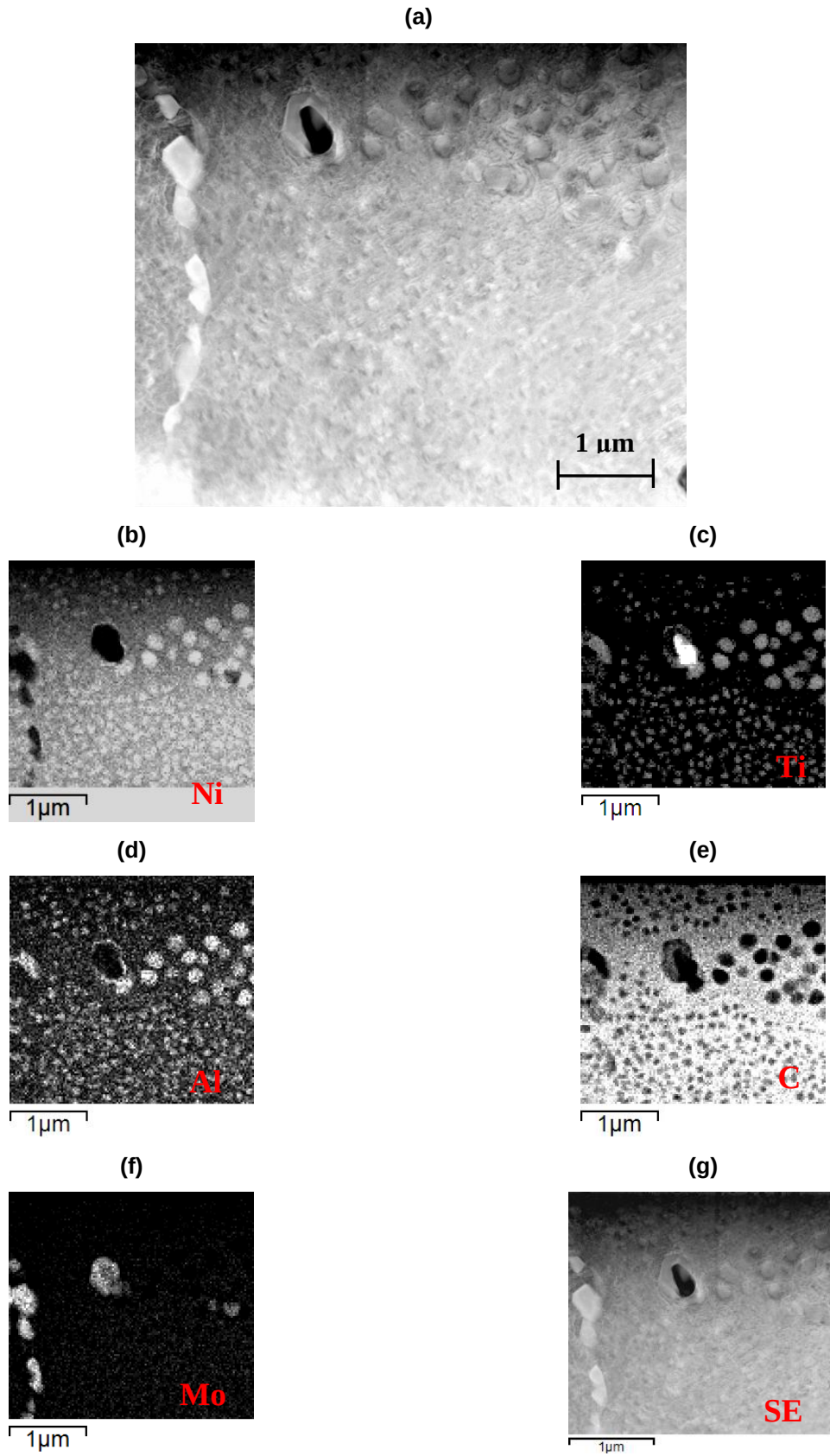


Figure 5.28 – Area 1 EDX maps showing (a) bright field image, (b) Ni, (c) Ti, (d) Al, (e) Cr, (f) Mo and (g) SE

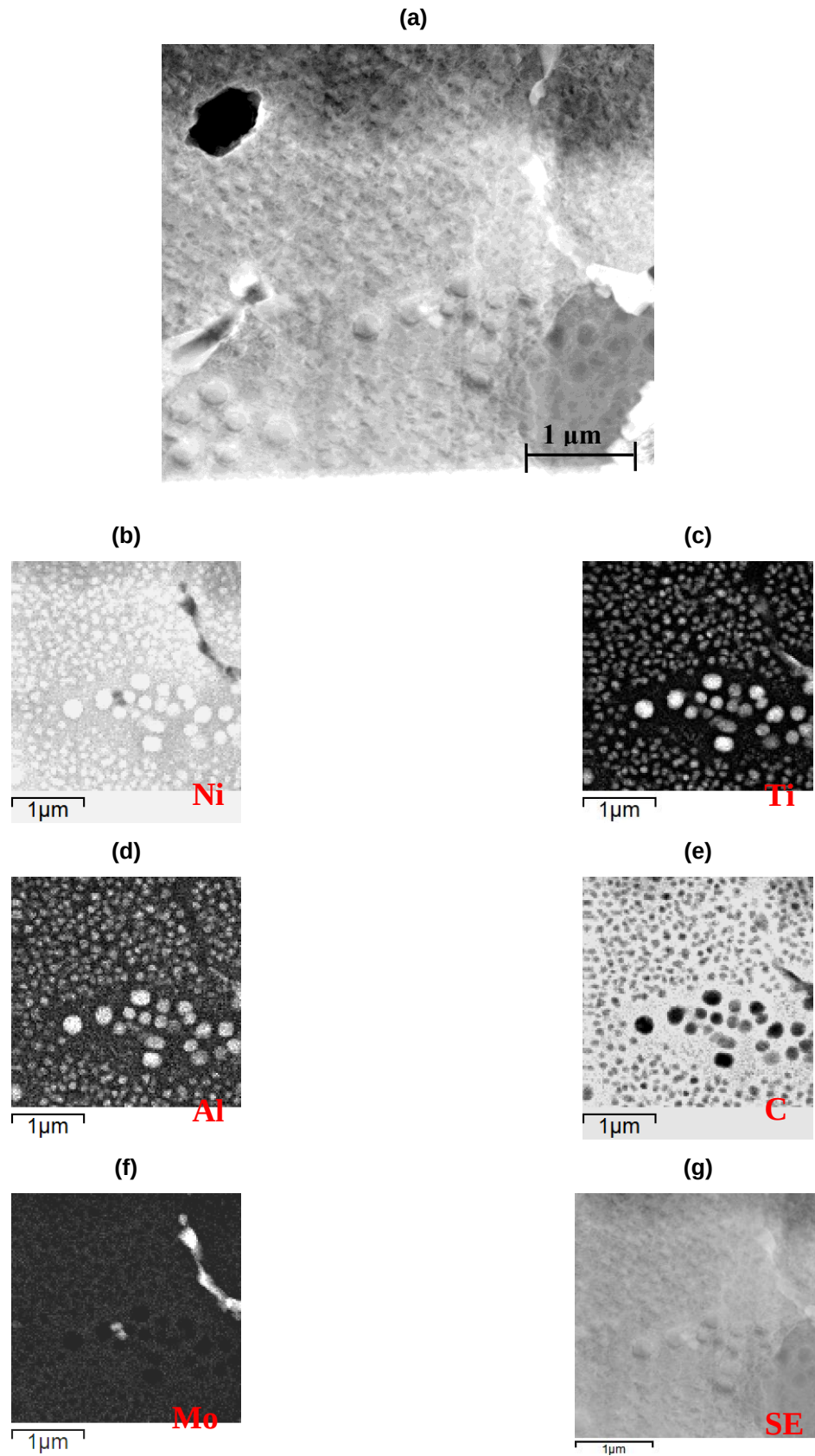


Figure 5.29 area 2 EDX maps showing (a) bright field image, (b) Ni, (c) Ti, (d) Al, (e) Cr, (f) Mo and (g) SE. The two EDX maps show similar results in terms of chemical concentrations in the scan area. The maps shown in Figure 2.8 and 2.9 indicate that the large interdendritic spherical phases

have the same composition as the smaller spherical phase known to be γ' . To further validate this theory, quantification on the maps spectra was carried out by using the software to trace around the large spherical phase and analyse their chemistry. Results are shown in Figures 5.30 (a) and (b) for 'areas' 1 and 2 respectively.

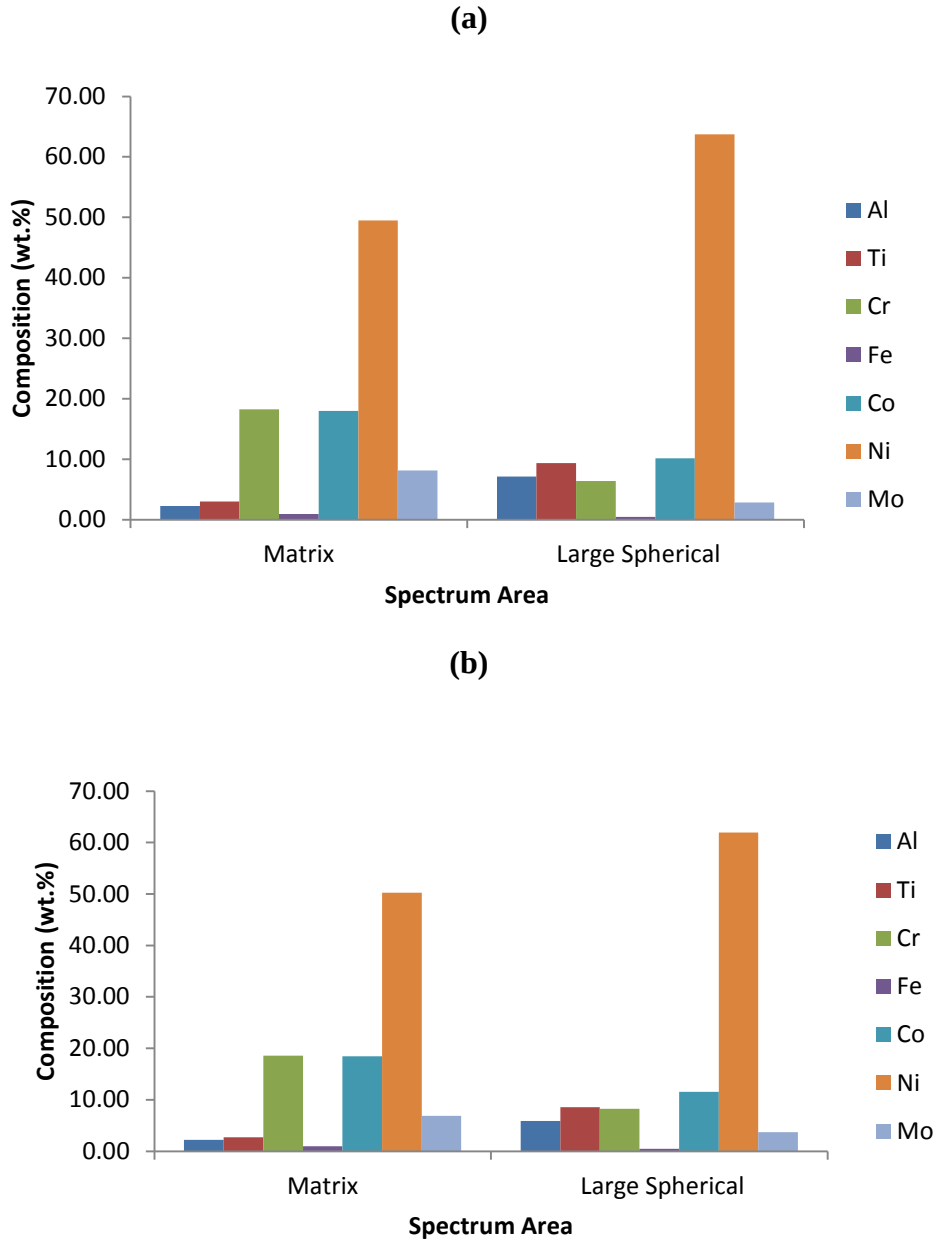


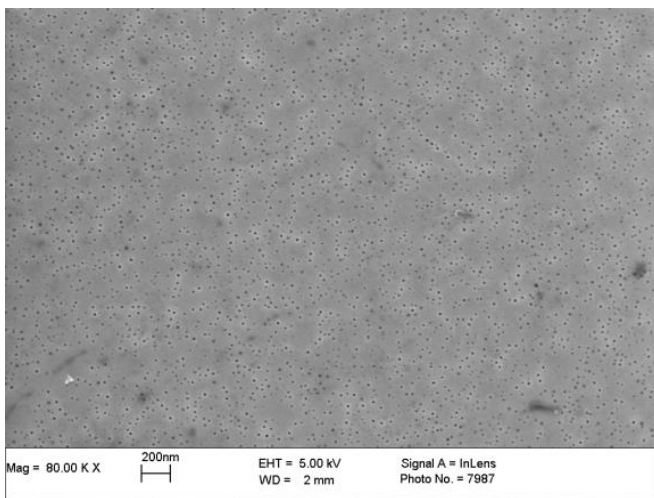
Figure 5.30 – EDX spectra results from (a) area 1 and (b) area 2 in the stress relieved weld metal

Both graphs indicate that, when compared to the matrix, the large spherical phases are higher in Ni, Ti and Al as would be expected of the $\text{Ni}_3(\text{Ti,Al})$ phase γ' .

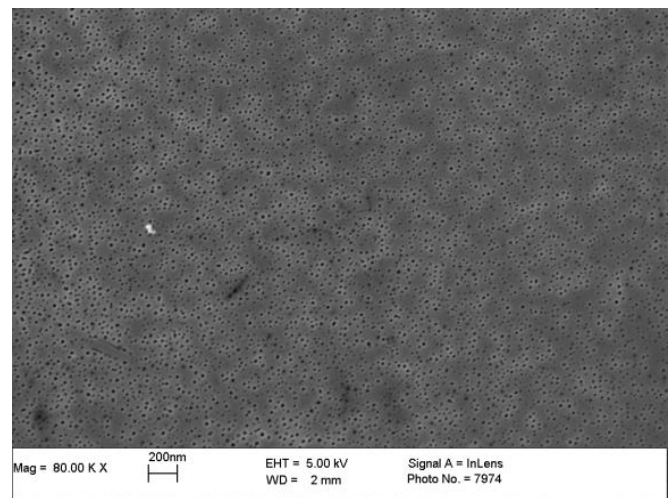
Hardened sample - IP (I)

Analysis of the weld sample given the hardening heat treatment in industry is discussed in the next section, and micrographs from this analysis are shown in Figures 5.31 (a – c). Both the parent and weld parts of the sample were found to contain γ' at 15.2 and 15.8 nm respectively. The area fraction of the γ' present in the weld was also significantly larger than that of the parent, 7% in the weld compared to 4.5% in the parent.

(a)



(b)



(c)

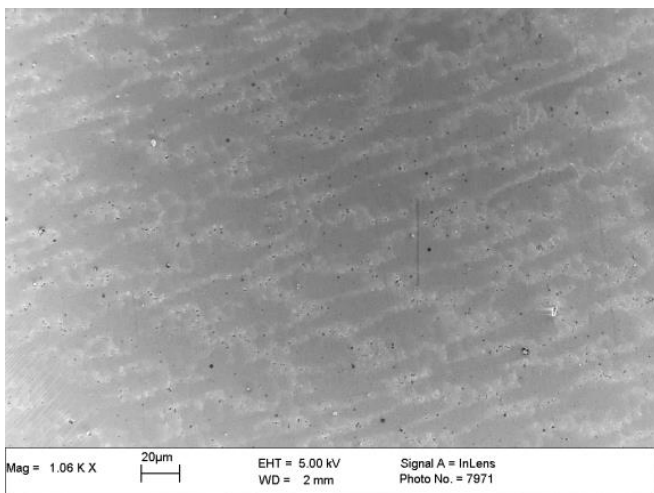
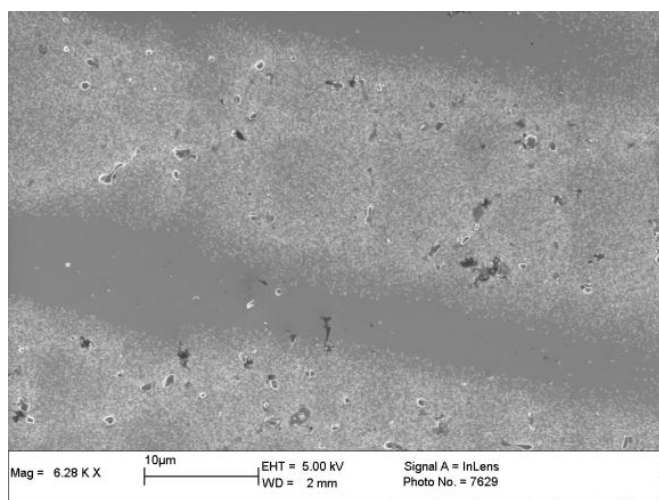


Figure 5.31 – Electron micrographs showing (a) presence of γ' in the parent, (b) presence of γ' in weld and (c) evidence of dendrites

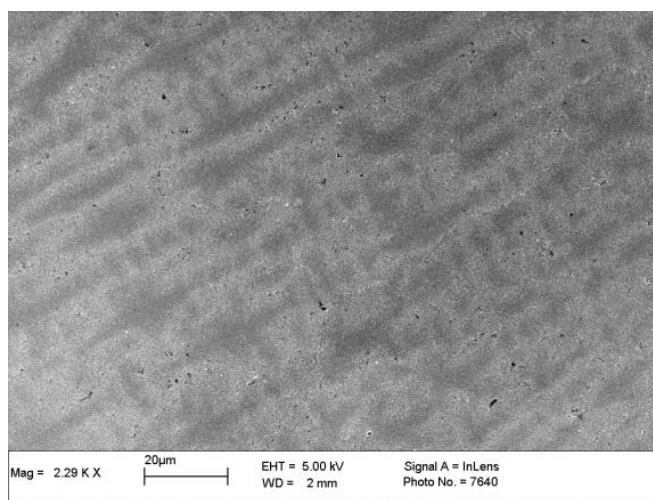
Stress relieved sample - laboratory heat treatment

The stress relieved sample produced in the laboratory showed no γ' to be present in the parent material, and only the high temperature MX precipitates remained after heat treatment. In the weld metal the dendritic zones also showed virtually no γ' precipitation, although γ' was present within and around the interdendritic regions as shown in Figure 5.32 (a). Evidence of the dendritic structure can be seen in Figures 5.32 (b) and (c). The average particle size of the γ' present in the interdendritic region is 38.7 nm.

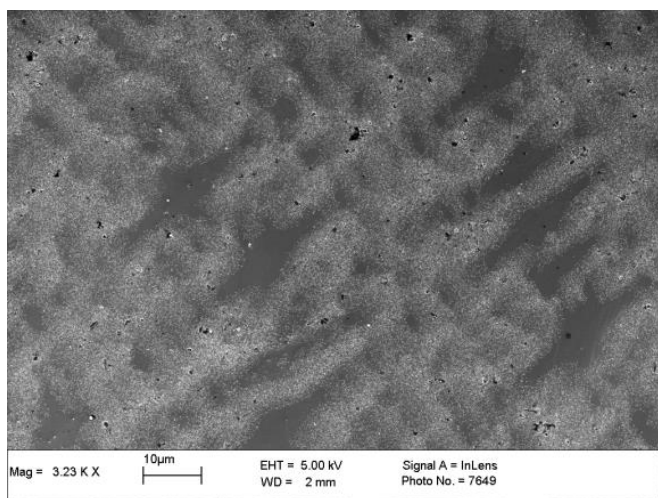
(a)



(b)



(c)



(d)

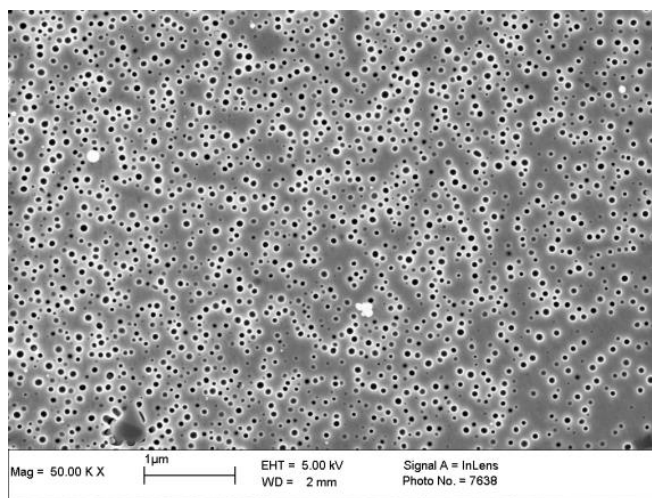


Figure 5.32 – Electronic micrographs (a), (b) and (c) showing interdendritic precipitation and (d) γ' present in interdendritic region

Hardened sample - laboratory heat treatment

The hardened sample produced in the laboratory showed γ' to be present in both the parent and weld metal. The dendritic structure present in previous samples is less evident than in the hardened lab produced sample, this can be seen in Figure 5.33 (a) and (b). Similarly to industrially hardened sample γ' is present in both the parent and weld metal at approximately the same size, 12.7 and 11.7 nm respectively. Again, in accordance to the results from the industrially hardened samples the area fraction of the γ' is higher in the weld at 8.5% compared to 6.1% in the parent.

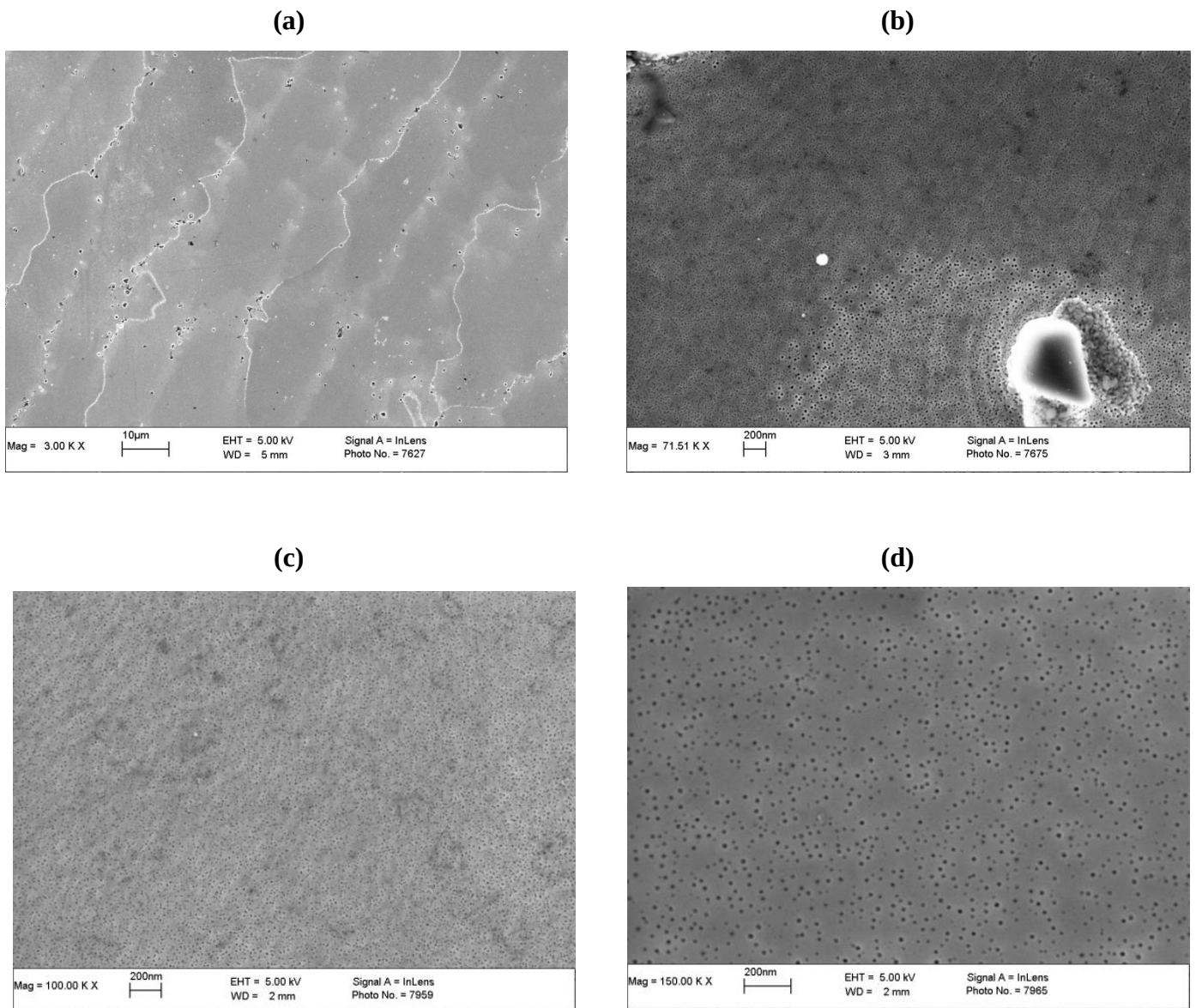


Figure 5.33 – Electron micrographs (a) showing an overview of the precipitation trends in the alloy, (b) the presence of larger γ' in the segregated region situated around MX precipitate (c) the γ' present in the parent material and (d) the γ' present in the weld

Results from the initial characterisation work suggest that there are significant differences in the precipitation trends of both the industrial and laboratory produced samples. The three post weld heat treatments have also produced different microstructures, as would be expected. Differences in precipitation trends between the dendritic and interdendritic regions were also noted.

Results from the two hardening post weld heat treatments show little difference, with similar hardness values recorded in both cases. The average γ' size of the two hardened samples showed variation between the industrial and laboratory produced sample but both the particle size in the parent and weld were similar in each sample. The hardness increase from parent to weld can be attributed to the area fraction variation of the γ' in each region. The stress relieved samples showed more marked differences between the industrial and laboratory heat treatments. The hardness in the parent metal of the laboratory heat treated sample is low when compared to the industrially produced sample, which can be linked to the lack of γ' observed in the parent region compared to the precipitation observed in the weld. The partial precipitation of γ' in the weld region of the laboratory produced samples can be seen to have little effect on its hardness when compared to that of the industrially produced weld metal. In the stress relieved samples, the γ' size was measured to be slightly larger in the industrially treated sample, although this can be attributed to slight coarsening due to slower cooling as a result of the larger section size.

Stress relieved + Hardened sample - IP (I) followed by laboratory heat treatment

A further post weld heat treatment sample was produced by combining the stress relief and hardened post weld heat treatments. This was carried out by sectioning a piece of the industrially heat treated stress relieved weld and heat treating it at 800°C for 4 hours in a furnace. Results are shown below in Figure 5.34 (a – d). The micrographs shown in Figure 5.34 (c) and (d) show γ' to be present in both the parent and weld regions of the sample at 17.2 and 45.2 nm respectively. The interdendritic regions observed in Figure 5.34 (b) containing the large spherical γ' were again observed, with no obvious changes in their area fraction or size of the precipitates contained.

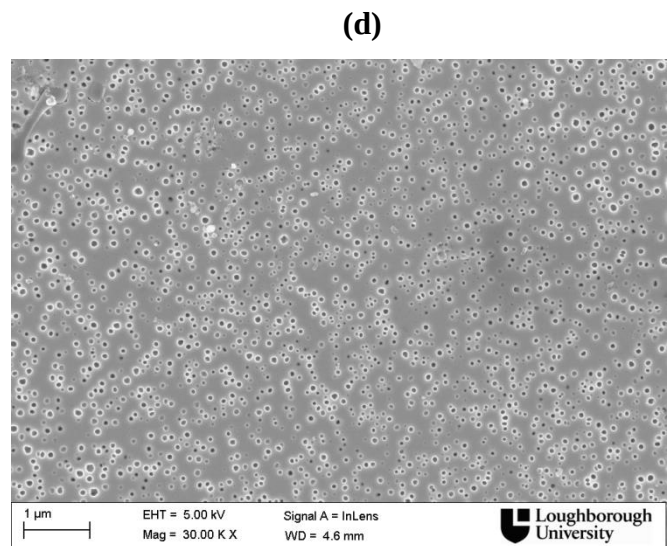
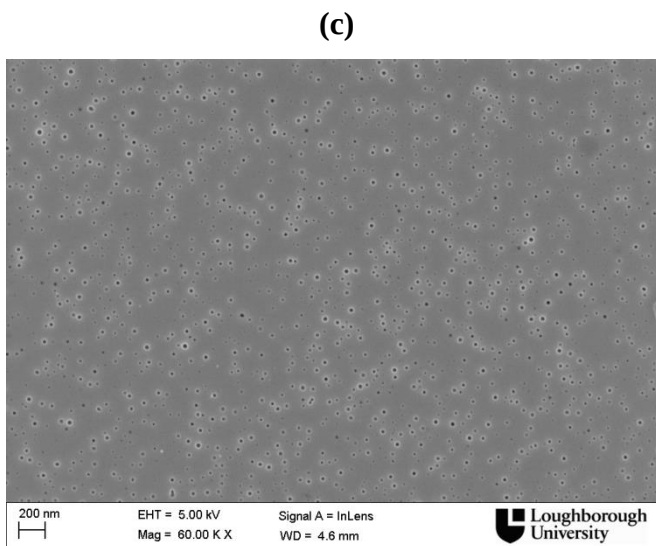
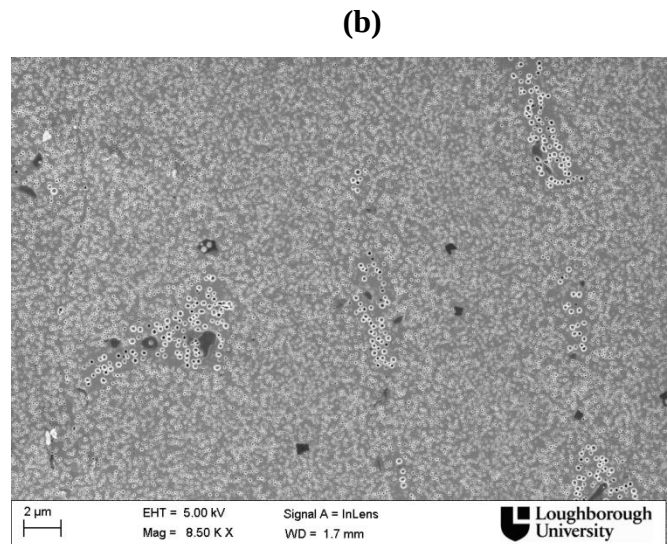
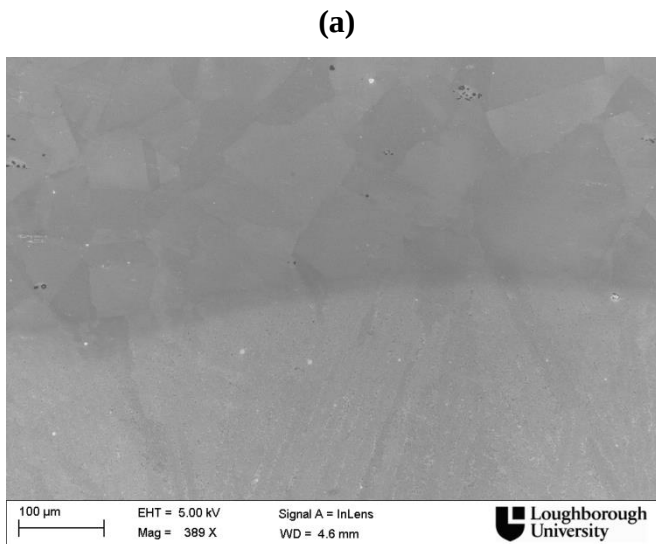


Figure 5.34 – Electron micrographs (a) showing an overview of the area surrounding the weld line, (b) the presence of larger γ' in the segregated regions (c) the γ' present in the parent material and (d) the γ' present in the weld

Microstructural characterisation has indicated that, after the stress relief heat treatment, the γ' phase is still completely present after industrial heat treatment and remained partially present after laboratory heat treatment. Its overall presence in the welds can be attributed to one of two causes or a combination of the two; either the γ' phase is not dissolved at 980°C or the γ' is dissolved during the heat treatment but re-precipitates out during cooling. To ensure that the stress relief heat treatment temperature of 980°C is high enough, samples of both standard Nimonic 263 (of similar composition to the parent) and the weld metal were heat treated in the dilatometer. Initially the standard precipitation heat treatment of 4 hours at 800°C was carried out to ensure full precipitation of the γ' phase, before attempting a dissolution. The stress relief heat treatment of 3 h at 980°C was then conducted, and after the heat treatment the samples were quenched down to room temperature at a rate of 100°Cs⁻¹ to preserve the microstructure of the alloys. Analysis of both the weld and parent samples found no γ' to be present, proving 980°C to be a sufficiently high temperature at which to dissolve the γ' . These results confirm that the precipitation observed during both stress relief heat treatments are as a result of re-precipitation on cooling. The industrial heat treatment would have been carried out on a large section of welded pipe, and after heat treatment such a large component would cool slowly. The laboratory heat treatments were carried out on significantly smaller weld sections, approximately 3 – 4 mm in thickness. The difference in γ' size between the two samples also suggests that the slow cooling rate of the large section is not only re-precipitating the γ' phase but coarsening it also. In order to verify this theory two more stress relief heat treatments were carried out using the dilatometer, this time cooling slowly from 980°C down to 500°C at 100°C h⁻¹. The γ' phase was observed in both the parent and weld at an average particle size of 11.1 and 53.4 nm respectively, an image of the weld metal showing γ' precipitation is shown in Figure 5.35 (a). Figure 5.35 (b) shows that there was little to no precipitation differences between the dendritic and interdendritic regions in the slow cooled weld metal. The laboratory stress relieved sample as seen in Figure 5.32 (a – c) showed γ' to be present in only the interdendritic regions of the laboratory stress relief sample. An explanation for the preferred precipitation of γ' in this region is probably the result of localised chemistry. Thermodynamic calculations carried out on the segregated composition whilst suspending the Eta phase actually predict higher dissolution temperatures and an increased fraction of the γ' phase in such regions.

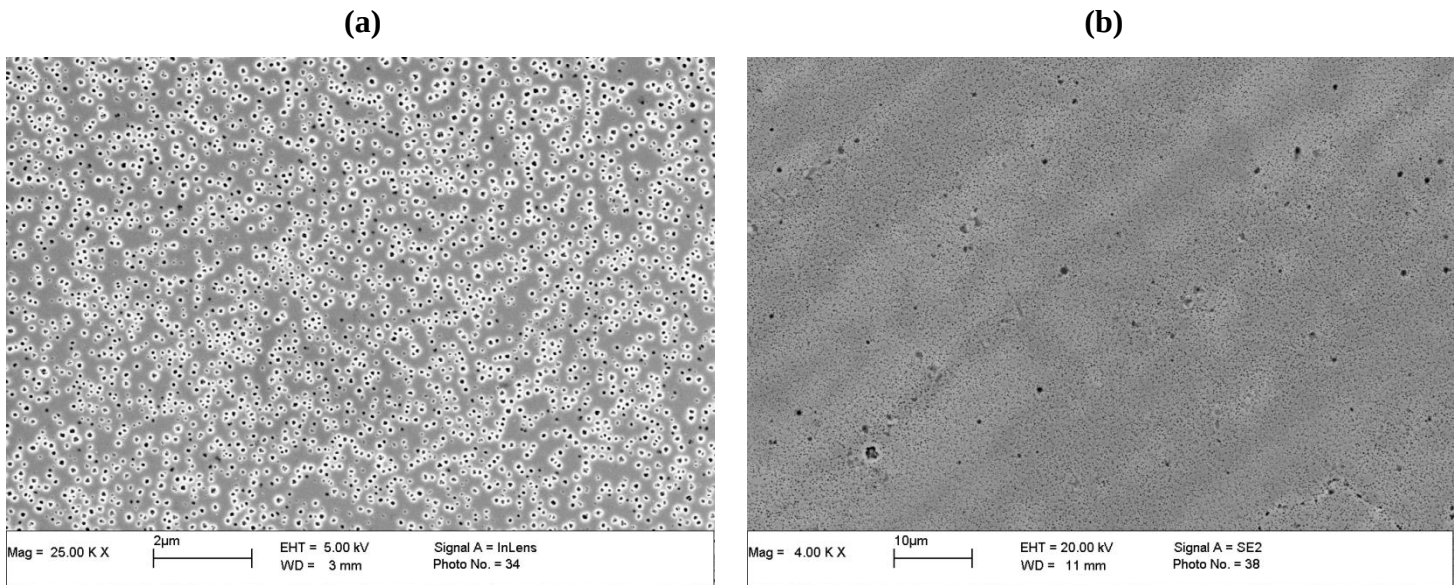


Figure 5.35 – Electron micrograph showing (a) γ' present in the weld metal of the dilatometer produced slow cooled stress relief heat treated sample and (b) a low magnification image showing both dendritic and interdendritic areas of weld

5.8 Summary of the effect of post weld heat treatment conditions

The microstructural evolution in Nimonic 263 welds was studied using a number of analytical techniques, with particular focus placed on the effects of different post weld heat treatments, section size and chemical segregation present within the weld.

Hardness measurements showed differences between the samples as a result of different post weld heat treatments and section size. Both the stress relief and hardening heat treatments were found to harden the welds in comparison to ‘as welded’ values, which was primarily attributable to the precipitation of the γ' phase. The effect of section size on the mechanical properties in the heat treated samples was minimal. The hardened samples showed little change, whereas as a result of the stress relief heat treatment, the parent region underwent significant softening and a small amount of softening was also seen in the weld.

The γ' precipitates were observed to be present in either the weld or the parent of every sample analysed. The work has shown that the hardness of the weld regions can be attributed to a combination of γ' particle size and area fraction. Links were established between the precipitation and coarsening of the γ' phase and the individual post weld heat treatments, section size and segregated microstructure of the welds.

5.9 Effect of aging in weld IP (I)

Whilst studying the welds in the ‘as welded’ state and after the three different post weld heat treatments is valuable, it is only a small step in understanding how the welds will perform in next generation plant. Therefore, the welds were then isothermally aged to create a sample set representative of some of the ageing temperatures to be experienced in industry.

Isothermal ageing was carried out in a high temperature furnace at 750°C for four different ageing times; 25 h, 100 h, 1000 h and 5000 h. These particular times were chosen to assess microstructural evolution in the weld and parent metal under conditions of both short and long term ageing. The ageing temperature of 750°C was chosen based on work carried out on the isothermally aged samples presented in Chapter 4. The work showed that ageing at 750°C accelerated coarsening of the γ' and resulted in earlier precipitation of the η phase when compared to samples aged at 700°C. Ideally two ageing temperatures of 700°C and 800°C would have been chosen, however, this was not possible due to material availability. Table 5.4 shows the aged weld samples presented in this Chapter.

Table 5.4: Summary of isothermally aged weld samples

Sample ID	Pre aged condition	Heat treatment temperature (°C)	Heat treatment time (h)
76	As welded	750	25
77	As welded	750	100
78	As welded	750	1000
79	As welded	750	5000
80	Stress relieved	750	25
81	Stress relieved	750	100
82	Stress relieved	750	1000
83	Stress relieved	750	5000
84	Hardened	750	25
85	Hardened	750	100
86	Hardened	750	1000
87	Hardened	750	5000
88	Stress relief + Hardened	750	25
89	Stress relief + Hardened	750	100
90	Stress relief + Hardened	750	1000
91	Stress relief + Hardened	750	5000

5.9.1 Hardness evolution of isothermally aged welded samples

After removing the aged welds from the furnace, each sample was prepared and then hardness tested. The hardness test was carried out every 1 mm in a traverse from the weld centreline towards the parent material. The results from these tests are shown in the graphs in Figure 5.36. Each graph shows the different hardness profiles for ageing time in the individual post weld conditions; as welded, stress relieved, hardened and stress relief + hardened.

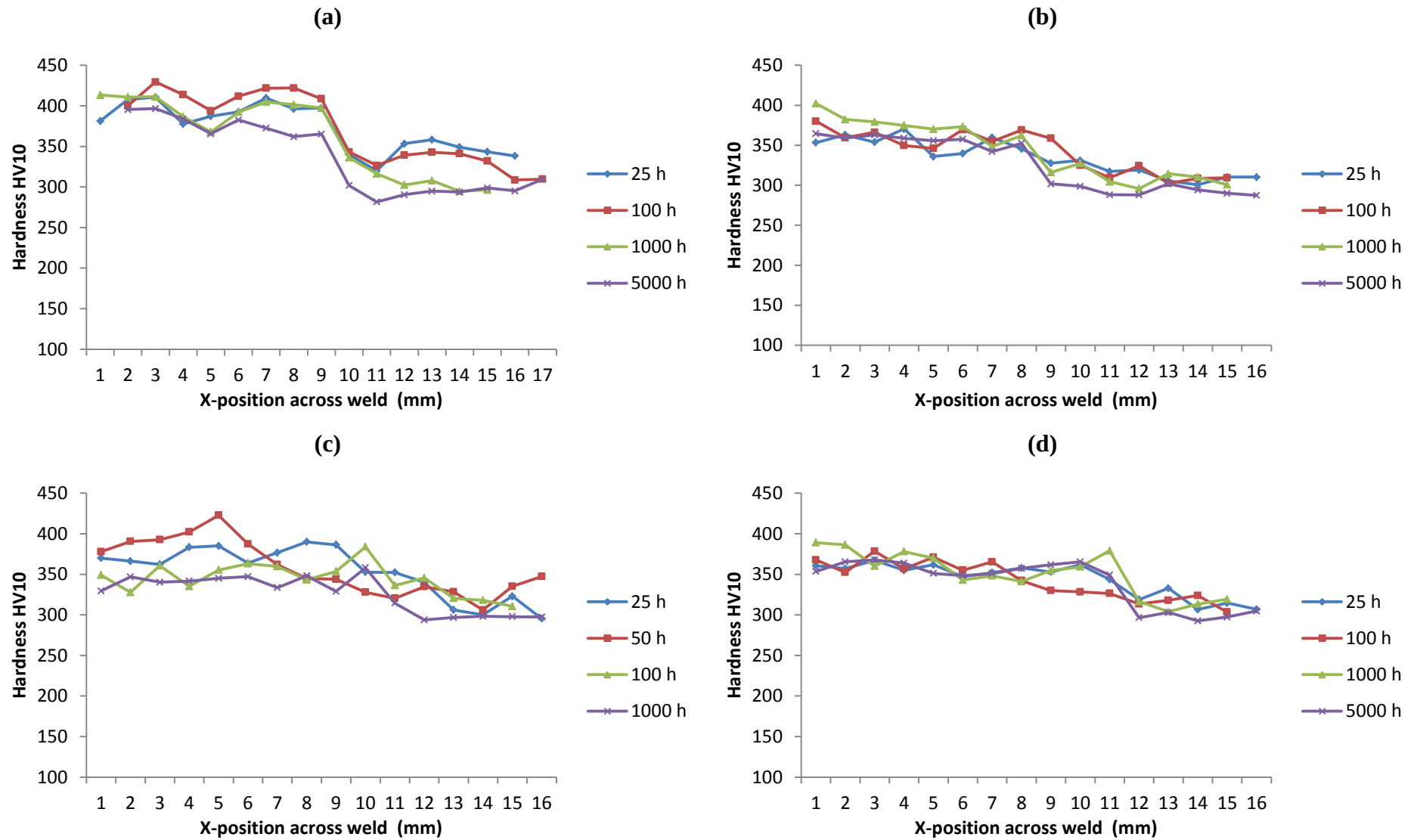


Figure 5.36 – Hardness evolution through welded samples at different ageing times for (a) as welded, (b) stress relieved, (c) hardened and (d) stress relieved + hardened

Results from hardness testing shown in Figure 5.36 (a – d) indicate that ageing at 750°C has a relatively small effect on the overall hardness of both the parent and weld material. Table 5.5 has been produced to show the average values of the parent and weld hardness in for each condition at each exposure time.

Table 5.5 – Average hardness results for both the weld and parent in different aged PWHT samples

Ageing 750°C	time	at	PWHT condition	Parent		Weld	
				Hardness (HV ₁₀)	Standard deviation	Hardness (HV ₁₀)	Standard deviation
25			AW	343.2	12.5	395.7	12.2
100			AW	328.6	14.4	405.0	25.7
1000			AW	309.0	15.5	398.5	14.6
5000			AW	292.5	5.9	369.6	28.4
25			SR	310.5	6.9	348.1	14.3
100			SR	313.2	9.3	361.6	10.7
1000			SR	309.9	10.6	374.1	15.6
5000			SR	294.7	6.1	356.7	7.0
25			H	313.0	18.4	371.7	13.5
100			H	330.5	13.2	385.0	24.0
1000			H	326.2	14.4	353.2	15.8
5000			H	300.2	8.2	341.9	9.1
25			SR + H	316.0	10.8	356.1	6.9
100			SR + H	320.5	9.5	361.1	11.7
1000			SR + H	313.2	6.7	364.4	17.1
5000			SR + H	297.4	4.2	357.7	7.4

Hardness testing of the aged, as-welded sample showed a significant softening in the parent material going from 343 HV₁₀ to 293 HV₁₀ after ageing for 5000 h, a reduction of 51 HV₁₀. In the un-aged condition the hardness in the weld metal from the as welded sample was recorded at 264 HV₁₀, ageing at 25 and 100 h showed an initial increase in hardness to 396 HV₁₀ and 405 HV₁₀ respectively. The increase is thought to be due to the precipitation of the γ' phase during early ageing at 750°C. A decrease in hardness to 370 HV₁₀ is recorded after long term ageing at 5000 h. A noticeable feature in the corresponding hardness graph in Figure 5.36 (a) is the large difference in hardness values between the parent and weld materials when compared to other aged PWHT conditions. Such a large difference in mechanical properties is undesirable for plant materials.

Hardness results from the stress relieved weld sample showed the parent hardness to remain stable during early ageing between 25 and 1000 h with 311 HV₁₀ and 310 HV₁₀ recorded respectively. There is a small drop in hardness to 293 HV₁₀ after long term ageing for 5000 h, however overall the parent material shows little change. The weld metal is seen to harden

from 349 HV₁₀ in the un-aged sample to 348 HV₁₀, 362 HV₁₀ and 374 HV₁₀ in the 25, 100 and 1000 h respectively. After 5000 h the weld metal softens to 357 HV₁₀, it is expected that longer exposure times would see a further decrease in hardness.

Results from the hardened samples showed that the parent material experienced some small hardness changes with ageing, hardness initially increased on ageing from 307 HV₁₀ in the un-aged sample to 313 HV₁₀ and 331 HV₁₀ in the samples aged for 25 and 100 h respectively. Further ageing was seen to soften the parent material to around 300 HV₁₀ after 5000 h thermal exposure. In the weld metal a small decrease in hardness was recorded after long term ageing from 388 HV₁₀ in the un-aged sample to 342 HV₁₀ after 5000 h thermal exposure.

The post weld heat treatment that combined both the stress relieved and hardening heat treatment showed that the parent material experienced little to no change in hardness up to 1000 h thermal exposure. Long term ageing at 5000 h showed softening in the parent metal from 313 HV₁₀ after 1000 h to 297 HV₁₀ at 5000 h. In the weld metal the hardness increases from 326 HV₁₀ in the un-aged to 356 HV₁₀ at 25 h. Further ageing was shown to have no effect with recorded hardness values of 361 HV₁₀, 364 HV₁₀ and 358 HV₁₀ in the 100, 1000 and 5000 h respectively.

In summary, ageing at 750°C has been shown to have some effect on the hardness properties of the weld assembly in both the parent and weld materials. Ageing of the parent material shows similar results to those observed in the parent material of the isothermally aged samples. In the as-welded and stress relieved material there is a constant reduction in hardness with ageing time. Samples which have undergone the hardening heat treatment, however, show a hardening up to 1000 h before decreasing after long term ageing. In all of the PWHT conditions, apart from as welded, the weld material is seen to harden on ageing up to 1000 h before softening at long term ageing of 5000 h, this is especially clear in the stress relieved sample.

5.9.2 Microstructural evolution of isothermally aged welded samples

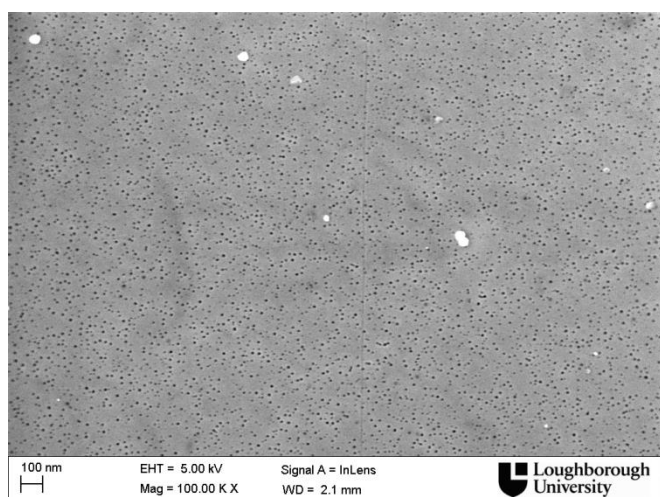
The last section showed how differently the parent and weld metals behaved when aged at 750°C. Electron microscopy has been carried out to establish the microstructural factors behind such changes and where possible to quantify them.

During analysis of each aged sample, the distribution and type of MX phase was noted. It was found that similar to results presented in Chapter 4, both the blocky Ti rich and the smaller elongated Ti-Mo rich phases were present throughout. As noted in section 5.7 it was clear that the MX phase was concentrated along the interdendritic regions of the weld material, this occurrence did not change with thermal exposure. At no point was the previously identified sub-micron spherical Ti-Mo rich MX phase observed. Detailed TEM microscopy was not carried out on the grain boundary precipitates such as $M_{23}C_6$, however, EDX mapping did reveal a Cr rich grain boundary phase to be present.

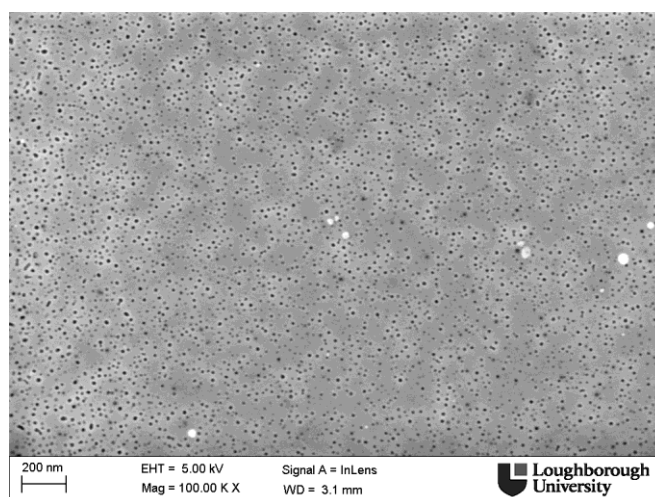
The γ' evolution was studied in both the parent and weld metals in addition to the interface between the two regions. The γ' evolution was studied in each condition using both etched and un-etched samples, in order to clarify any effect of etching on the features observed.

Figures 5.37 (a), (c) and (e) show the γ' present in the parent material for the as welded samples aged for 25, 1000 and 5000 h respectively. Figures 5.27 (b), (d) and (f) show the γ' present in the corresponding weld metal for samples aged for 25, 1000 and 5000 h respectively. Although not shown in Figure 5.37, a 100 h aged sample was also produced, and the data for the sample are included in the analyses. The size of the average parent γ' particle coarsened from 12.8 nm in the un-aged parent to 11.6, 17.8, 33 and 53.2 nm in the 25, 100, 1000 and 5000 h respectively. The area fraction of the γ' phase showed little change with ageing, averaging at 5.5% across all four aged samples. Analysis of the un-aged sample originally observed no γ' to be present in the weld, ageing for 25 h at 750°C cause precipitation of the γ' at 12.9 nm, further ageing at 100, 1000 and 5000 h coarsened the γ' to 20.2, 34.5 and 66.2 nm respectively. Similarly to the parent metal the area fraction showed little change during ageing, averaging at 7.5% across all four aged samples.

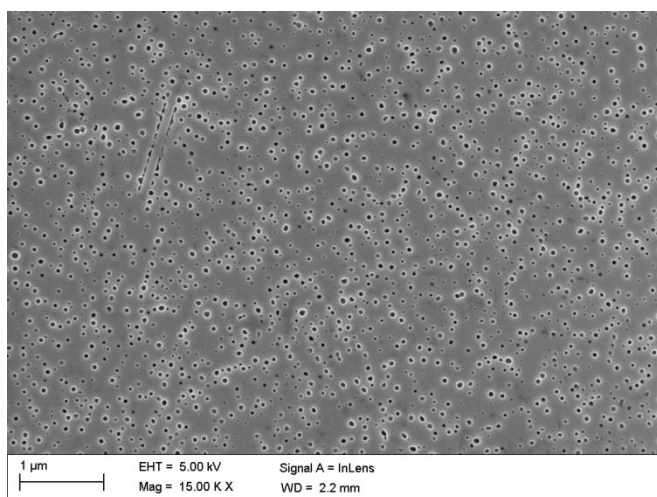
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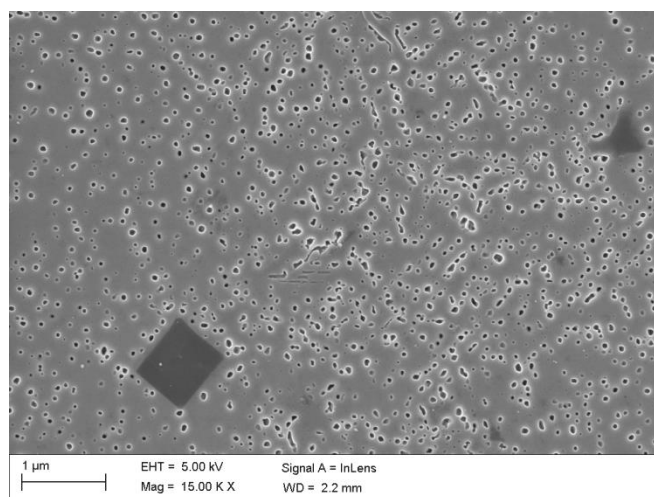
(b)



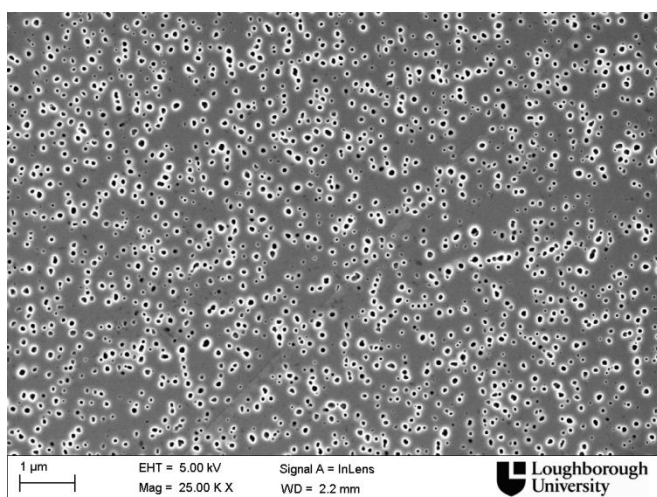
(c)



(d)



(e)



(f)

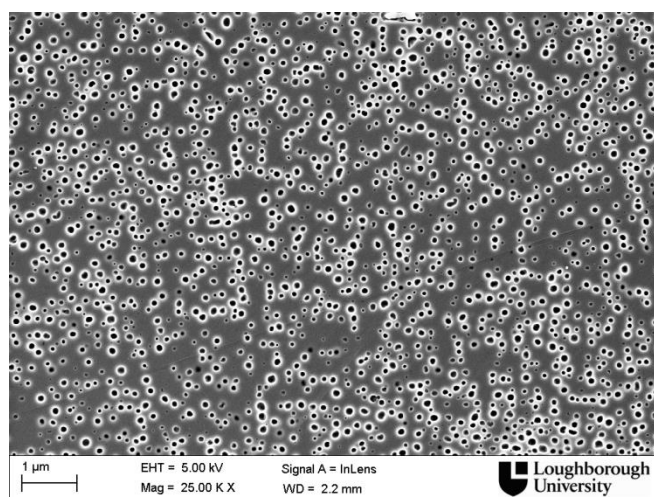
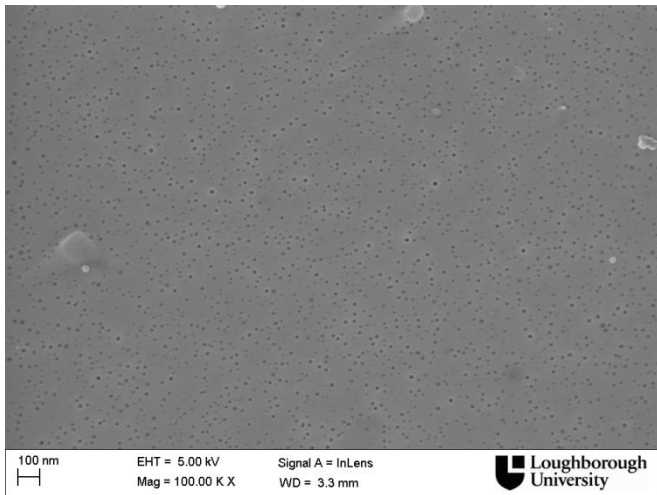
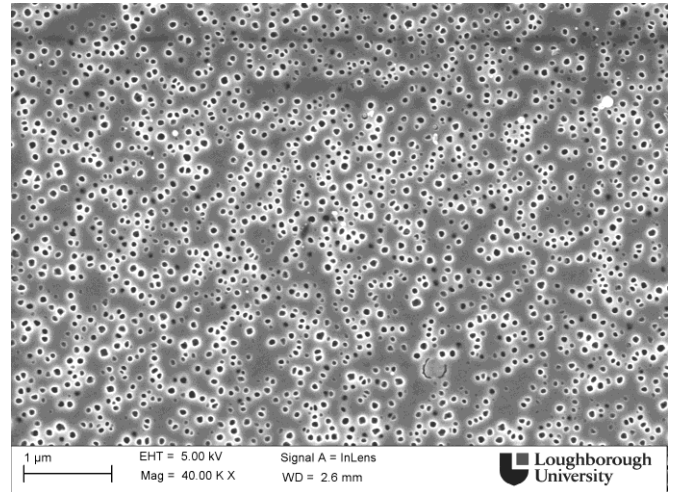


Figure 5.37 – Electron micrographs showing the isothermally aged as welded samples of (a,b) parent and weld aged for 25 h at 750°C, (c,d) parent and weld aged for 1000 h at 750°C and (e,f) parent and weld aged for 5000 h at 750°C

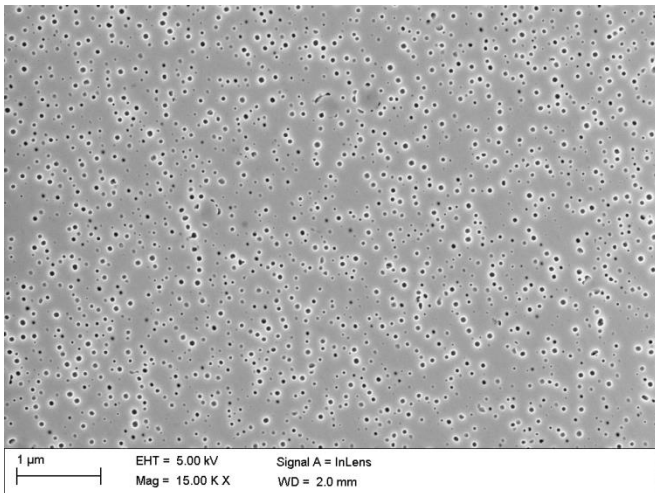
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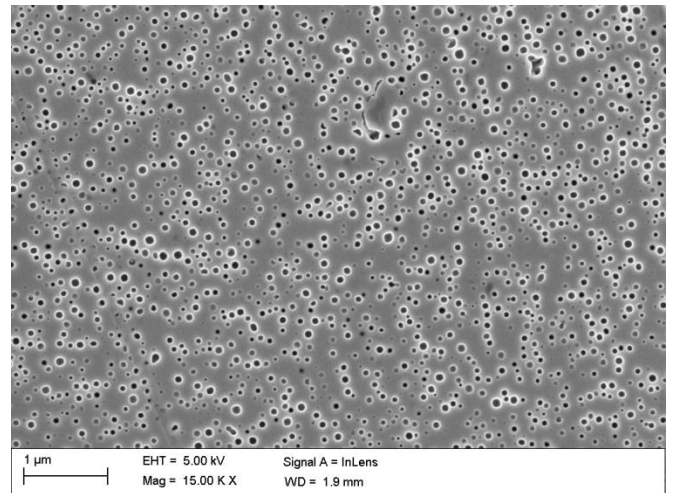
(b)



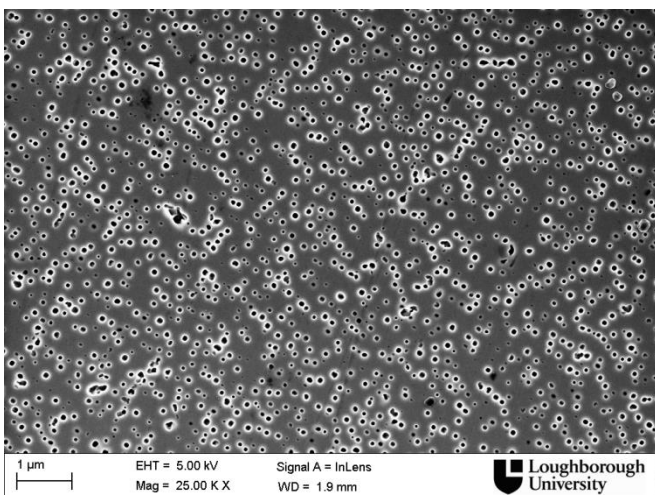
(c)



(d)



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(f)

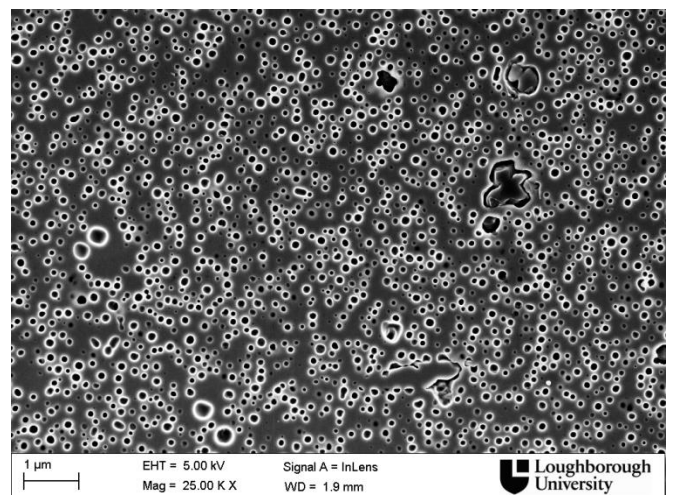
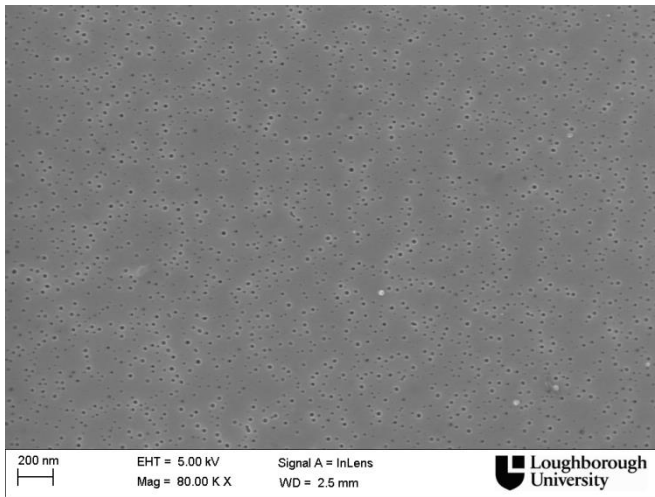
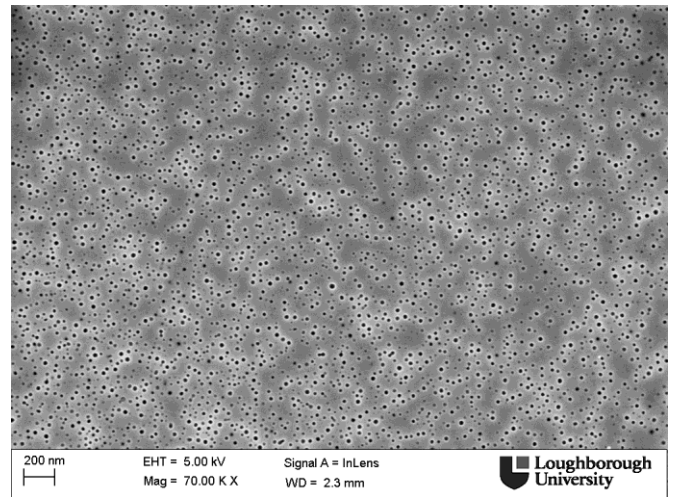


Figure 5.38 – Electron micrographs showing the isothermally aged stress relieved weld samples of (a,b) parent and weld aged for 25 h at 750°C, (c,d) parent and weld aged for 1000 h at 750°C and (e,f) parent and weld aged for 5000 h at 750°C

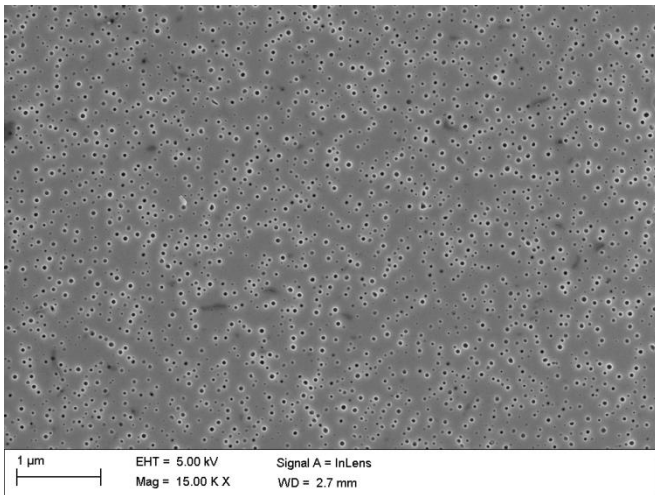
(a)



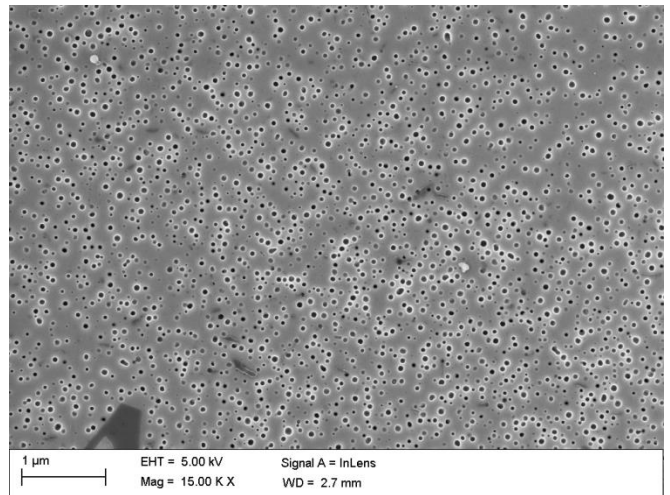
(b)



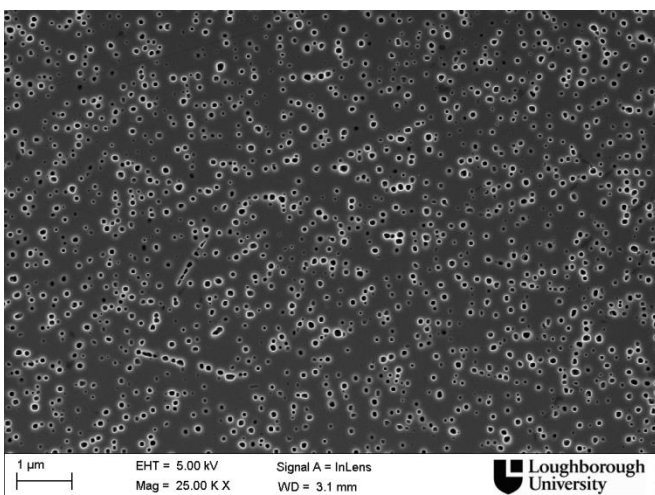
(c)



(d)



(e)



(f)

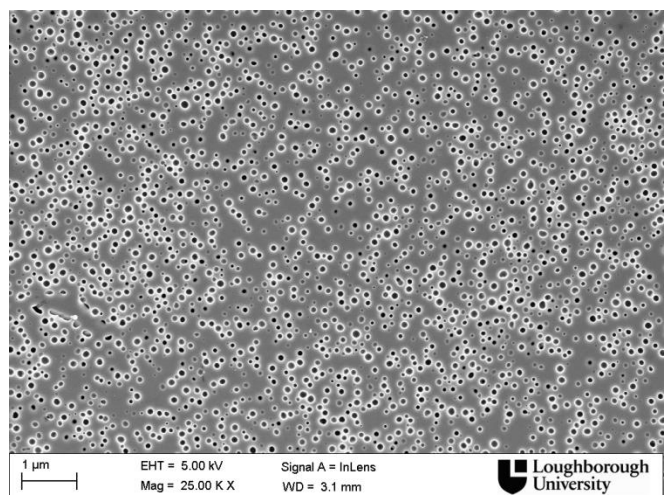
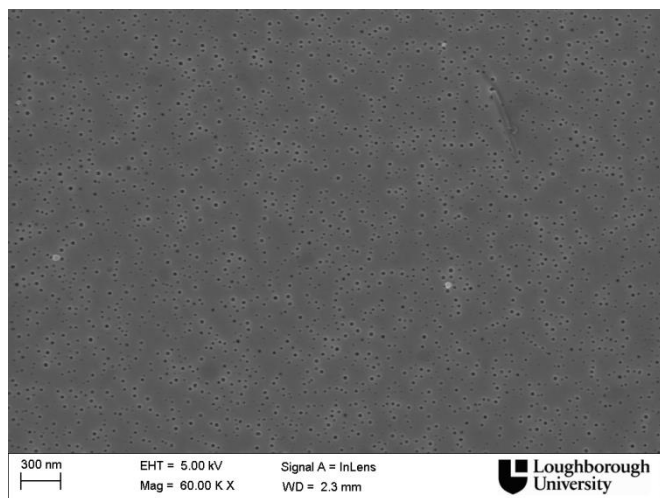
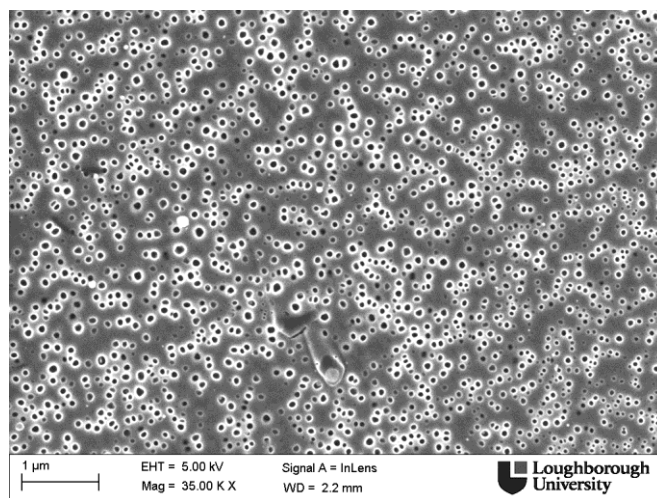


Figure 5.39 – Electron micrographs showing the isothermally aged hardened weld samples of (a,b) parent and weld aged for 25 h at 750°C, (c,d) parent and weld aged for 1000 h at 750°C and (e,f) parent and weld aged for 5000 h at 750°C

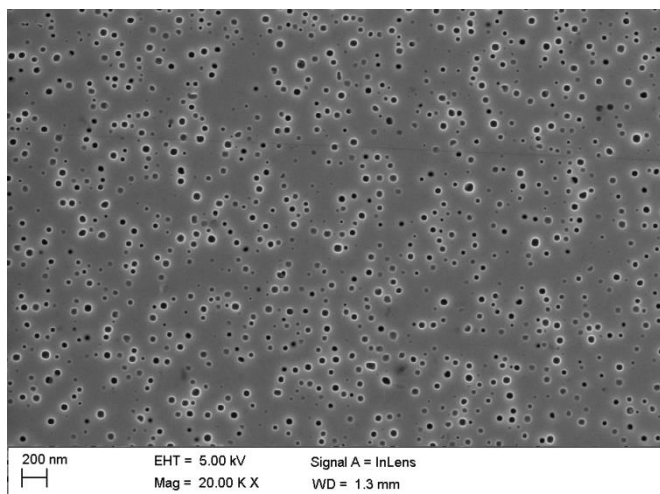
(a)



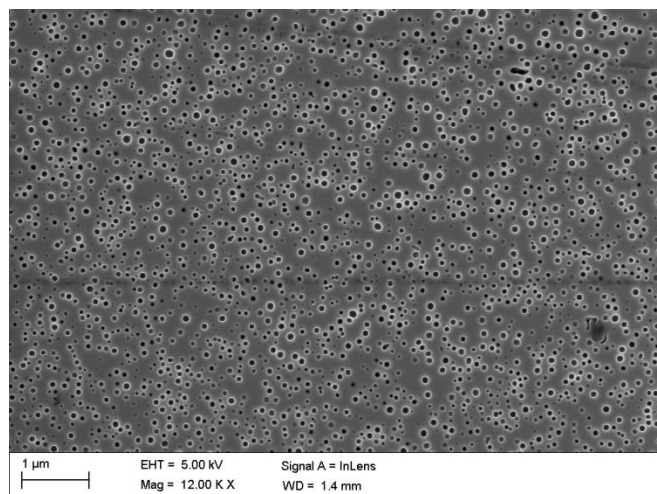
(b)



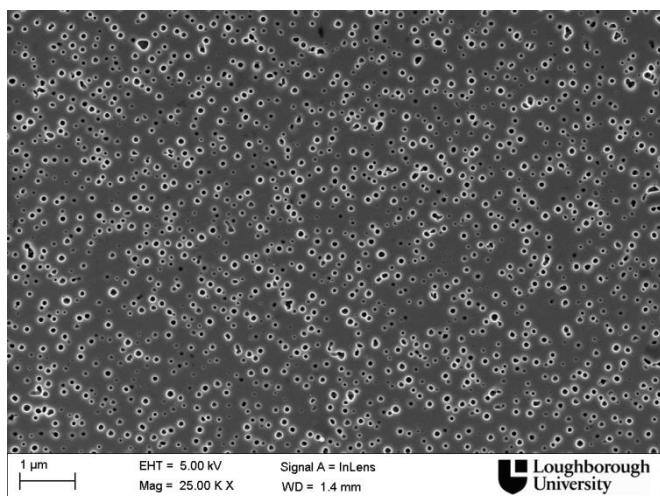
(c)



(d)



(e)



(f)

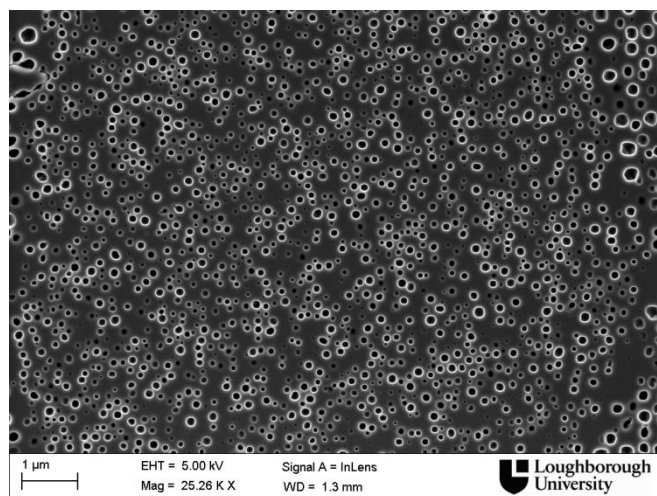


Figure 5.40 – Electron micrographs showing the isothermally aged SR + H weld samples of (a,b) parent and weld aged for 25 h at 750°C, (c,d) parent and weld aged for 1000 h at 750°C and (e,f) parent and weld aged for 5000 h at 750°C

Figures 5.38 (a), (c) and (e) show the γ' present in the parent material for the stress relieved samples aged for 25, 100 and 5000 h respectively. After analysis of the electron micrographs, the γ' phase was observed to coarsen from 12.5 nm in the un-aged stress relieved sample to 14.6, 16.7, 35.8 and 55.6 nm after ageing at 25, 100, 1000 and 5000 h respectively. The area fraction of γ' in the parent material again showed no change with an average value of 5.4 %. In the un-aged stress relieved weld metal two separate distributions of γ' were observed, dendritic and interdendritic at 39.9 and between 100 – 200 nm respectively. The evolution of the γ' contained in the dendritic region was observed at 40, 33.8, 46.9 and 68.4 nm when aged at 25, 100, 1000 and 5000 h respectively.

The large interdendritic γ' was observed not to change with ageing at 750°C, and Figures 5.41 (a), (b), (c) and (d) show the interdendritic γ' when aged for 25, 100, 1000 and 5000 h respectively. Cracking was observed in the samples aged for 100, 1000 and 5000 h exclusively within the interdendritic regions. Un-etched samples were also studied to understand whether the observed cracking was present only after exposure to the etchant. Micrographs from the 100 h aged sample shown in Figure 5.42 (a) and (b), show cracks to be present in the interdendritic regions. The cracking of the interdendritic regions is currently not understood and requires further investigation. One possible cause is the difference in the coefficient of thermal expansion between the matrix and interdendritic precipitates.

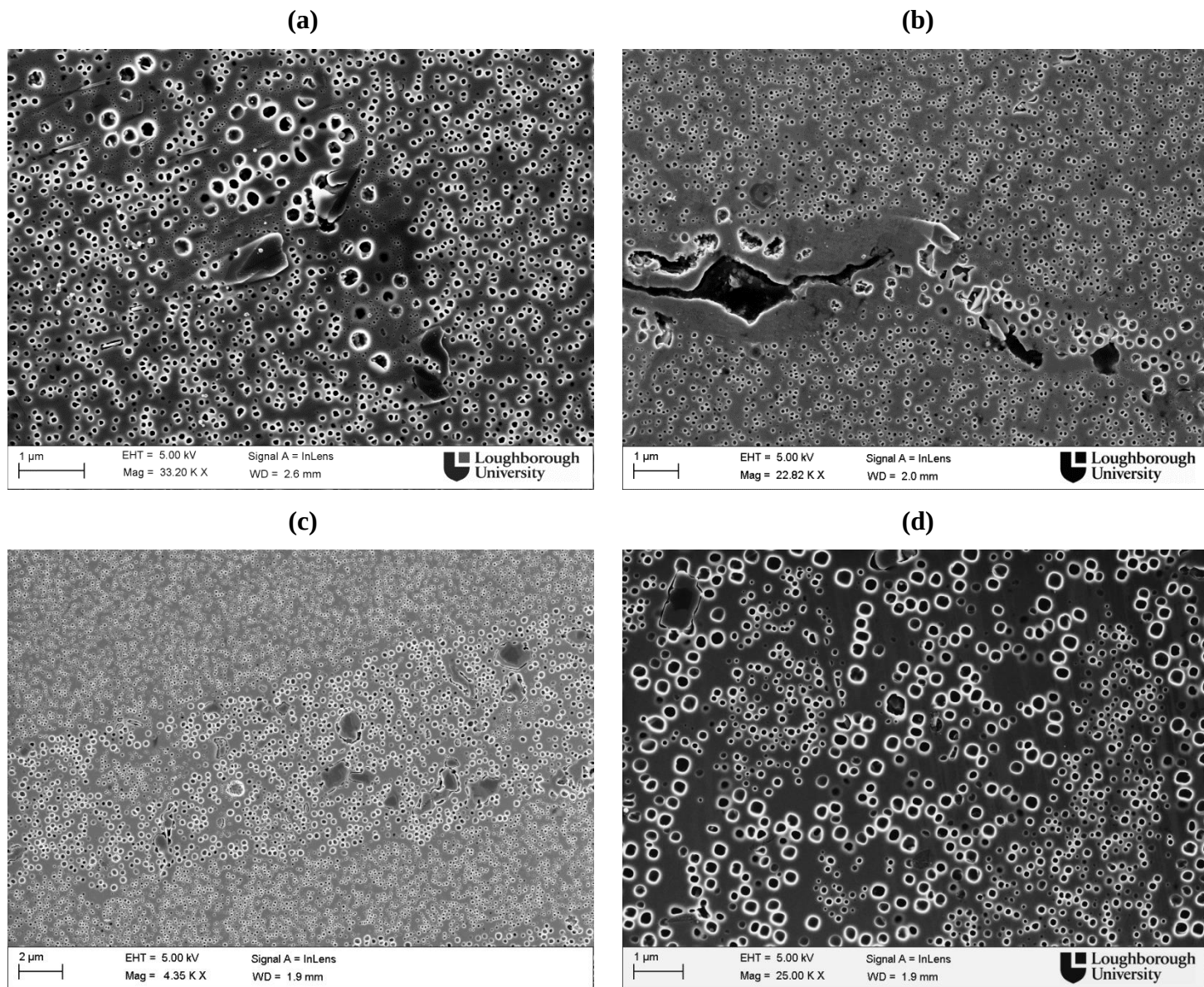


Figure 5.41 – Electron micrographs showing the large γ' contained in the interdendritic regions of the 750°C ageing set for (a) 25 h, (b) 100 h, (c) 1000 h and (d) 5000 h.

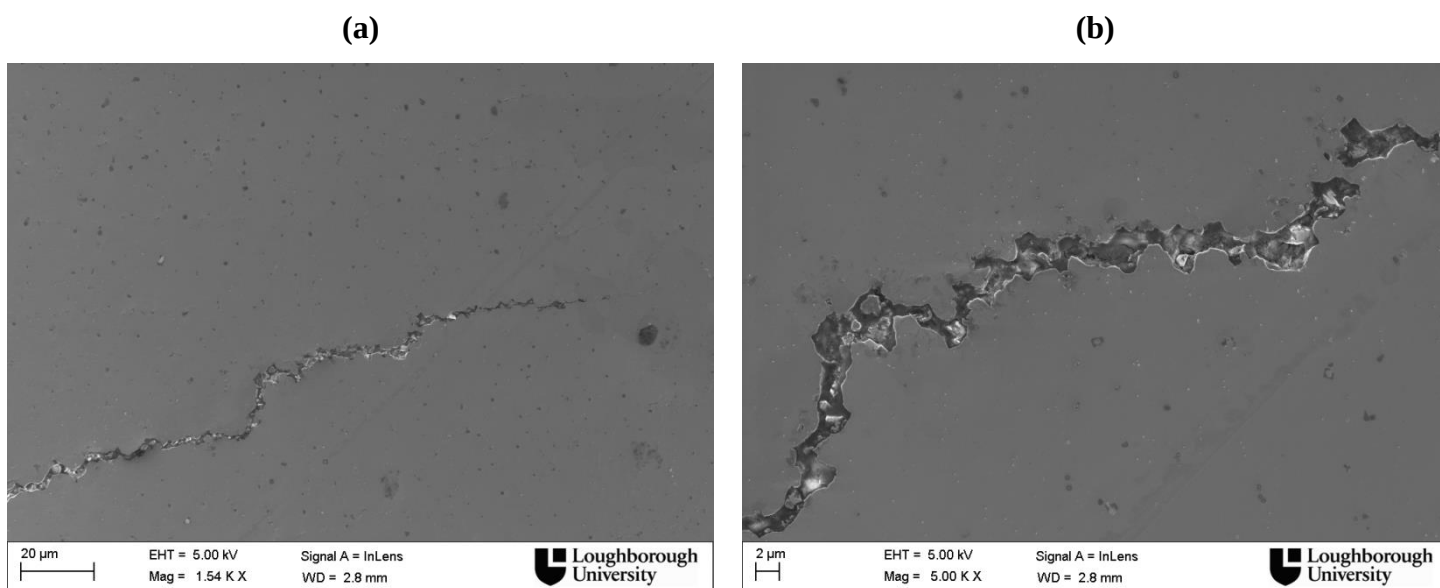


Figure 5.42 – (a, b) Electron micrographs showing the cracks with interdendritic region in the sample aged at 750°C for 100 h

The combined post weld heat treatment, denoted SR + H, used the industrially produced stress relieved weld as a base for the subsequent hardening heat treatment. Due to this, the large interdendritic γ' are also a feature of the weld microstructure. Cracking in the interdendritic regions was not observed in any of the aged samples from 25 – 5000 h. Due to the difference in precipitation between the dendritic and interdendritic regions it was possible that the regions could be cracking as a result of heating or cooling rate. In order to study this phenomenon, a piece of the un-aged stress relieved weld metal was aged for 100 h, an ageing time in which cracking had been previously observed, before cooling using one of three different techniques. Cooling was carried out in air, by quenching in water and also in a furnace or slow cool. The resultant samples were analysed in both the etched and un-etched states, and no cracks were found after any of the three different cooling heat treatments.

Figures 5.39 (a), (c) and (e) show the γ' present in the parent materials at 25, 1000 and 5000 h respectively. The γ' was observed to coarsen from 15.2 nm in the un-aged hardened sample to 17.2, 22.5 31.3 and 53.6 nm in the samples aged for 25, 100, 1000 and 5000 h respectively. The area fraction of the γ' again remained consistent during ageing at 5.7 % when averaged across all four conditions.

Figures 5.39 (b), (d) and (f) show the γ' evolution in the weld metal when aged for 25, 1000 and 5000 h respectively. Ageing at 750°C was found to coarsen the γ' phase from 15.8 nm in the un-aged sample to 18.8, 22.1, 38.6 and 62.3 in the samples aged for 25, 100, 1000 and

5000 h respectively. The average area fraction of the γ' phase was calculated to be 8.4%, ageing was seen to have little effect on the area fraction of the γ' phase.

Figures 5.40 (a), (c) and (e) show the evolution of the γ' present in the parent material for the SR + H condition when aged at 25, 1000 and 5000 h respectively. The γ' phase was observed to coarsen from 17.2 nm in the un-aged sample to 20.2, 19.3, 33.4 and 55.4 in the samples aged for 25, 100, 1000 and 5000 h respectively. The average area fraction of the γ' phase was calculated to be 5.1% and not observed to change with ageing time.

Figures 5.40 (b), (d) and (f) show the γ' present in the SR + H weld metal when aged for 25, 100, 1000 and 5000 h respectively. Ageing at 750°C was seen to coarsen the γ' from 45.2 nm in the un-aged condition to 42.6, 53, 52.1 and 71.1 nm in the 25, 100, 1000 and 5000 h respectively. Again the area fraction of the γ' remained consistent with ageing, an average of 8.53 % was observed in the weld metal.

The evolution of the γ' phase has been summarised for all conditions and at all exposure times in Table 5.6 and Figures 5.43 (a – d).

Table 5.6 – Summary of γ' evolution in welded samples

Sample index	PW condition	Ageing time (h)	Area fraction parent (%)	Parent γ' (nm)	Parent γ' SD	Area fraction weld (%)	Weld (nm)	Weld γ' SD
57	AW	~	5.1	12.8	0.2	-	-	-
58	SR	~	5.6	12.5	0.4	6.3	39.9	3.8
59	H	~	4.6	15.2	1.4	7	15.8	0.6
63	SR + H	~	2.9	17.2	1.7	6	45.2	2.1
76	AW	25	6.21	11.6	0.4	7.8	12.9	0.2
77	AW	100	5.5	17.8	0.3	8.9	20.2	1
78	AW	1000	5	33	0.52	4.6	34.5	1.3
79	AW	5000	5.4	53.2	1.1	8.8	66.2	1.2
80	SR	25	6.2	14.6	0.5	7.7	40	1
81	SR	100	5.3	16.7	0.7	7.8	33.8	0.6
82	SR	1000	5.1	35.8	0.9	8.8	46.9	2.91
83	SR	5000	4.9	55.6	1.9	8.7	68.4	0.8
84	H	25	5.6	17.2	0.6	8.4	18.8	0.4
85	H	100	6.5	22.5	0.3	8.2	22.1	0.7
86	H	1000	5.5	31.3	0.4	8.2	38.6	0.5
87	H	5000	5.0	53.6	1.3	8.7	62.3	1.6
88	SR + H	25	5.6	20.2	0.4	6.9	42.6	5.1
89	SR + H	100	4.3	19.3	0.9	9.3	53	1.9
90	SR + H	1000	5.4	33.4	0.9	9.5	52.1	4.1
91	SR + H	5000	5.1	55.8	0.5	8.4	71.1	2.4

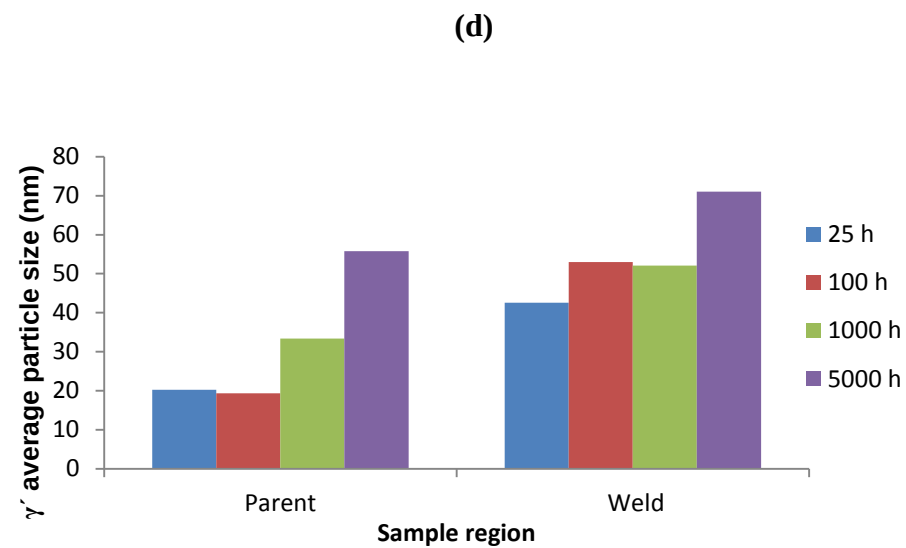
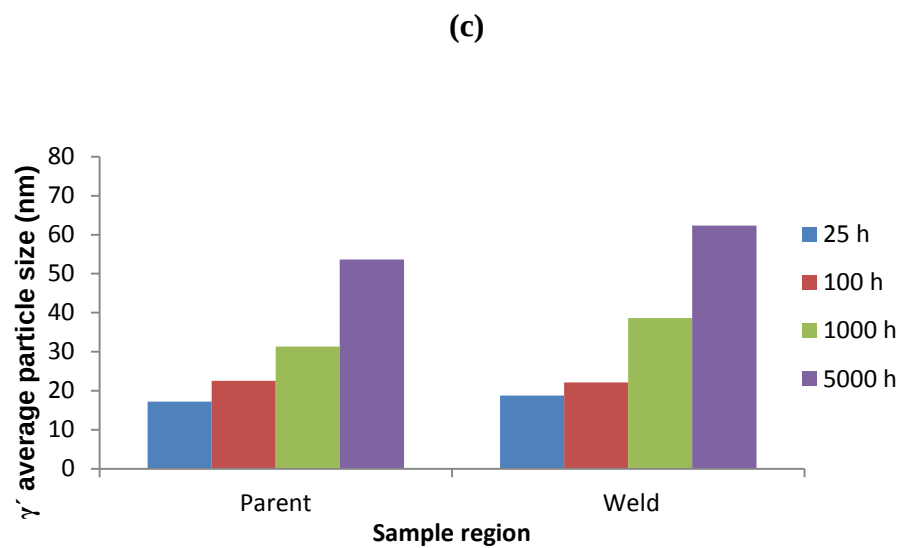
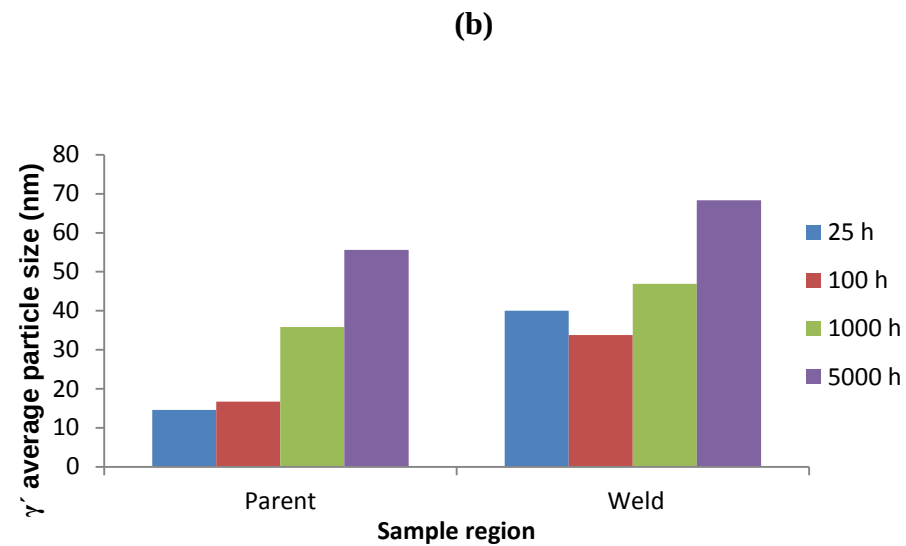
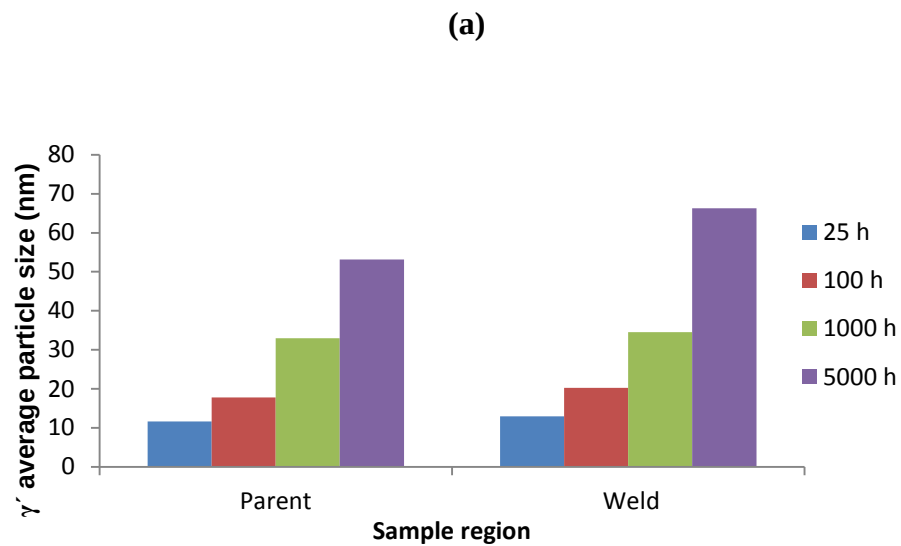


Figure 5.43 - Bar charts showing the γ' evolution in terms of change in the average γ' size for each of the PWHT condition for each thermal exposure in both the parent and weld metal for (a) as-welded, (b) stress relieved, (c) hardened and (d) SR + H.

Results clearly show that ageing at 750°C has resulted in coarsening of the γ' phase in both the parent and weld metal. Further analysis indicated that, although the weld metal contained larger γ' , the coarsening rate between the two remains similar, as shown by plotting the average γ' size against $t^{1/3}$ in Figures 5.44 (a – d). A differing gradient between the lines of best fit for each data set would represent such a change, a steeper gradient would be indicative of a faster coarsening rate, however, this is not seen in any of the Figures shown in 5.44. It is also noted that those samples which had received the industrial stress relief heat treatment of 980°C for 3 hours showed little to no coarsening in the weld material during short to medium ageing (25 – 1000 h), although these samples did, however, show significant coarsening after long term ageing for 5000 h. The suspected slow cooling rate, as a result of heat treating a large component is thought to be the cause of initial larger γ' . This theory was verified using the dilatometer to heat treat samples precisely with a high degree of control over both heating and cooling rates. It is interesting however that no further coarsening occurs until after long term ageing at 5000 h.

Significantly, in both the aged and un-aged conditions the weld metal was found to contain a much higher area % of γ' than in the parent material. Figure 5.22 (a) shows the predicted mass % of the γ' phase present in the four different experimental materials based on the Nimonic 263 composition. Although the experimentally observed values for area percentage are unable to be compared directly to predicted mass %, the calculated and observed results can be seen to follow the same trend. The same is true of the interdendritic areas contained in samples originating from the industrial stress relief heat treatment, the predictions in Figure 5.22 (b) are again in agreement with the observations showing an increased area % of the γ' present in such regions.

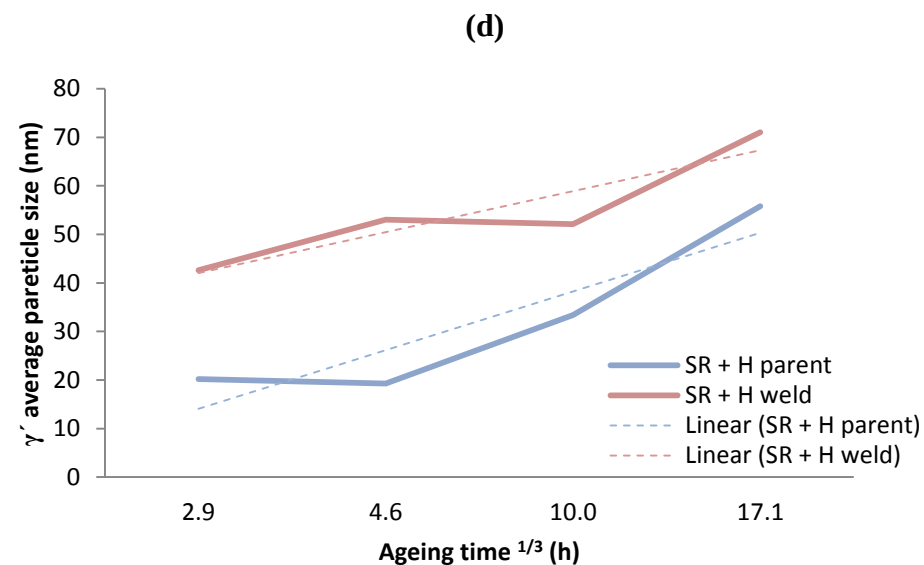
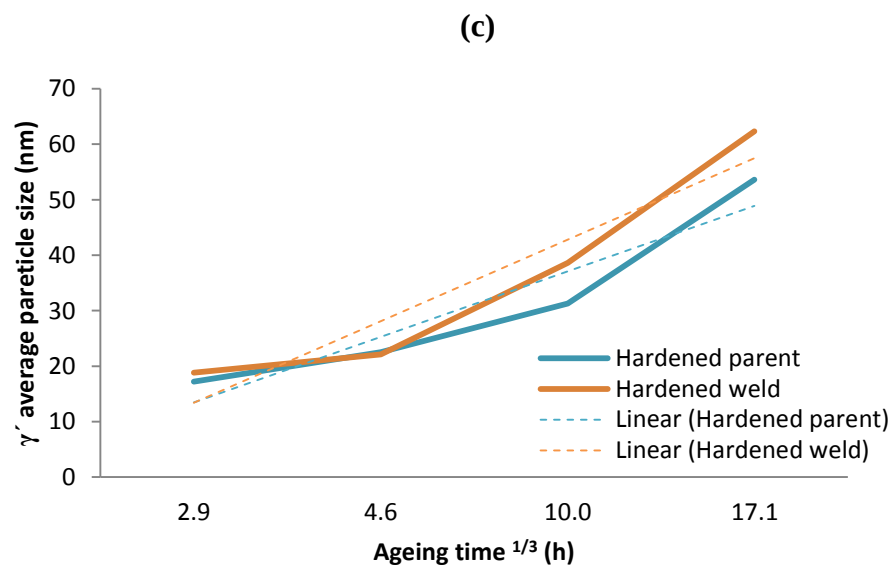
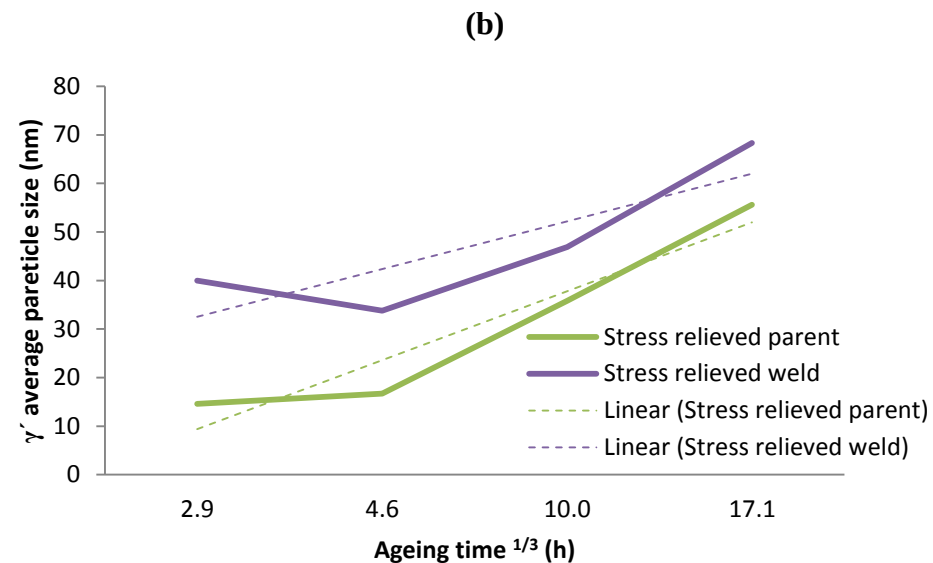
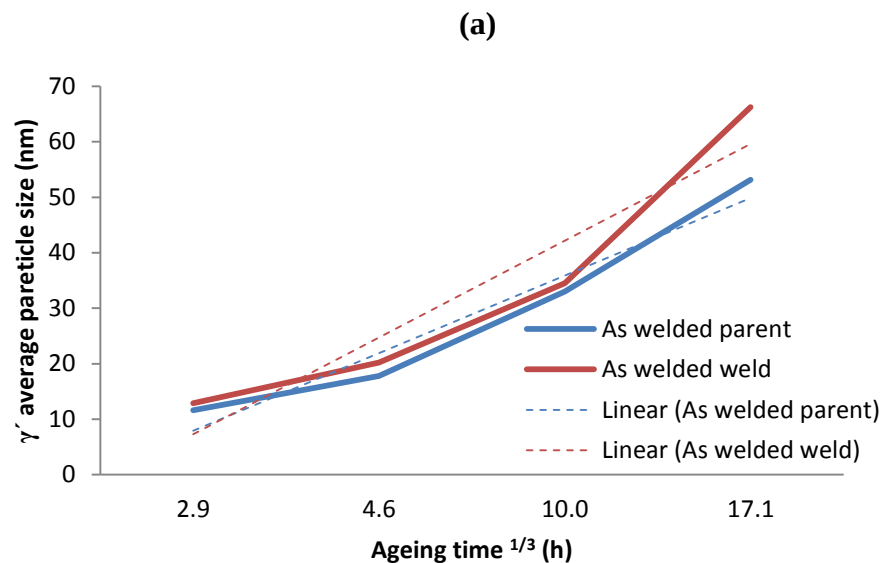


Figure 5.44 - Graphs showing the average γ' particle size against $t^{1/3}$ for each of the PWHT condition for each thermal exposure in both the parent and weld metal for (a) as-welded, (b) stress relieved, (c) hardened and (d) SR + H.

In Section 5.3, thermodynamic calculations predicted significant precipitation of the Eta phase in highly segregated areas of the weld such as the interdendritic regions. Through literature and previous work it is known that although the Eta phase is thermodynamically stable at equilibrium, its transformation from the γ' phase is relatively sluggish. Results from the isothermally aged samples showed that widespread transformation of the Eta phase did not occur until 10,000 h of exposure at 750°C. Time constraints prohibited the production of longer term aged samples such as 10,000 h. Alternatively, a shorter term ageing trial was carried out at a higher temperature of 800°C, known to facilitate the transformation of Eta phase at shorter exposure times, due to the faster kinetics brought about by the increase of 50°C.

Three small sections of the stress relieved weld metal, approximately 5 mm³, were heat treated at 800°C for 100, 1000 and 5000 h. Due to the size of the samples heat treated they were sealed in quartz to protect them from oxidation, which in the smaller samples would have been significant. After thermal exposure hardness testing was carried out on each sample to assess the mechanical property evolution. Several indents were made throughout each welded specimen, the average hardness was determined to be 329, 326 and 290 HV₁₀ for the samples aged for 250, 1000 and 5000 h respectively. The γ' phase was observed to be present in all of the thermal exposures and the average particle size was calculated utilising the same method applied in previous sections. Micrographs showing the evolution of the γ' phase can be seen in Figures 5.45 (a), (b) and (c) for the samples aged at 800°C for 250, 1000 and 5000 h respectively.

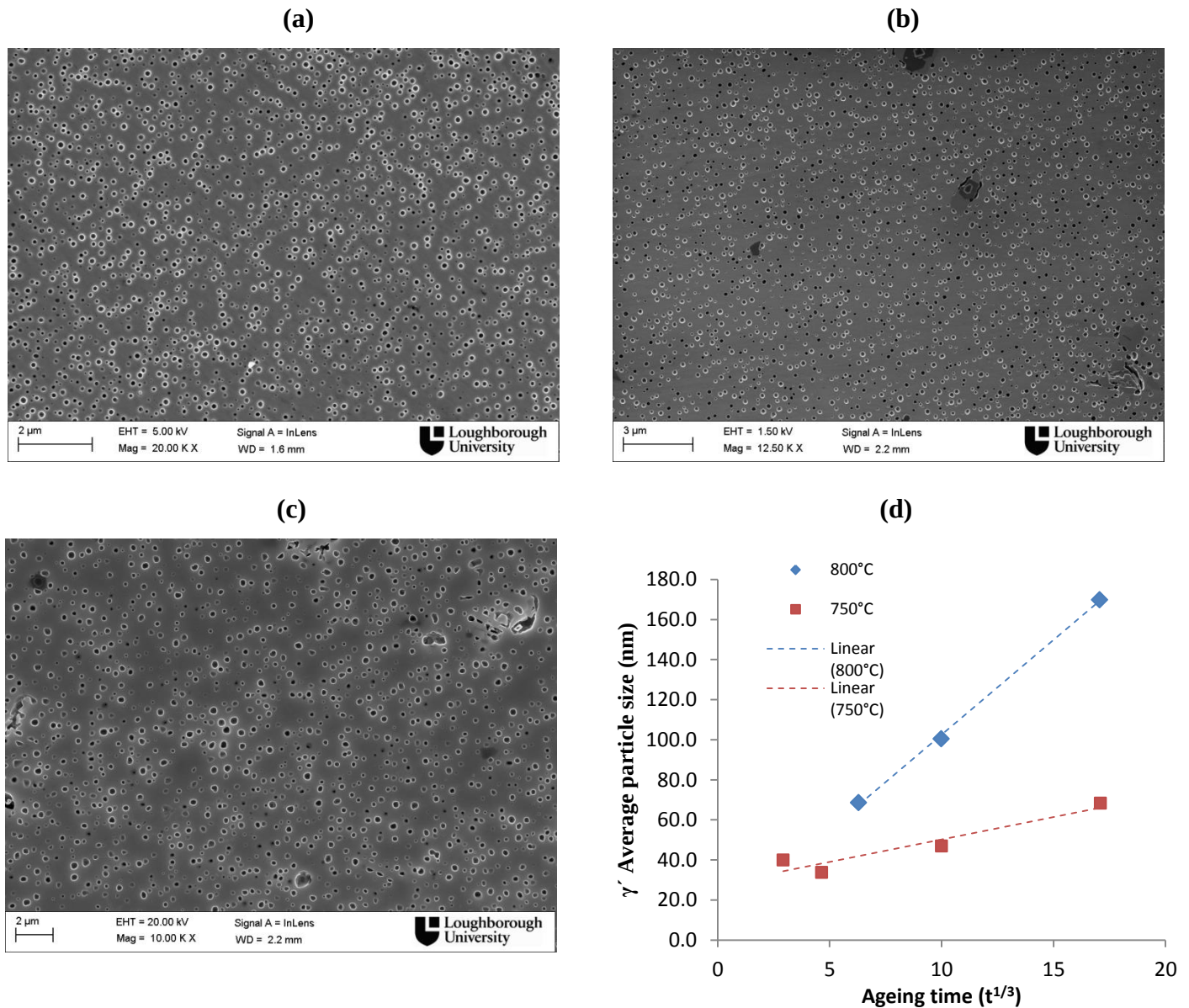


Figure 5.45 – Micrographs showing γ' evolution in stress relieved weld metal when aged at 800°C for (a) 250 h, (b) 1000 h, (c) 5000 h and (d) a graph plotting the average particle size of the γ' phase against $t^{1/3}$ for the stress relieved weld metal when aged at 750 and 800°C.

The average γ' particle size was calculated to be 68.6, 100.5 and 169.8 nm for samples aged at 800°C for 250, 1000 and 5000 h. Figure 5.45 (d) is a graph indicating how the average particle size of the γ' phase evolves as a result of ageing the stress relieved weld metal at both 750 and 800°C. It is clear that coarsening of the γ' phase occurs at an increased rate when compared to ageing at 750°C. Each exposure was also studied to see whether any of the Eta phase was observed to be present. None of the Eta phase was observed after 250 h of ageing, whilst evidence of early Eta transformation was present after 1000 h in the form of γ' alignment in grain boundary areas. After long term exposure at 5000 h, a significant amount

of the Eta phase was observed in and around the interdendritic regions of the weld metal as shown in Figures 5.46 (a – d). The presence of the Eta phase in these regions was predicted in by thermodynamic calculations using a segregated composition thought to be typical of these regions.

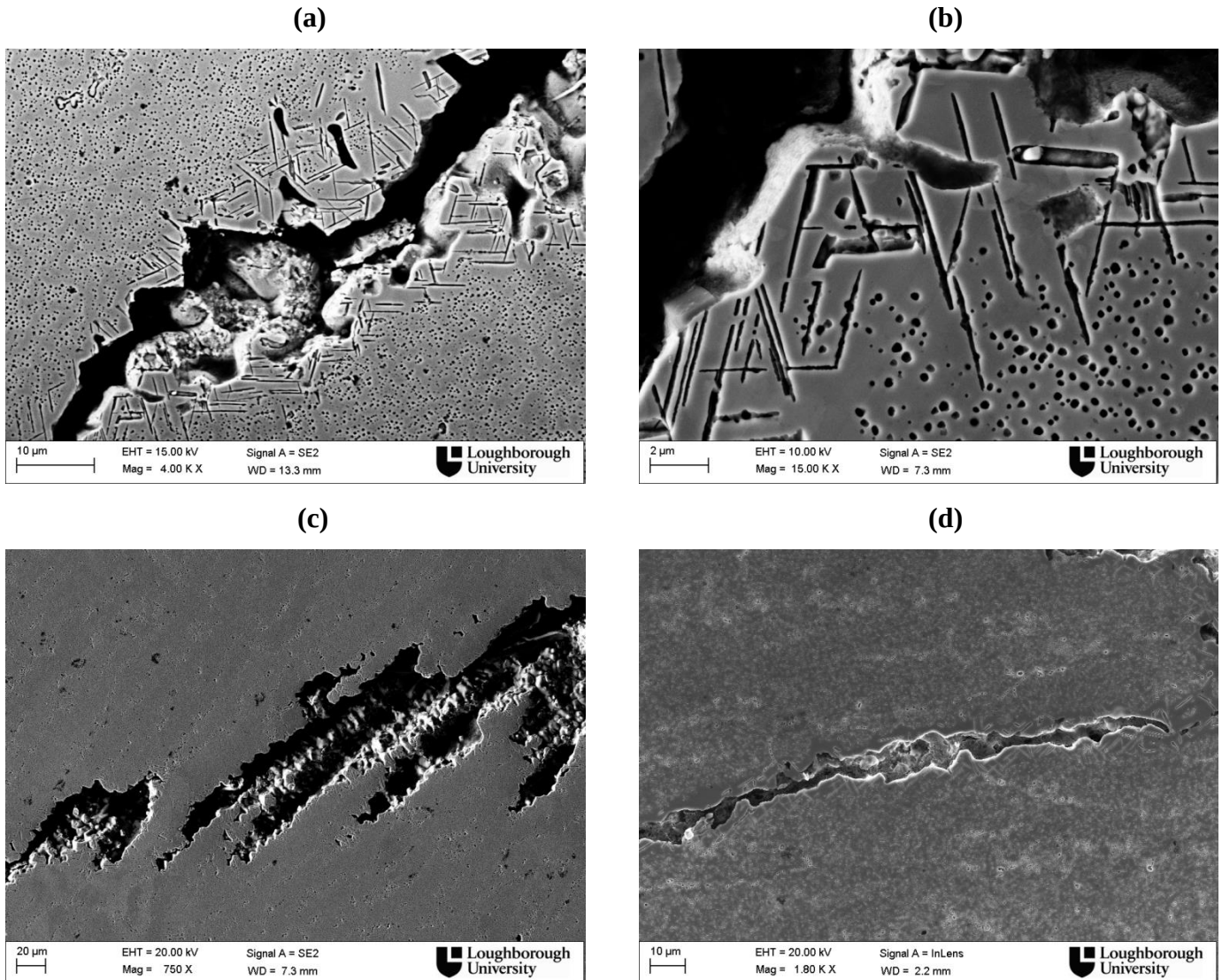


Figure 5.46 – Micrographs showing (a), (b) the presence of the Eta phase around a defect in ID area of weld metal and (c), (d) lower magnification micrographs showing some of the different sizes of defects present

5.10 Microstructural evolution of IP (II)

The first part of this chapter was primarily focused around the study of a weld material designated IP (I). The material was an experimental Nimonic 263 filler material and differed significantly from the nominal composition set by Special Metals; the composition of all the materials studied in this chapter can be seen in Table 5.1. The parent material is not listed, although it is known to be from the same pipe studied in Chapter 4. This next section will detail the characterisation on a sample set based on a weld filler material much closer to the nominal composition. Industrial partners provided five samples as shown in Table 5.7; an as welded sample in addition to samples aged for 3000 and 10,000 h at 700 and 725°C.

Table 5.7 – Table showing welded samples and heat treatment conditions IP (II)

Sample index	Ageing temperature (°C)	Ageing time (h)
97	-	-
98	700	3000
99	700	10,000
100	725	3000
101	725	10,000

Welding was carried out using the circumferential narrow gap TIG butt process, in the aim to produce welded Charpy impact test specimens. Post welding no solution / stress relief type heat treatment was carried out. The welds were, however, given the standard precipitation heat treatment of 800°C for 4 hours before ageing.

Thermodynamic calculations were carried out to predict the stable phases in the weld material and their evolution with temperature. Similarly to the work in section 5.3 based on the filler material supplied by IP (I), two initial equilibrium calculations were produced, the first allowing all phases and the second with suspension of the Eta phase. Non-equilibrium calculations were also produced showing the same trends seen previously with enrichment of the last liquid to form in Mo and Ti and dilution of Al. Due to the similarity of the results produced when modelling the IP (II) weld composition and the extensive thermodynamic modelling already carried out on compositions close to that of nominal Nimonic 263 only a small selection of the calculations are shown in Figure 5.47 (a – d).

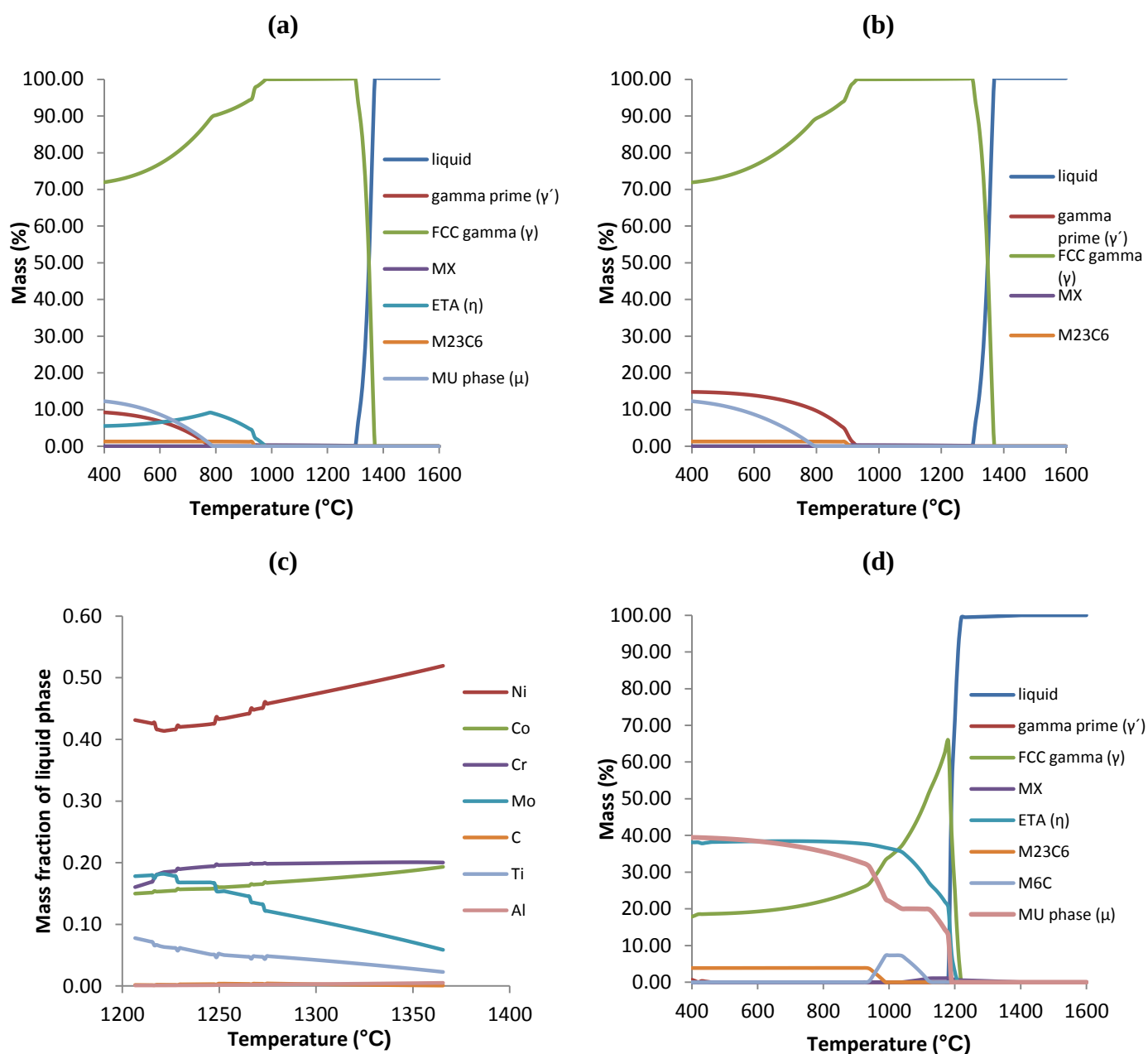


Figure 5.46 – Thermodynamic calculations showing (a) predicted phases against temperature for weld metal allowing for all phases, (b) predicted phases against temperature for weld metal with the Eta phase suspended, (c) Scheil calculation showing the change in chemical composition of the liquid phase during solidification and (d) the resultant equilibrium calculation from the segregated composition calculated using Scheil

The predicted microstructure was very similar in terms of the presence, thermal stability and quantities of minor phases such as $M_{23}C_6$ and MX, the currently unobserved Mu phase is once again predicted, as is M_6C in the calculation using the segregated composition. Differences in predicted γ' precipitation were calculated as would be expected given the two individual compositions used during calculations.

Figure 5.47 shows a modification of a graph previously displayed and shows how the predicted γ' precipitation varies between the two weld assemblies as a whole.

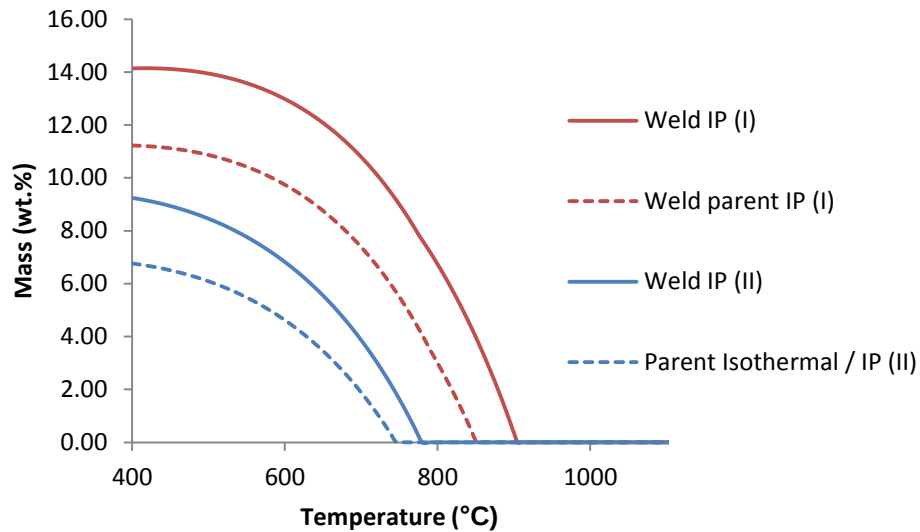


Figure 5.47 – Thermodynamic equilibrium calculation of the mass wt.% of γ' predicted to be present in four different Nimonic 263 based compositions

The weld filler material supplied by IP (II) was predicted to contain a smaller amount of γ' compared to the weld filler material supplied by IP (I), at values of 9.2 wt.% and 14.1 wt.% respectively. The parent materials are also calculated to contain a different amount of γ' with 6.8 and 11.2 wt.% predicted to be present in IP (II) and IP(I) parent material respectively.

The mechanical property evolution of each weld assembly was assessed using a traverse across from the parent metal into the weld. The results are plotted on the graphs contained in Figure 5.48 (a – f). Results indicate that the weld is on average harder than the parent metal in all conditions, however, the difference between the two regions is less pronounced when compared with those results seen in IP (I). In the as-welded sample the average weld hardness was calculated to be 330 HV₁₀ compared to 307 HV₁₀ in the parent metal. After ageing for 3000 h at 700°C the average weld hardness was calculated to be 360 HV₁₀ compared to 341 HV₁₀ in the parent metal. Further ageing at 700°C for 10,000 h found the average hardness to be 332 HV₁₀ compare to 302 HV₁₀ in the parent metal. Ageing carried out at the slightly higher ageing temperature of 725°C for 3000 h found the average weld hardness to be 350 HV₁₀ and 322 HV₁₀ in the parent metal. Longer exposure time of 10,000 h at 725°C only had enough weld metal to provide one data point in the traverse direction at 363 HV₁₀, further indent in the longitudinal direction proved this indent accurate. The average for parent material was calculated to be 323 HV₁₀.

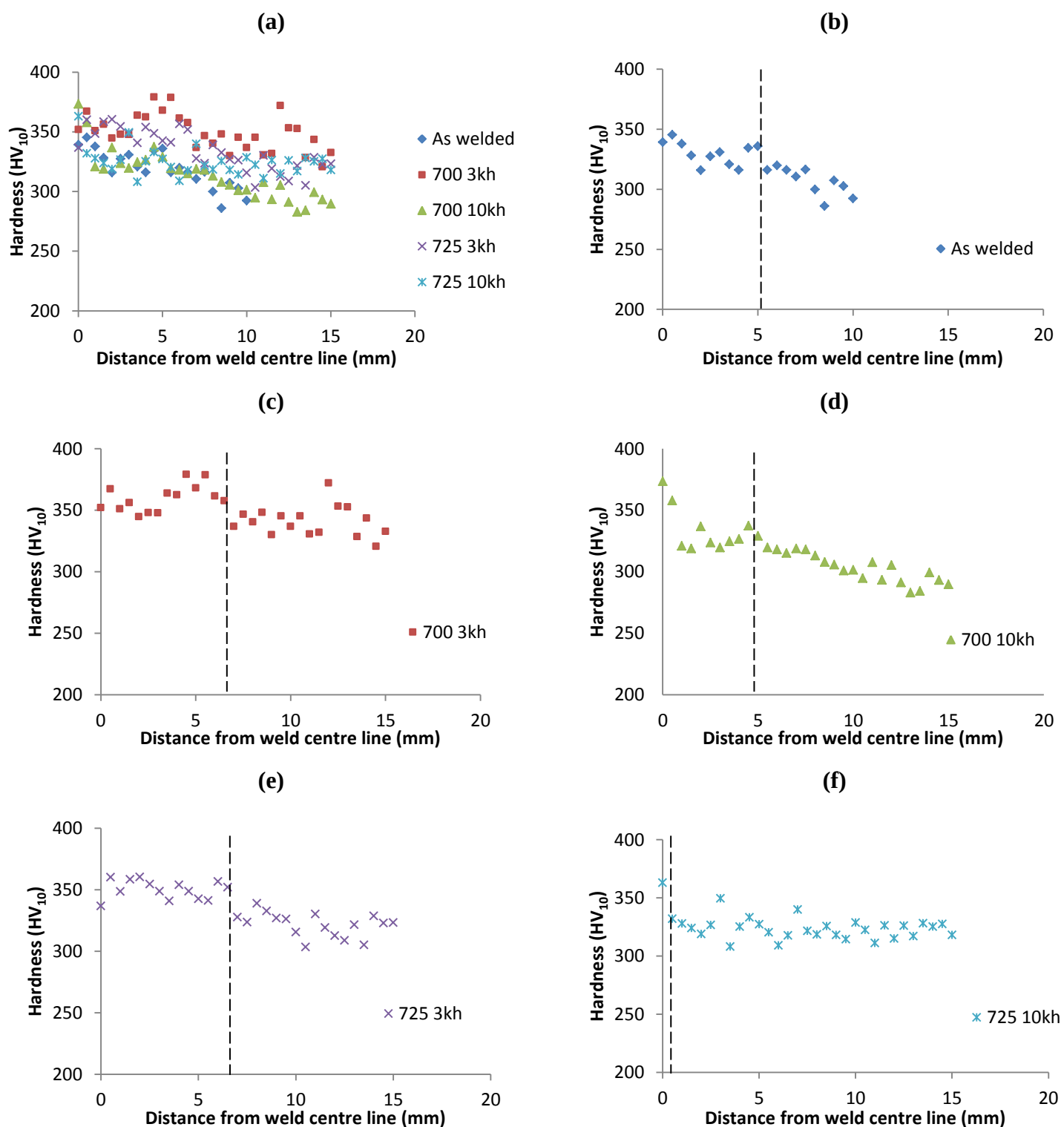


Figure 5.48 – Graphs showing the hardness evolution of welds in the following conditions (a) all conditions, (b) as welded, (c) 3000 h at 700°C, (d) 10,000 h at 700°C, (e) 3000 h at 725°C and (f) 10,000 h at 725°C

In the IP (II) sample set, the γ' was observed in both the parent and weld metals of all the welded samples including the as-welded. This differs from the IP (I) sample set where the as-welded weld material was found to contain no γ' in the un-aged condition. It is, however, difficult to compare the two sample sets as the welds were produced in different materials, material sizes and using unknown welding procedures. The γ' was studied in order to understand the data gathered from hardness testing, and in turn explain why the two sample sets showed such differences in mechanical properties.

Figures 5.49 (a – c) show micrographs taken from the as-welded sample. Figure 5.49 (a) shows a SE image of the interface between the parent and weld material, the micrograph shows no distinct HAZ. The grain structure of each material is also clearly different with the parent metal displaying the polycrystalline grain structure containing twins, typical of a 263 forged grain structure. The weld metal shows a microstructure with an elongated grain structure containing serrated boundaries. The spherical γ' phase was found to be present in both the parent and weld material at 13.3 and 13.4 nm respectively. The area percentage of γ' between both regions was also found to be similar at 6.2 and 6.4%. Analysis of the sample aged at 700°C for 3000 h found the average γ' particle size to be 26.6 and 27.3 nm in the parent metal and weld material respectively. In a repeat of the result observed in the as-welded sample the area % of γ' remained similar at 6.7 and 6.8 % for the parent and weld material respectively. Further exposure time at 700°C for 10,000 h found the γ' coarsened to 33.2 and 32.5 nm in the parent and weld material respectively. The area percentage was again close at 4.7 and 5.2% for the parent and weld metal respectively. Ageing at the higher temperature of 725°C unsurprisingly saw an increase in γ' size when compared to the same ageing time for the 700°C sets. The γ' size was calculated to be 38.8 and 39.9 nm in the parent and weld material for the 3000 h sample. The 10,000 h sample observed the γ' precipitates to coarsen to 53.9 and 53.7 nm in the parent and weld material respectively. At both thermal exposures the area % between the two regions remained close. The closer alignment of hardness values compared to IP (I) can be explained through the γ' phase being present at the same amount and size.

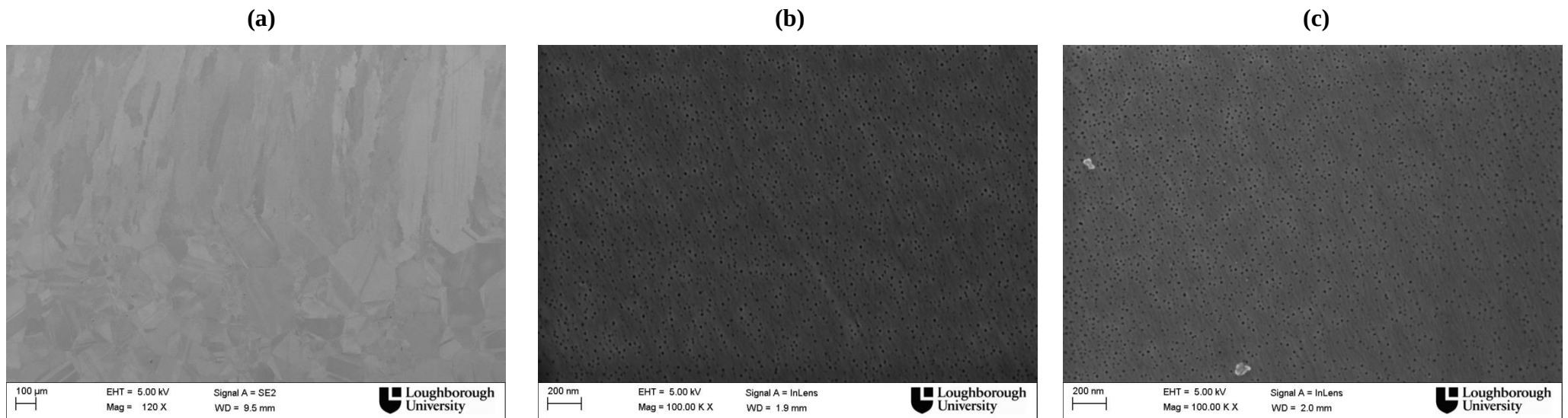


Figure 5.49 – Micrographs of the as welded sample showing (a) Interface of weld and parent material, (b) γ' in the parent material and (c) γ' in weld material

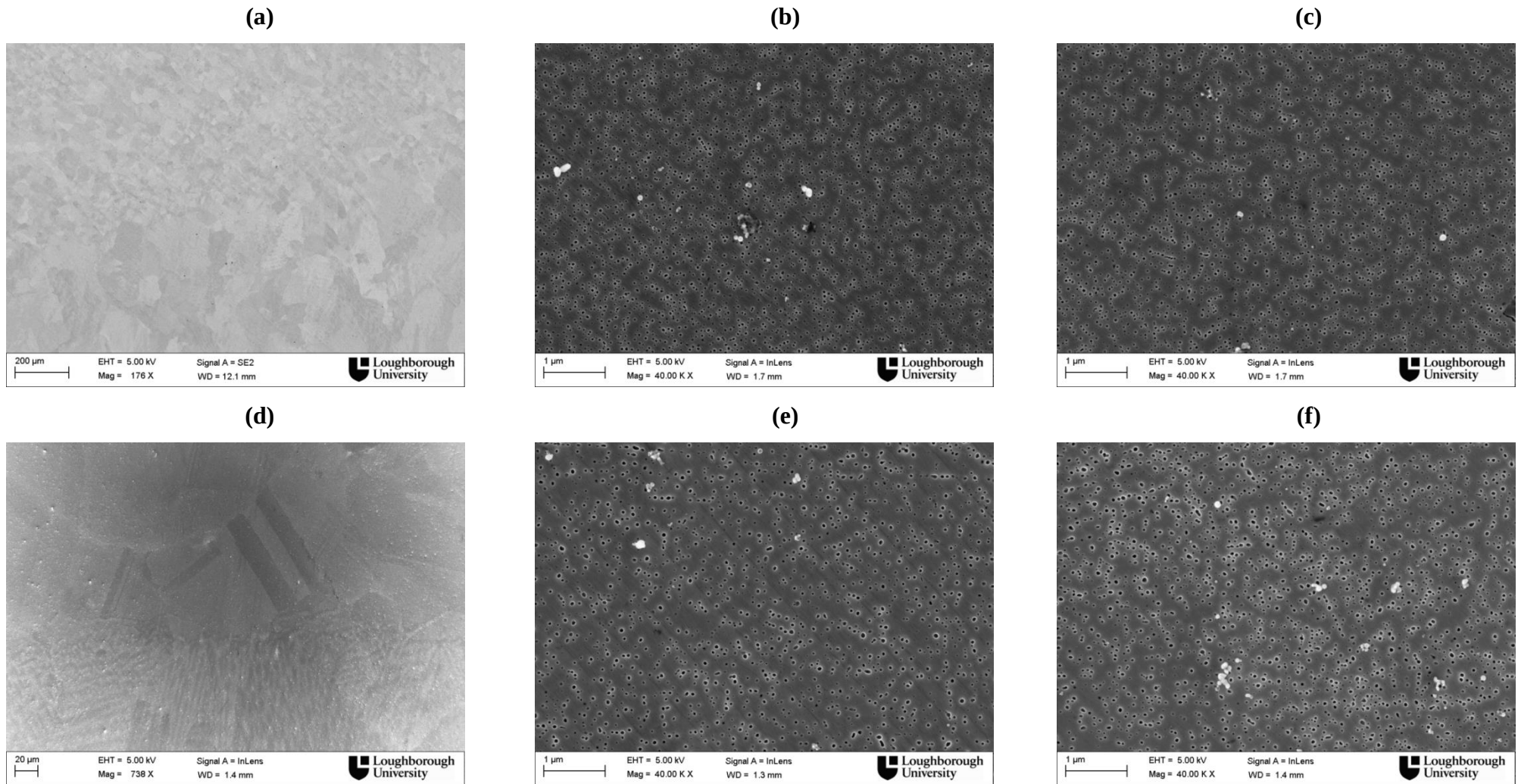


Figure 5.49 – Micrographs of the 700°C aged weld sample showing (a) Interface of weld and parent material for 3000 h sample, (b) γ' in the parent material for 3000 h sample, (c) γ' in weld material for 3000 h sample, (d) interface of weld and parent material for 10,000 h sample, (e) γ' in the parent material for 10,000 h sample and (f) γ' in the weld material for 10,000 h sample

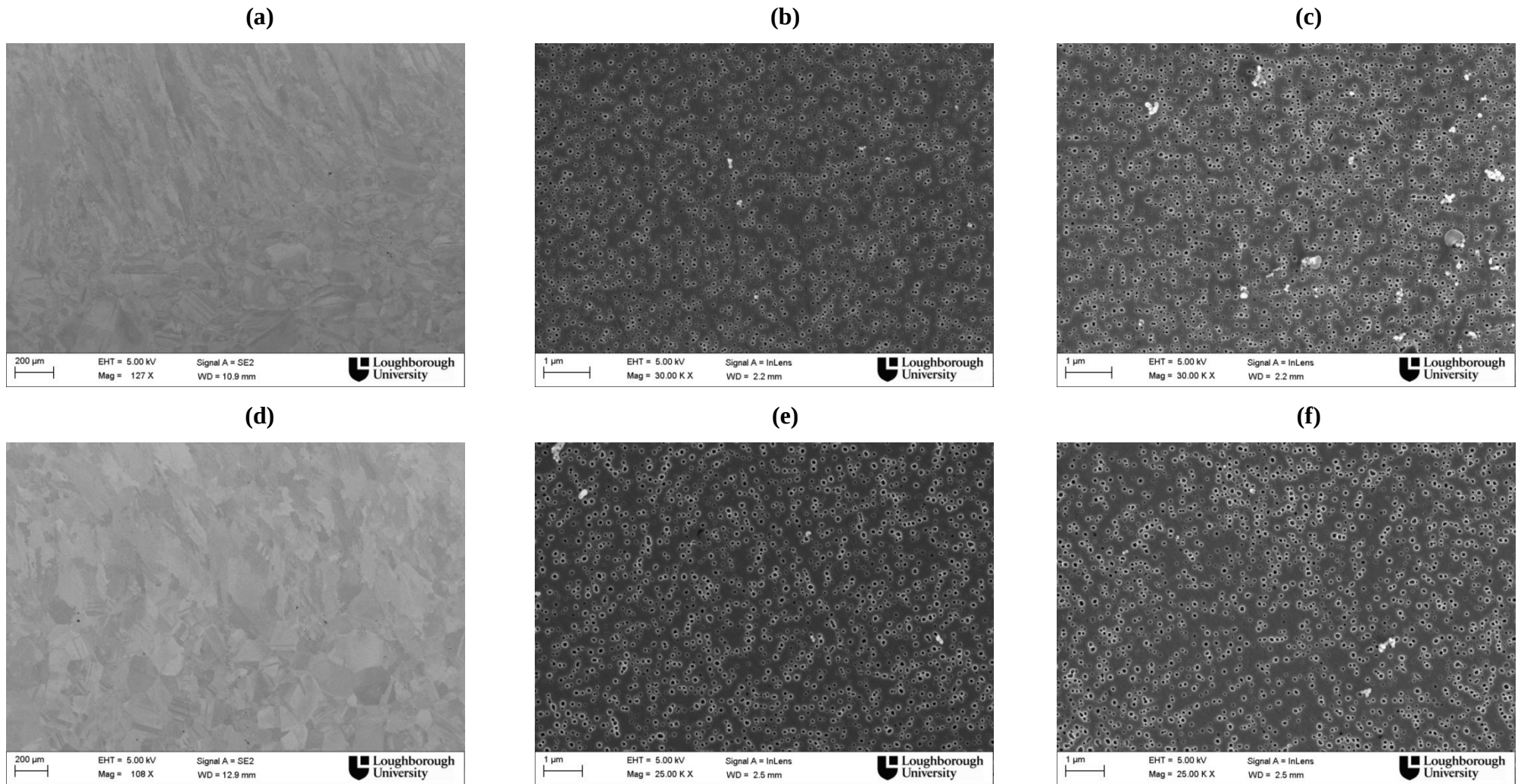


Figure 5.50 – Micrographs of the 725°C aged weld sample showing (a) Interface of weld and parent material for 3000 h sample, (b) γ' in the parent material for 3000 h sample, (c) γ' in weld material for 3000 h sample, (d) interface of weld and parent material for 10,000 h sample, (e) γ' in the parent material for 10,000 h sample and (f) γ' phase in the weld material for 10,000 h sample

The presence and effect of segregation was studied in this sample set to see if there was any segregation present and whether there were any precipitation differences in these regions. Segregation was evident in all samples at low magnification images such as that shown in Figure 5.51 (a), and similar to previous work, the dendrites were found to be present in both the equiaxed and elongated forms heterogeneously throughout the alloy. Precipitation trends also showed some variation with area fraction and γ' particle size increased in the interdendritic areas, an example of this is shown in Figure 5.51 (b). Eta transformation was observed in the 700°C sample aged for 10,000 h shown in Figure 5.51 (c), existing Eta phase and alignment of the γ' phase can be clearly seen in this micrograph. Localised and more extensive regions of the Eta phase were found to be present in the 725°C aged for 10,000 h, this can be seen in Figure 5.51 (d).

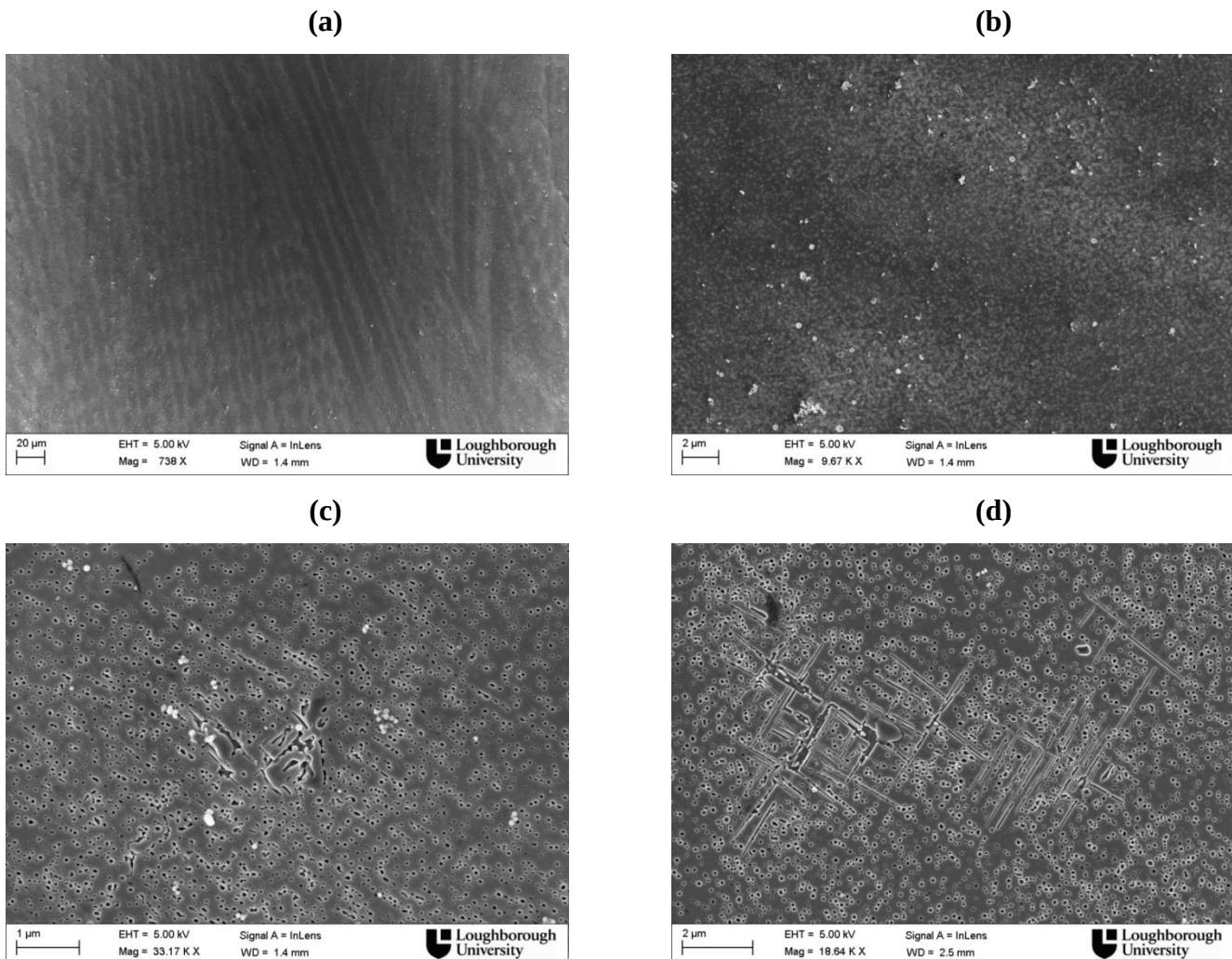


Figure 5.51 – Micrograph showing (a) presence of dendrite in sample aged for 10,000 h at 700°C, (b) higher magnification image of same sample showing increase area fraction and γ' size in these areas, (c) early transformation of Eta phase in 10,000 h sample aged at 700°C and (d) region containing significant precipitation of Eta phase in sample aged for 10,000 h at 725°C

5.11 Summary of work on welded Nimonic 263

This chapter studied two welded sample sets, designated IP (I) and IP (II), originating from two different industrial partners. Research into both sample sets has enabled comparisons to be drawn regarding the effect of varying filler material compositions, different post weld heat treatments and ageing at a range of temperatures. Work has also been carried out, successfully predicting the precipitation products across different regions and conditions of the weld. The predicted microstructures across both sample sets were found to be broadly similar, predicting the same phase constituents and approximate compositions to be present. Non-equilibrium calculations found that both weld metals were prone to chemical segregation, the last liquid to solidify was predicted to contain an increase in titanium and molybdenum with a decrease in aluminium content. Experimental observations across both sample sets showed that different microstructural features were present as a result of this segregation. Both sample sets showed preferential Eta transformation within and around segregated areas upon ageing, although to different extents.

The IP (I) sample set contained four pre-service conditions which were observed to contain different microstructures. The microstructural evolution of the four pre-service conditions was later studied as an effect of ageing. Samples studied in the as-welded or hardened pre-service condition presented a microstructure which contained a homogenous distribution and sizing of the γ' phase in addition to other phases typical to Nimonic 263. The two pre-service conditions which originated from the stress relieved condition were observed to contain significantly different microstructures when compared to the aforementioned pre-service conditions, in which the distribution and size of γ' phase was found to vary in segregated areas. The interdendritic regions were found to have significantly larger γ' when compared to that of the dendritic regions and those of other pre-service conditions. Upon ageing, the Eta phase was found to heavily populate the interdendritic regions, this was not unexpected due to the predicted shift in Ti-Al ratio as a result of segregation. The presence of voids were also observed along segregated areas, the cause of these voids was not determined. Heat treatment trials were carried out using the dilatometer in an attempt to reproduce the industrially heat treated stress relieved microstructure. These trials ultimately proved unsuccessful but helped to convey important links between cooling rate and the subsequent coarsening rate of γ' . The individual pre-service heat treatments had a significant effect on the hardness properties of each weldment. The hardness in both the weld and parent materials was found to soften after isothermal ageing at 750°C.

The results have clearly demonstrated that the filler material IP (II) which was closely aligned to the nominal composition of Nimonic 263 showed a high degree of similarity in both mechanical properties and microstructural features observed between the parent and weld metals. Furthermore, no cracking was observed in any region of the weld metals studied.

Chapter 6

Microstructural characterisation of cast Nimonic 263

6.1 Introduction

Chapters 4 and 5 have focused on Nimonic 263 as a forged alloy and the effect that heat treatment, ageing and welding have on its microstructure and performance. As discussed at the beginning of Chapter 5, concerned with welding, advanced plant will be manufactured through a complex network of pipes and fittings. Part of these complex boiler assemblies will include components such as valves, steam glands and connectors etc. Such components often have intricate internal and external features which are extremely difficult and time consuming to machine from a billet. Therefore, to produce such large power plant components the casting route is chosen. An example of such a casting is shown in Figure 6.1.

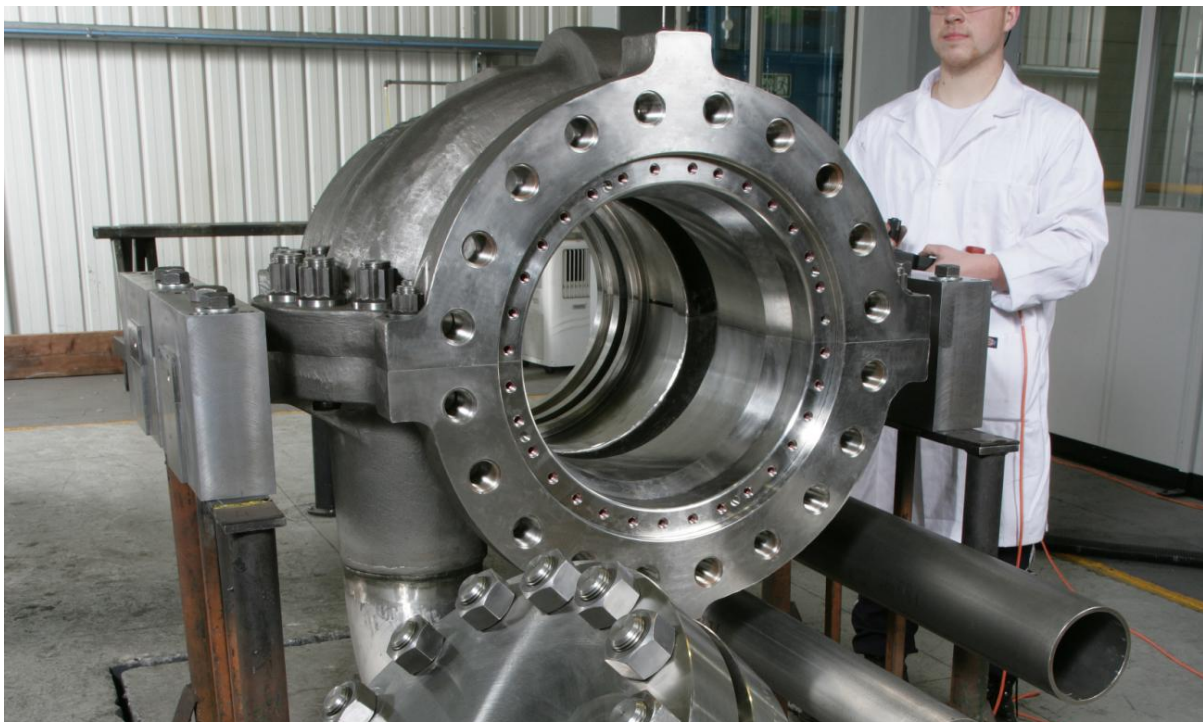


Figure 6.1 – Nickel steam gland casting (image courtesy of Goodwin Steel Castings)

Casting is the preferred manufacturing method for a number of reasons. Firstly, the casting method allows complex external and internal geometries to be realised. The cast product will also be near net shape, meaning that very little machining has to be done. This is especially important as machining of nickel base alloys can be expensive and time consuming, with specialist machinery often required. The steam gland casting, shown in Figure 6.1, had to be produced in two halves and bolted together to achieve the finished product. A steam gland is located at the exhaust end of a high temperature gas turbine. Steam temperatures in this area

are in excess of 700°C, which is why nickel base alloys are again the material of choice for such components in A-USC plant.

Nimonic 263 is a candidate material along with other nickel base alloys including; Nimonic 105, Inconel 625, Inconel 740, Inconel 617 and Haynes 282 for both large and small castings in high temperature parts of the plant.

6.2 Sample conditions

A Nimonic 263 step block casting similar to that shown in Figure 6.2 was produced to simulate the manufacture of a Nimonic 263 casting. Production of the step block was carried out using a gravity fed sand casting technique. Production of a step block will also provide information regarding the effect of different section sizes on the microstructure and the different precipitation products present as an effect of cooling rate.



***Figure 6.2 – Typical step block, approximately 1 meter in height
and similar to those shown in experimental section***

The Nimonic 263 castings were supplied in three conditions: As-cast; solution treated; and fully processed. The cast alloy is solution treated for a number of reasons firstly to remove /

reduce any segregation that is present as a result of the casting process. The alloy is also solution treated to dissolve any phases that may have formed during solidification or on cooling after casting. Finally, the aim is to have a casting with a homogeneous composition throughout and free from all lower temperature phases such as γ' and $M_{23}C_6$. Solution treatment of the cast condition is a two-step process which includes:

- Homogenise @ $1100^{\circ}\text{C}^{+/-20^{\circ}\text{C}}$ for 6 h;
- Ramp to $1200^{\circ}\text{C}^{+/-20^{\circ}\text{C}}$ for 12 h – WQ.

The above heat treatment differs from the standard solution heat treatment used in the rest of the research. The specific heat treatment was chosen by the foundry and takes into account section thickness and the as-cast dendrite arm spacing measurements.

The Nimonic 263 sample described as ‘fully processed’ has been given both the solution treatment above and a precipitation hardening heat treatment. The fully processed condition in the step block was produced by precipitation heat treating a piece of the cast material supplied in the solution treated condition. The precipitation heat treatment has been designed to result in a controlled precipitation of strengthening phases such as $M_{23}C_6$ and γ' . This final heat treatment makes up the standard pre heat treatments before the alloy goes into service:

- Precipitation hardened for 800°C for 8 h – air cool

It should be noted that the precipitation heat treatment is 4 h longer than that used in other sample conditions. This is due to a specification which states piping material or welds must pass a bend test, and shorter precipitation heat treatments can facilitate this.

The composition for Nimonic 263 as supplied by Goodwins SC is shown below in Table 6.1.

Table 6.1 – Composition of Nimonic 263 in the cast product form

Element	Ni	Co	Cr	Mo	C	Ti	Al	Fe	N
Composition (wt.%)	51.99	19.59	19.85	5.61	0.06	2.05	0.42	0.07	0.007

6.3 Thermodynamic calculations and predicted microstructure

The composition in Table 6.1 falls within the specification set by Special Metals for the alloy. Based on the composition of the cast material, thermodynamic calculations were carried out to produce a prediction of the phases present and how the fraction of each phase varies with temperature. The first prediction is an equilibrium calculation allowing for all possible phases and is shown in Figure 6.3 (a). An expanded view of this calculation which highlights changes in the two carbide phases MX and $M_{23}C_6$ is shown in Figure 6.3 (b). A separate calculation shown in Figures 6.3 (c) and (d) has also been produced suspending the Eta phase; suspension of this phase gives a more accurate prediction of the alloys early microstructure.

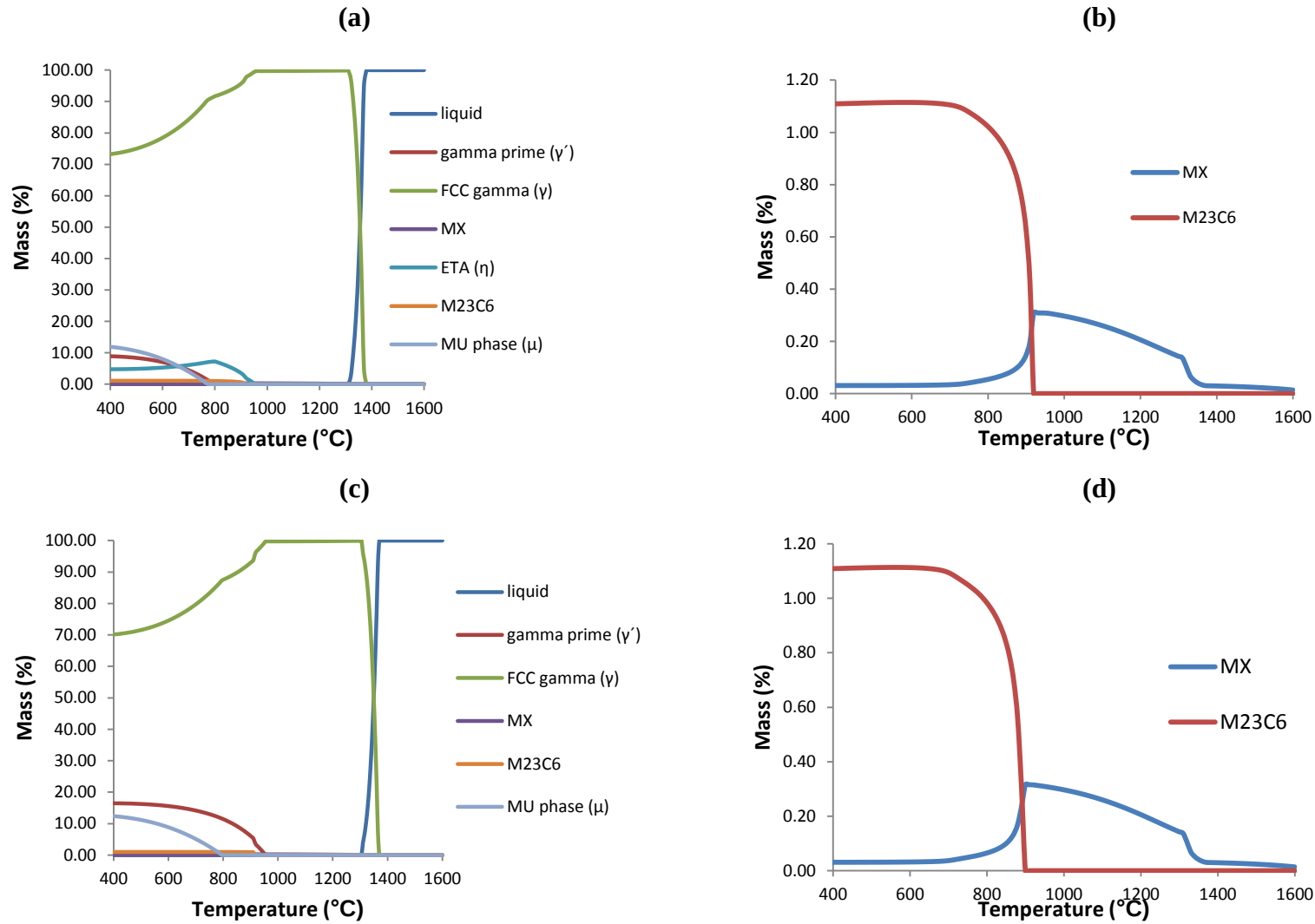


Figure 6.3 - Thermodynamic calculation showing predicted microstructure for (a) supplied composition, (b) enlarged calculation of supplied composition showing $M_{23}C_6$ and MX in particular, (c) supplied composition with the η phase suspended and (d) enlarged calculation of supplied composition with the η phase suspended, showing in $M_{23}C_6$ and MX in particular

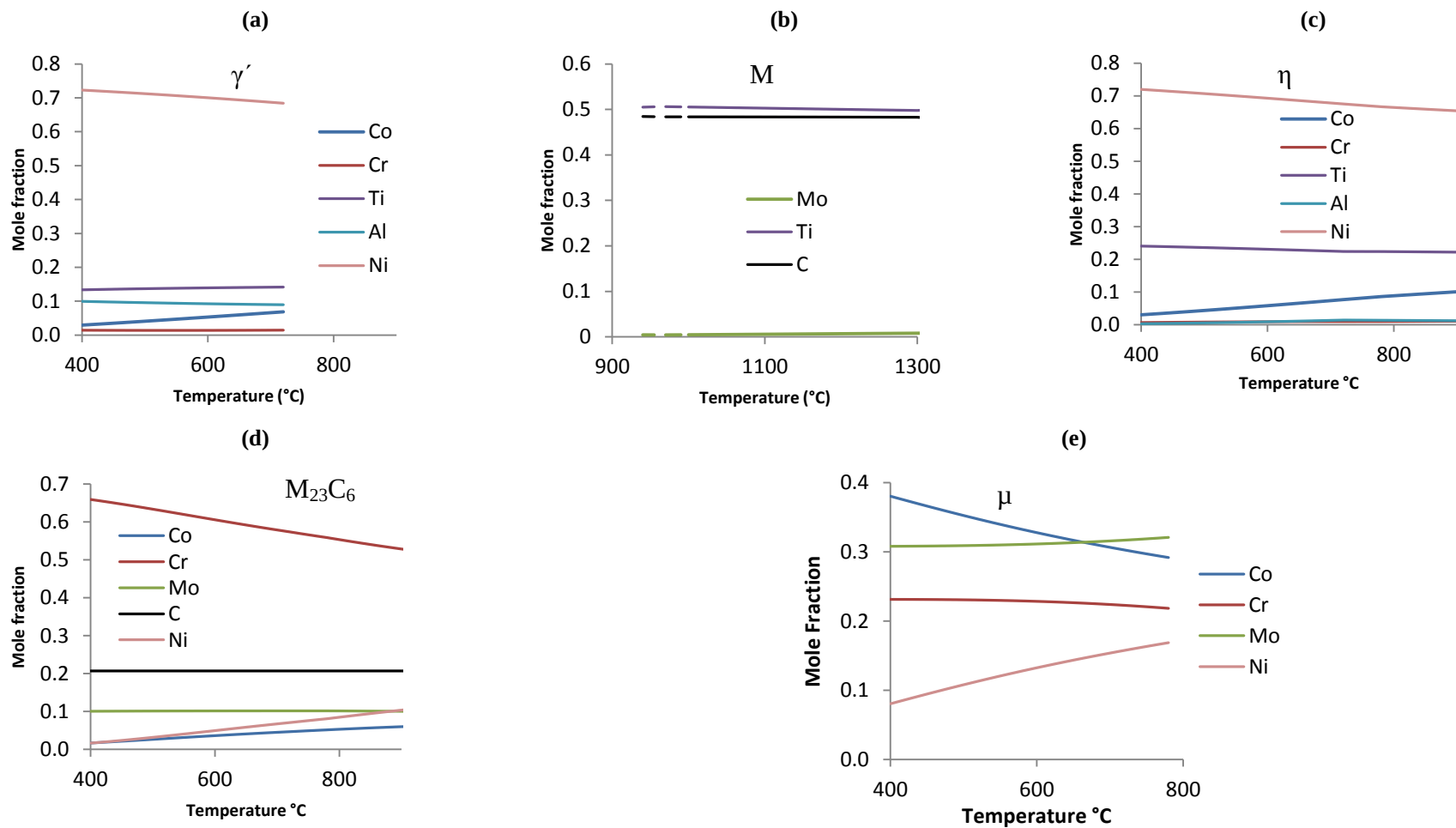


Figure 6.4: Phase composition calculations for average Nimonic 263 composition: (a) γ' , (b) MC, (c) η , (d) $M_{23}C_6$ and (e) μ phase as a function of temperature

The composition of the major phases predicted to be present in the cast alloy can be seen in Figure 6.4 (a – e). The composition of each phase shows little difference from the compositions of those predicted in the chapters concerned with isothermal ageing and welding.

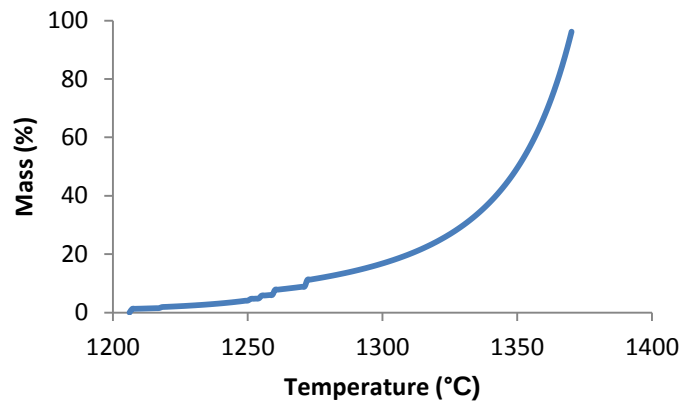


Figure 6.5: Solidification range of cast Nimonic 263

Due to the nature of the casting process, cast Nimonic 263 will have experienced significant segregation during solidification. Scheil calculations were carried out to model this segregation and will be discussed in detail later in the chapter. Figure 6.5 shows that the liquid phase solidifies over a range of 164°C, beginning to solidify at 1370°C before being fully solidified at 1206°C.

To understand the complexities of the cast microstructure and the effect of heat treatment several variables were investigated. In addition to data relating to thermal exposure it is also important to note the location each specimen was sampled from. This is especially important when focusing on cast alloys, because the thickness and geometry significantly influence the properties and microstructure of the alloy. The samples examined in this chapter are detailed in Table 6.2.

Table 6.2: Sample list used in cast chapter

Sample ID	Origin	Heat treatment	Notes (location, ageing conditions etc)
94	Test bar	Fully processed	Test bar
95	Test bar	Fully processed	Centre
96	Test bar	Fully processed	Edge
108	Test bar	Fully processed	100 h @ 700°C
109	Test bar	Fully processed	1000 h @ 700°C
110	Test bar	Fully processed	2000 h @ 700°C
111	Test bar	Fully processed	5000 h @ 700°C
112	Test bar	Fully processed	100 h @ 800°C
113	Test bar	Fully processed	1000 h @ 800°C
114	Test bar	Fully processed	2000 h @ 800°C
115	Test bar	Fully processed	5000 h @ 800°C
118	Step casting	As cast	-
119	Step casting	ST	Evaluate effect of ST
122	Step casting	Fully processed	Replicate fully processed test bar sample
123	Test bar	Fully processed	20 h @ 1200°C
124	Test bar	Fully processed	30 h @ 1200°C
125	Test bar	Fully processed	40 h @ 1200°C
126	Test bar	Fully processed	50 h @ 1200°C
127	Test bar	Fully processed	165 h @ 1200°C

6.4 Pre-service conditions

The fully processed casting (test bar) was sectioned and samples taken from both the centre and the edge of the casting. Due to the geometry of the test bar, it was not expected to contain the same degree of segregation when compared to thicker section areas of the casting. Samples were etched with Kallings No. 2 reagent to reveal a heavily segregated dendritic microstructure. Analysis of these two areas showed distinctly different dendrite morphologies. Figure 6.6 shows a number of optical micrographs stitched together to show (a) etched centre sample and (b) etched edge sample. It was also clear that the homogenisation heat treatment had not fully homogenised the casting as the dendritic microstructure was still present in both the centre and edge samples. To investigate the effectiveness of the homogenisation heat treatment, several heat treatments were performed on the ‘fully processed’ test bar. Samples were exposed to a temperature of 1200°C for periods between 20 – 160 h. Samples given the longer term homogenisation heat treatment were etched with Kallings No2 and analysed using optical microscopy. Evidence of a dendritic microstructure was still present with no visible difference observed across the sample set in terms of dendrite size or distribution.

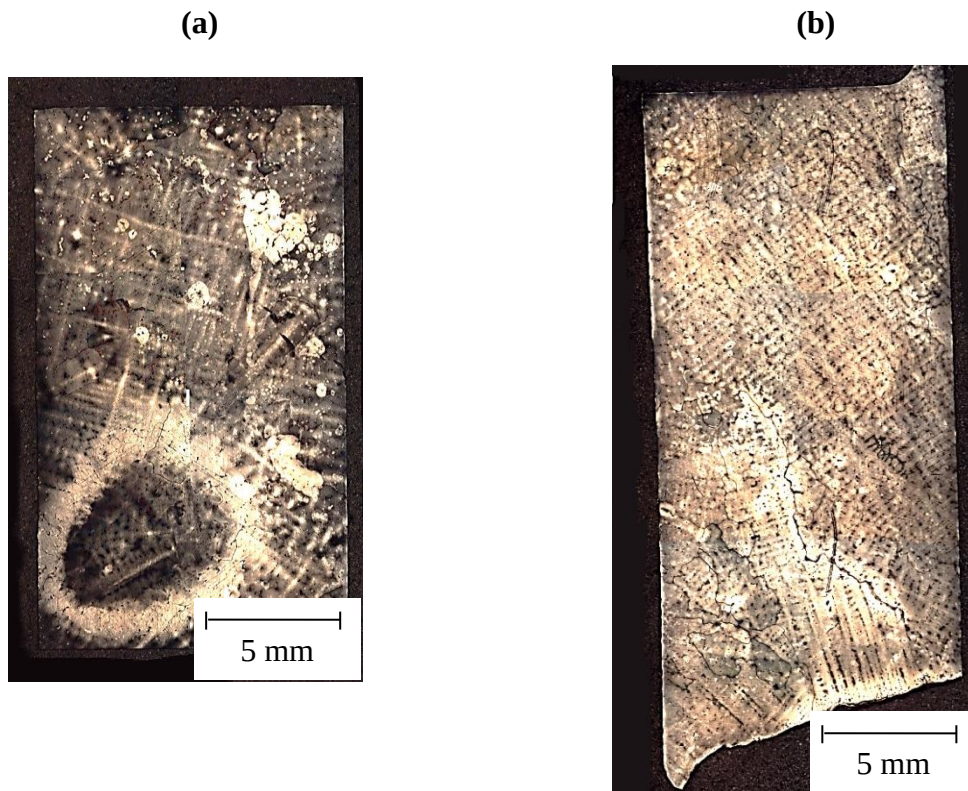


Figure 6.6: Stitched micrographs showing the centre (a) and edge (b) of the etched test bar

The dendritic microstructure observed in specimens from the test bar points to a heavily segregated microstructure. The Scheil method has again been used to model this segregation for the cast composition. The predicted composition of the last liquid to form is shown in Table 6.3. The segregated composition was then used to perform an equilibrium calculation, predicting the microstructure present in such segregated regions. Figure 6.7 (a) shows that the microstructure is predicted to be a gamma matrix with large amount of the Eta and Mu phase, approximately 40% in both cases. There is little γ' (0.86%) predicted due to preferential precipitation of the Eta phase as a result of the high Ti-Al ratio.

Table 6.3: Chemical composition of 263 casting and calculated composition of segregated region using Scheil modelling

Element	Ni	Co	Cr	Mo	C	Ti	Al	Fe	N
Composition (wt.%)	51.99	19.59	19.85	5.61	0.057	2.05	0.42	0.07	0.007
Segregated composition (wt.%)	42.82	15.23	16.14	17.90	0.17	7.67	0.07	-	-

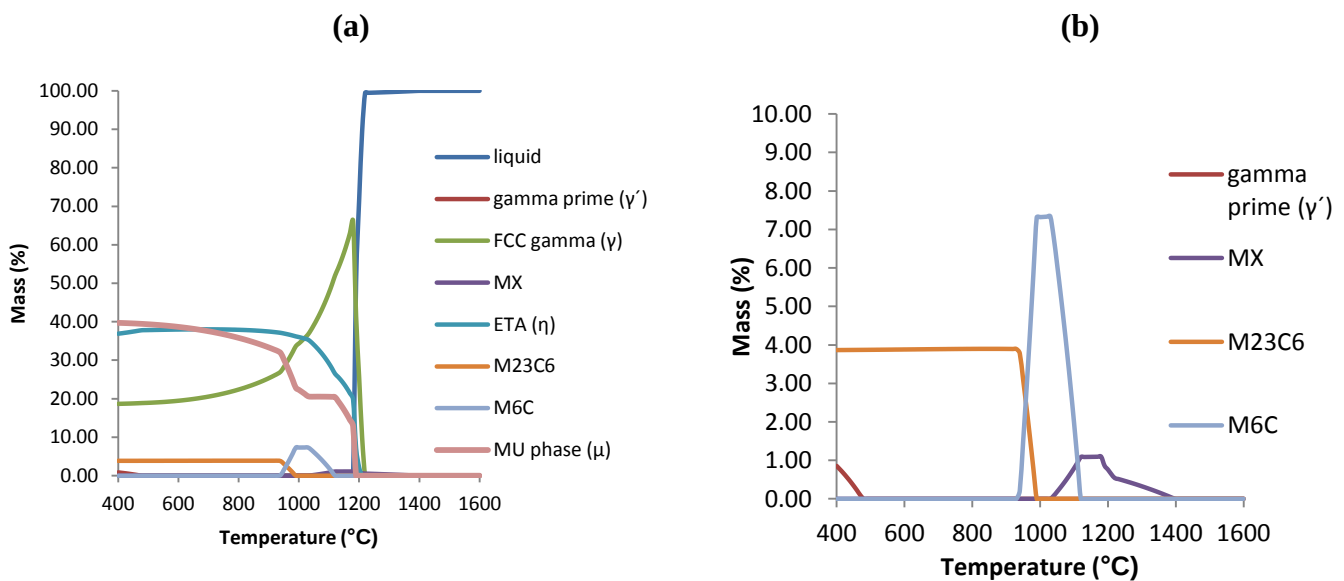


Figure 6.7: Thermodynamic calculations showing predicted microstructure for (a) the segregated composition and (b) expanded calculation

Figure 6.7 (b) shows an expanded view of the same calculation focusing on the minor precipitation phases such as MX, $M_{23}C_6$ and M_6C . The $M_{23}C_6$ carbide is present at approximately 4 % and is stable up until 900°C before it begins to dissolve; the carbide is fully dissolved at 1000°C. At approximately 900°C when the $M_{23}C_6$ precipitates begin to dissolve, the M_6C carbide is stable over a temperature range between 940 and 1110°C at a maximum of 7.34 %. From literature the M_6C phase is known to be prone to cracking ^[33]. Last to go into solution is the high temperature MX phase which is stable from 1040 to 1390°C at a maximum of 1.1 %. Results from the non-equilibrium thermodynamic calculations are in line with those described in Chapters 4 and 5.

It is important to understand how the alloy microstructure evolves as a result of the pre-service heat treatment. To do this the as-cast microstructure should be fully evaluated before studying the changes observed after each subsequent heat treatment step. Furthermore the mechanical effects of each heat treatment step on the alloy were also investigated by determining the hardness. The hardness evolution of the alloy as a result of the pre-service heat treatment is shown below in Figure 6.8.

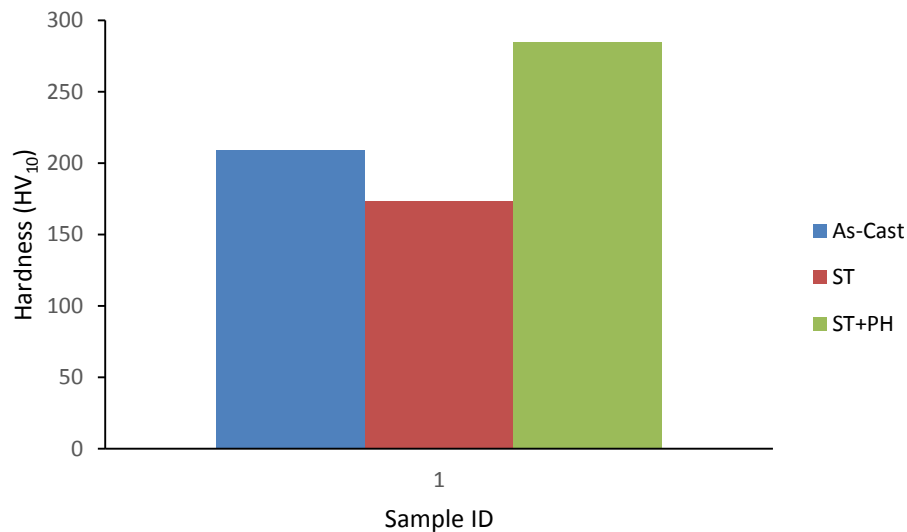


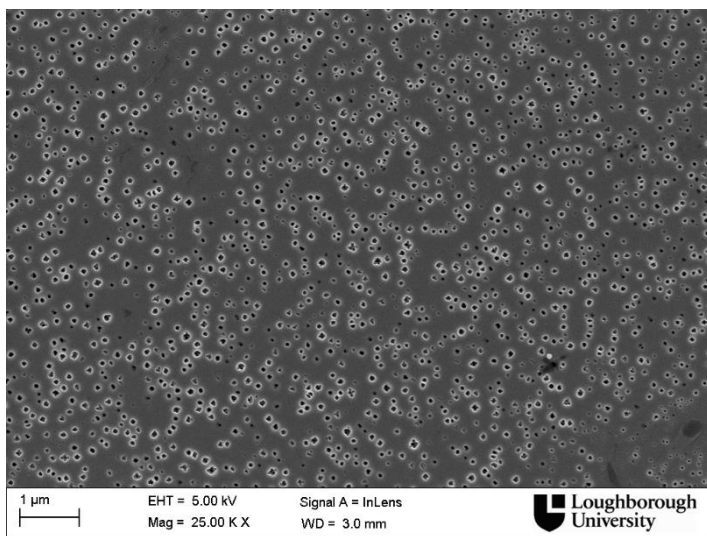
Figure 6.8: Effect of pre service heat treatment on hardness of cast Nimonic 263

The hardness of the as-cast sample was measured at 209 HV¹⁰, the alloy then softens to 173 HV¹⁰ as would be expected after solution treatment, which is designed to dissolve any of the strengthening precipitates formed as a result of the casting process. After the precipitation heat treatment the alloy increases in hardness to 284 HV¹⁰, this increase is attributed to the precipitation of the γ' phase which forms first within the microstructure. The standard

deviation of the As-cast, ST and fully processed sample was 10.5, 2.9 and 11.0 HV₁₀ respectively.

Electron micrographs shown in Figures 6.9 (a) and (b) indicate the presence of γ' precipitates in the as-cast sample. The γ' precipitate size was determined to be an average of 40 nm at an area fraction of 0.04 and was similar in size and evenly dispersed throughout the microstructure. Figure 6.9 (b) does show a clear denuded zone at close proximity to the grain boundary; this type of feature is typical for the alloy when comparing across other sample sets. However, the denuded region does look more pronounced in the cast alloy and was measured to be up to 3 μm using electron micrographs in Figure 6.10 (a, b).

(a)



(b)

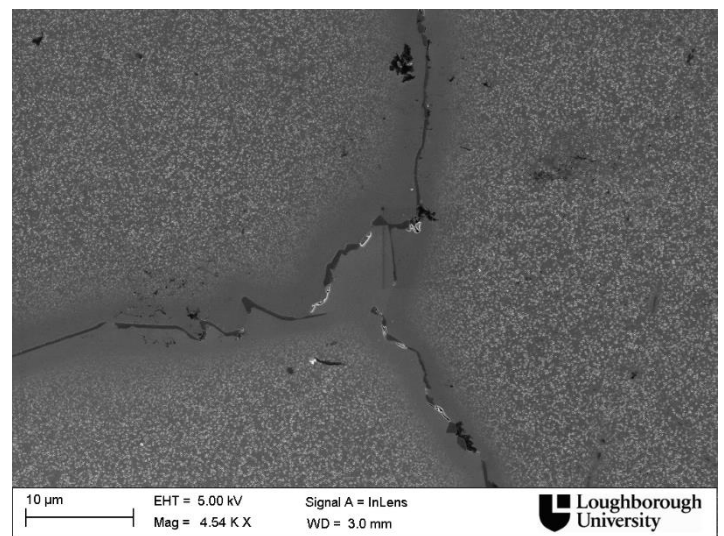
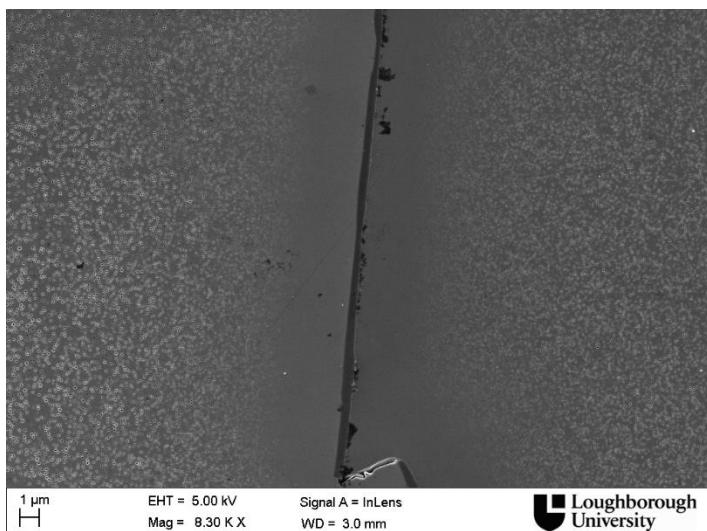


Figure 6.9: Electron micrographs of the as-cast sample showing (a) the γ' phase and (b) the denuded region of γ' precipitates in close proximity to the grain boundary – note that there is also a continuous grain boundary phase

(a)



(b)

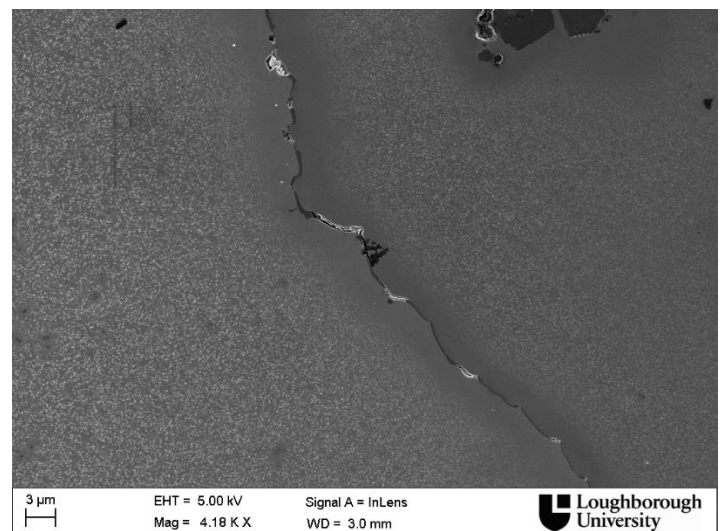


Figure 6.10: (a, b) Electron micrographs of as cast sample showing further evidence of continuous grain boundary phase and denuded region of γ' precipitates

A continuous grain boundary phase was observed throughout the as-cast microstructure. This phase was determined to be the Ti-Mo rich MX phase observed in previous chapters, and was confirmed through chemical mapping in Figure 6.11 and the average composition from EDX results presented in Table 6.4. The high titanium content of this phase is thought to be the reason for the much larger denuded zone of the Ti rich γ' phase. Small defects such as porosity and cracks were found to exist along the continuous boundaries and throughout the alloy. The specimen was examined in the as-polished condition which showed that these defects were still present and not a result of any etching effects.

Table 6.4: EDX data for the continuous grain boundary phase

	C	N	Al	Si	Mo	Ti	Cr	Co	Ni
<i>Continuous grain boundary phase Wt %</i>	8.43	3.51	0.26	0.44	28.29	45.16	4.00	3.04	6.89
<i>Continuous grain boundary phase At %</i>	27.69	10.32	0.43	0.69	12.14	38.81	3.11	2.10	4.71
<i>Matrix Wt %</i>	3.79	1.41	0.41	0.68	5.68	2.51	17.51	18.13	49.89
<i>Matrix At %</i>	15.30	4.87	0.75	1.17	2.88	2.54	16.34	14.93	41.24

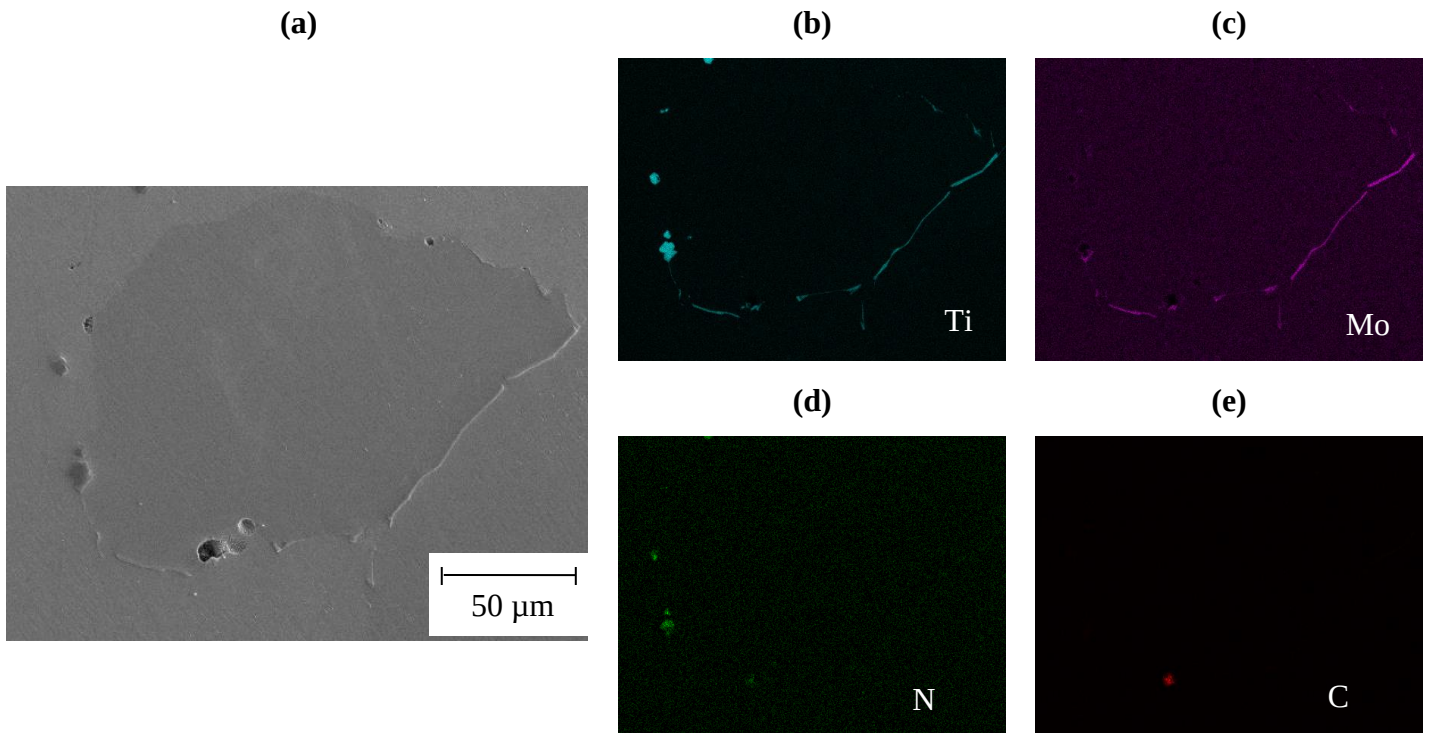


Figure 6.11: Chemical information of area in fully processed sample which contained elongated grain boundary phase (a) electron micrograph of area, (b) EDX map showing Ti concentration, (c) EDX map showing Mo concentration, (d) EDX map showing N concentration and (e) EDX map showing carbon concentration

After the two stage solution heat treatment, no γ' was observed to be present anywhere in the sample. The amount of the continuous MX phase along grain boundaries also appeared to be reduced. The electron micrographs in Figure 6.12 (a) and (b) show the microstructure after solution heat treatment. Grain boundary porosity was again observed throughout the alloy.

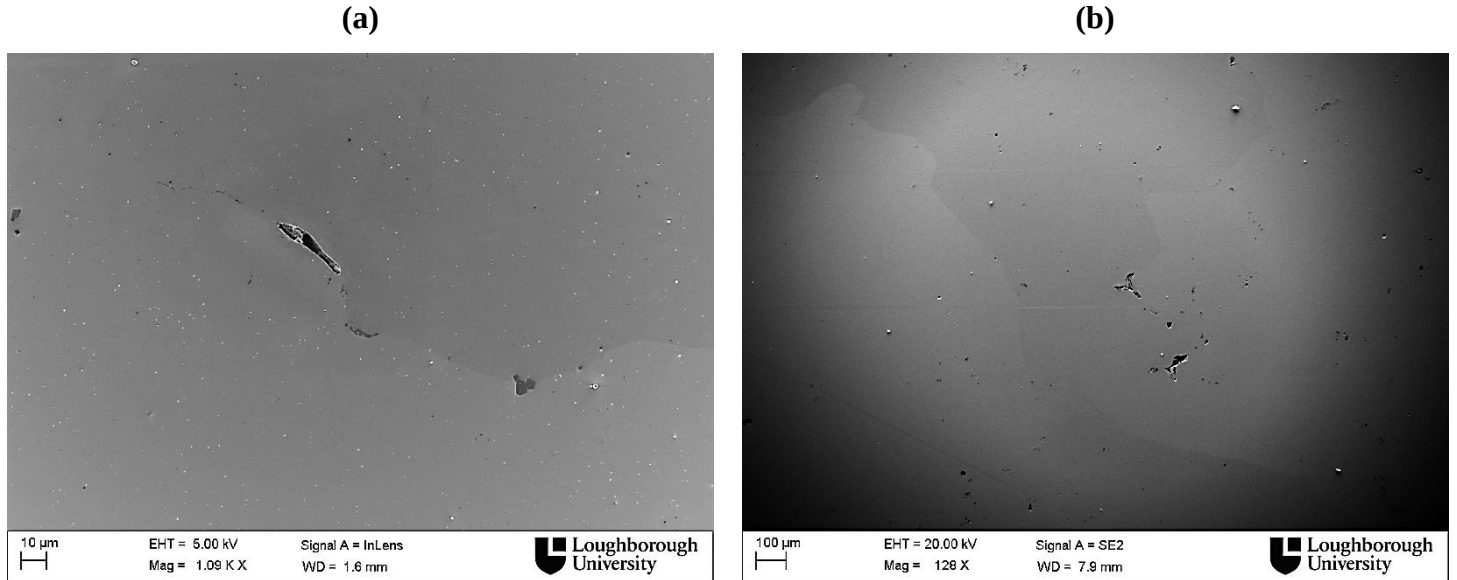
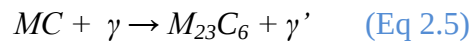
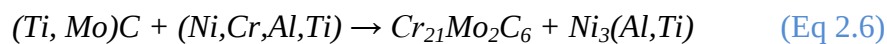


Figure 6.12: Electron micrograph of solution heat treated sample showing reduced amount of continuous grain boundary precipitates and grain boundary porosity

It is understood from literature that, during heat treatment and service, the MX phase decomposes slowly, releasing carbon into the surrounding matrix. Equations 2.5 and 2.6 from the literature review are repeated below:



or more specifically:



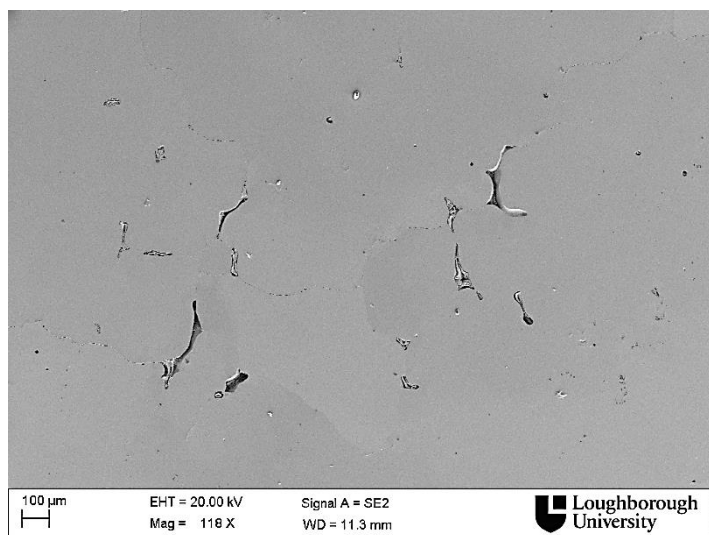
The precipitation heat treatment utilises the dissolved carbon present as a result of solution heat treatment and completes its transformation into $M_{23}C_6$ and γ' . The result of this transformation is evident after the precipitation heat treatment of 800°C for 8 hours. The γ' phase shown in Figure 6.13 (b) is found to be present at ~14 nm in size at an area fraction of 0.03. The grain boundary phase $M_{23}C_6$ was also present and was observed using carbon extraction replicas on the TEM. The chemical composition of this type of precipitate was determined using EDX analysis and is shown in Table 6.5.

Table 6.5: Chemical analysis of grain boundary precipitates in the fully processed cast Nimonic 263

Element	Cr	Co	Ni	Mo
Composition (wt.%)	74.88	3.73	3.92	17.48
Standard deviation	4.06	0.45	2.18	4.6

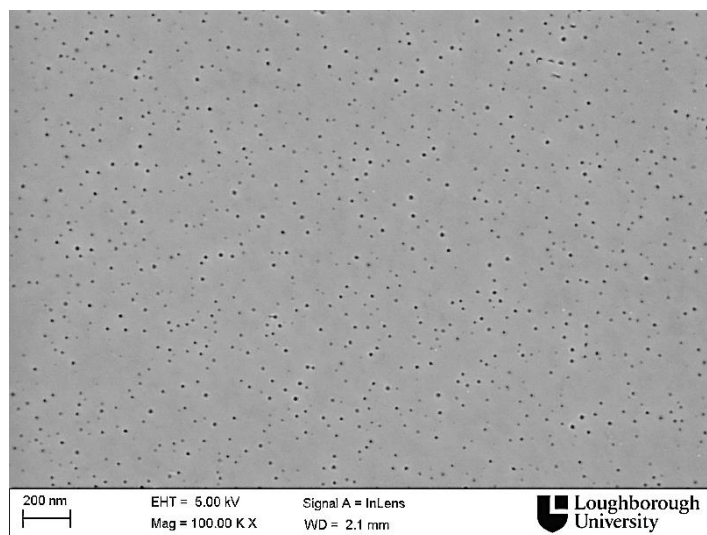
Voids are evident throughout the microstructure along grain boundaries. Although similar features were observed in the as-cast samples the amount and extent of these cavities appears to have increased after solution heat treatment.

(a)



(c)

(b)



(d)

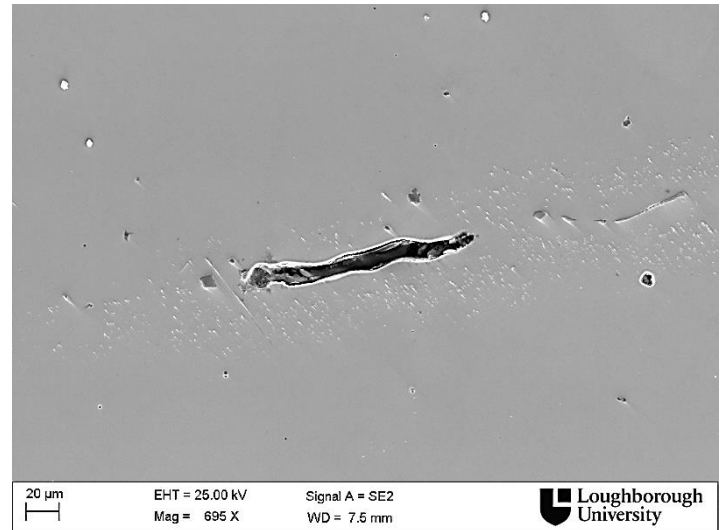
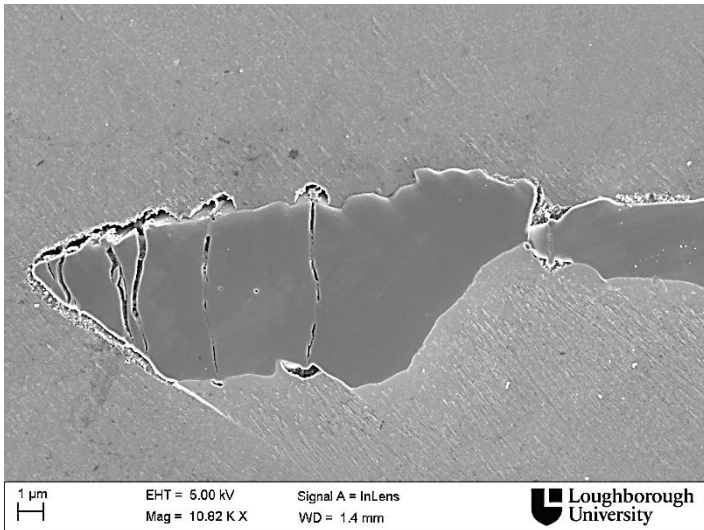


Figure 6.13: Electron micrographs showing (a) voids around grain boundaries, (b) high magnification image of γ' precipitates, (c) cracked MX precipitate and (d) another void along grain boundary

These voids could be present due to the dissolution of the MX phase during the solution heat treatment. There were some examples of cracked MX precipitates as shown in Figure 6.13 (c). Cracking is unlikely to have been introduced as a result of the polishing process. To establish this further work could be carried out sectioning a precipitate using the dual beam prior to any polishing. If cracking is still observed it discounts the possibility that these precipitates are cracking during specimen preparation.

EDX mapping shown in Figure 6.14 shows evidence of Ti segregation in the matrix.

(a)

(b)

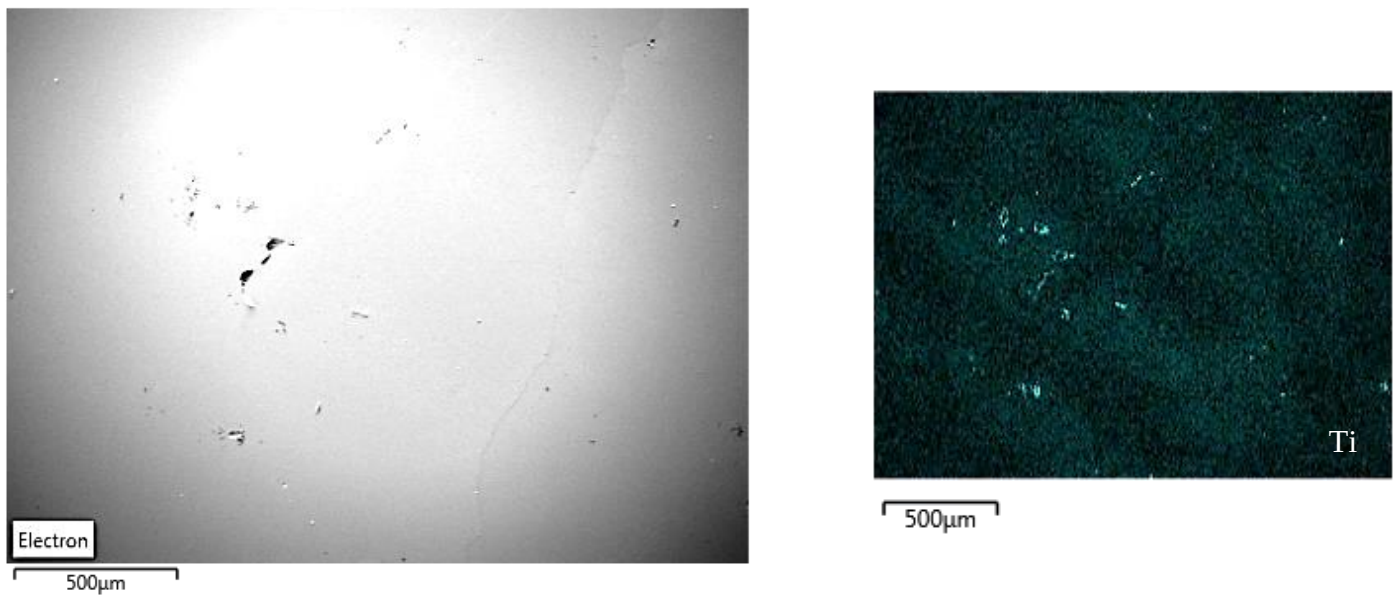


Figure 6.14: (a) Electron micrograph of as-cast microstructure accompanied by (b) associated Ti map showing segregated regions of titanium

6.5 Aged castings

Cast samples in the fully processed condition were aged at two different ageing temperatures of 700°C and 800°C. The ageing temperatures chosen are consistent with those in the previous chapters with the aim of comparing the aged microstructures across all three sample sets. Samples were aged at these temperatures for up to 5000 h as shown in Table 6.2.

Initial optical microscope observations from both the 700°C and 800°C sample sets showed the alloy to present a similar grain size to the pre-service conditions, with the bulk of grains measuring between 100 and 300 μm, with the inclusion of some very large grains greater than 1 mm in size. Attempts to reveal the grain structure of Nimonic 263 through etching proved extremely problematic, with some areas etching well and other areas either over or under etching. To avoid this problem the EBSD technique was employed in conjunction with ion beam imaging. Ion beam imaging was used to assess the grain structure and look for areas of interest before performing a later scan. Figure 6.15 shows the resultant IPF maps of two EBSD scans from the (a) As-cast alloy and (b) long term aged sample at 800°C for 5000 h. Figure 6.15 (b) shows that whilst the majority of grains are greater than 1 mm, some grains as small as 30 μm can be observed to be present along the grain boundary.

(a)

(b)

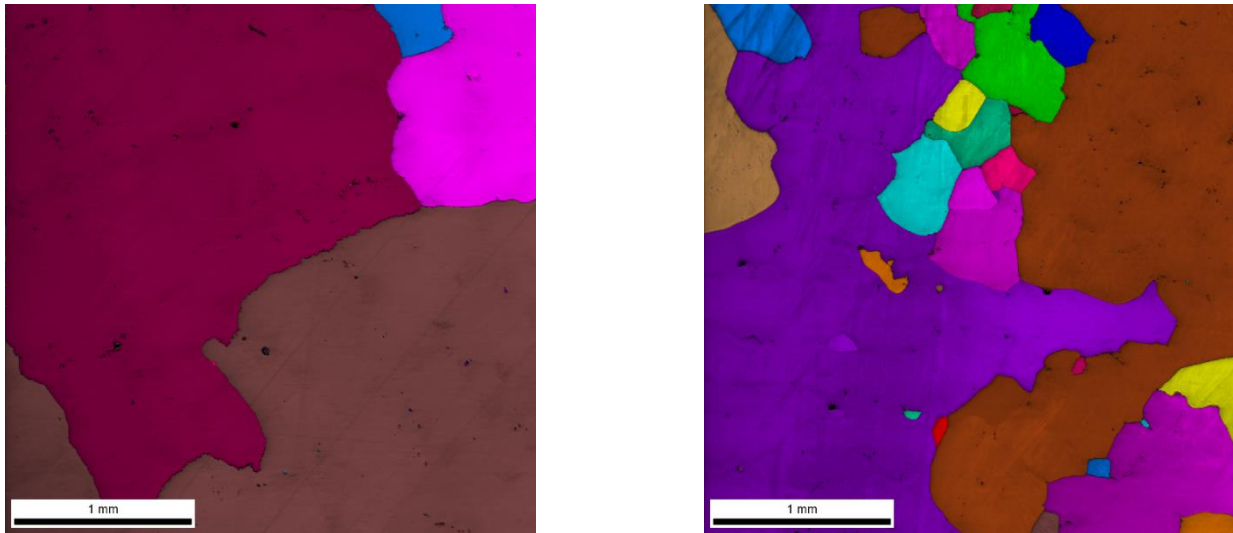


Figure 6.15: IPF maps showing grain orientation in (a) As-cast alloy and (b) long term aged sample 800°C for 5000 h

Understanding the γ' evolution during ageing and its effect on the properties is paramount when assessing the alloys candidacy for next generation plant. Figure 6.16 shows how the hardness of the alloy changes over time when exposed to two different ageing temperatures. When aged at 700°C the hardness of the alloy can be seen to remain relatively stable at approximately 300 HV¹⁰ up until 5000 h. Ageing at 800°C shows early softening at 100 h to 267 HV¹⁰, and then the alloy further softens after long term ageing for 5000 h to 227 HV¹⁰. An average standard deviation of 18.9 was calculated for the hardness readings across the sample, indicating that the segregation observed in the pre-service conditions did not appear to have any significant effects on the material's mechanical properties

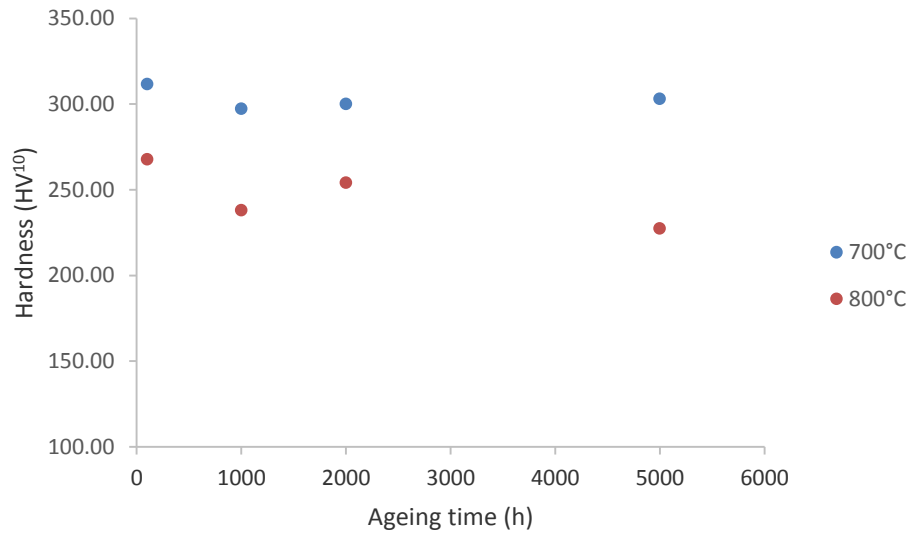


Figure 6.16: Graph showing hardness evolution for 700°C and 800°C ageing sets

Figures 6.17 (a – d) show the coarsening of the γ' precipitate when aged at 700°C. The average particle size for samples aged for 100, 1000, 2000 and 5000 h were 19, 22, 25 and 31 nm respectively. There was no evidence of a heterogeneous γ' distribution in the alloy in terms of area fraction or size. It was originally thought that the highly segregated microstructure could result in a heterogeneous distribution of the γ' precipitates or changes in the coarsening rate between different areas in the microstructure. There was some alignment of the γ' phase along twin boundaries not previously observed in other forms of the alloy. This has been highlighted in Figure 6.17 (b). It had been previously noticed in Chapter 4 that the Eta phase would not transform or extend through a twin boundary.

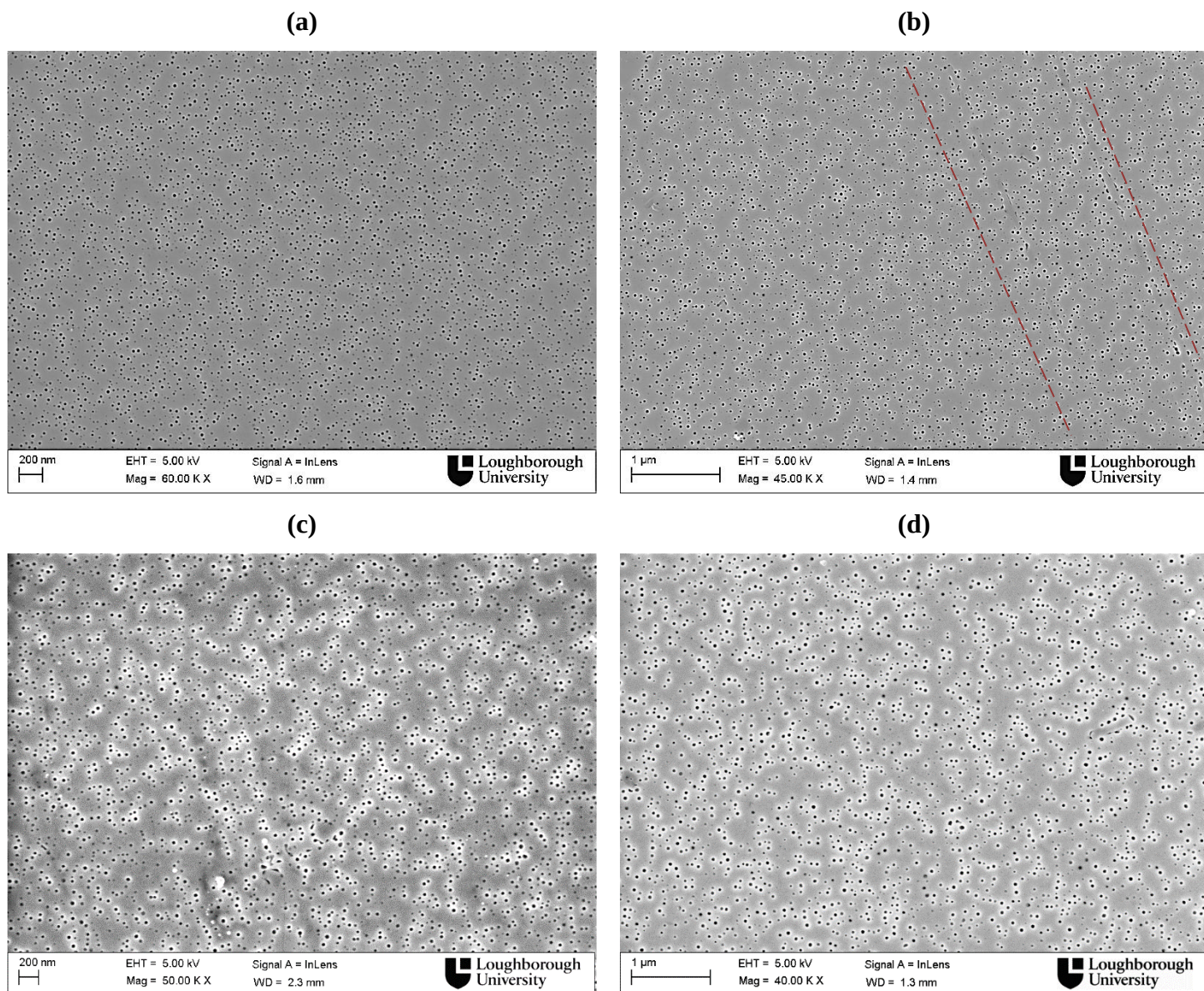


Figure 6.17: Electron micrographs showing γ' evolution as a result of ageing at 700°C for (a) 100 h, (b) 1000 h, (c) 2000 h and (d) 5000 h

Figure 6.18 shows further examples of the typical microstructure observed for cast Nimonic 263 aged for 700°C. Figure 6.18 (b) shows early transformation of the Eta phase along a grain boundary containing a Ti-Mo rich continuous MX precipitate. Figure 6.18 (c) shows further evidence of the porous microstructure typical of this cast alloy. In the long term aged sample significant lengthening of the Eta phase was observed, as can be seen in Figure 6.18 (d).

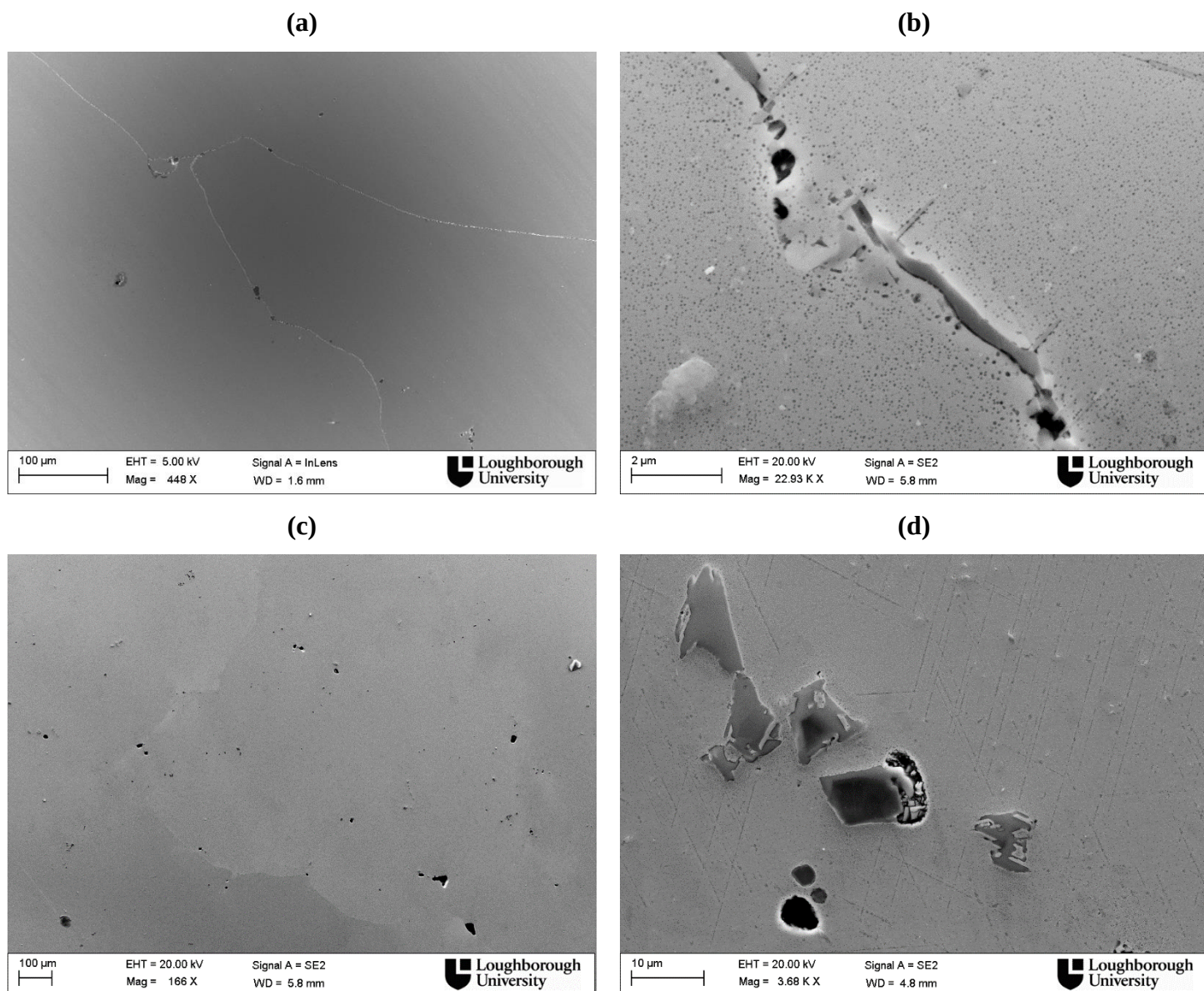


Figure 6.18: Electron micrographs showing (a) grain boundary triple point in 700°C 100 h sample (b) Early Eta transformation along grain boundary in 700°C 2000 h sample (c) Porosity present in 700°C 2000 h and (d) Eta precipitates surrounding MX precipitates in 700°C 5000 h sample

Ageing at the higher temperature of 800°C resulted in larger γ' precipitates and an increased coarsening rate. The average particle size analysis of the γ' phase found that ageing for 100, 1000, 2000 and 5000 h resulted in average γ' sizes of 40, 83, 146 and 259 nm. Examples of the γ' precipitates observed at each ageing time can be seen in Figure 6.19 (a – d). After ageing at 800°C for 5000 h the morphology of the γ' precipitates appeared cuboidal, as opposed to spherical; this can be clearly seen in Figure 6.19 (d).

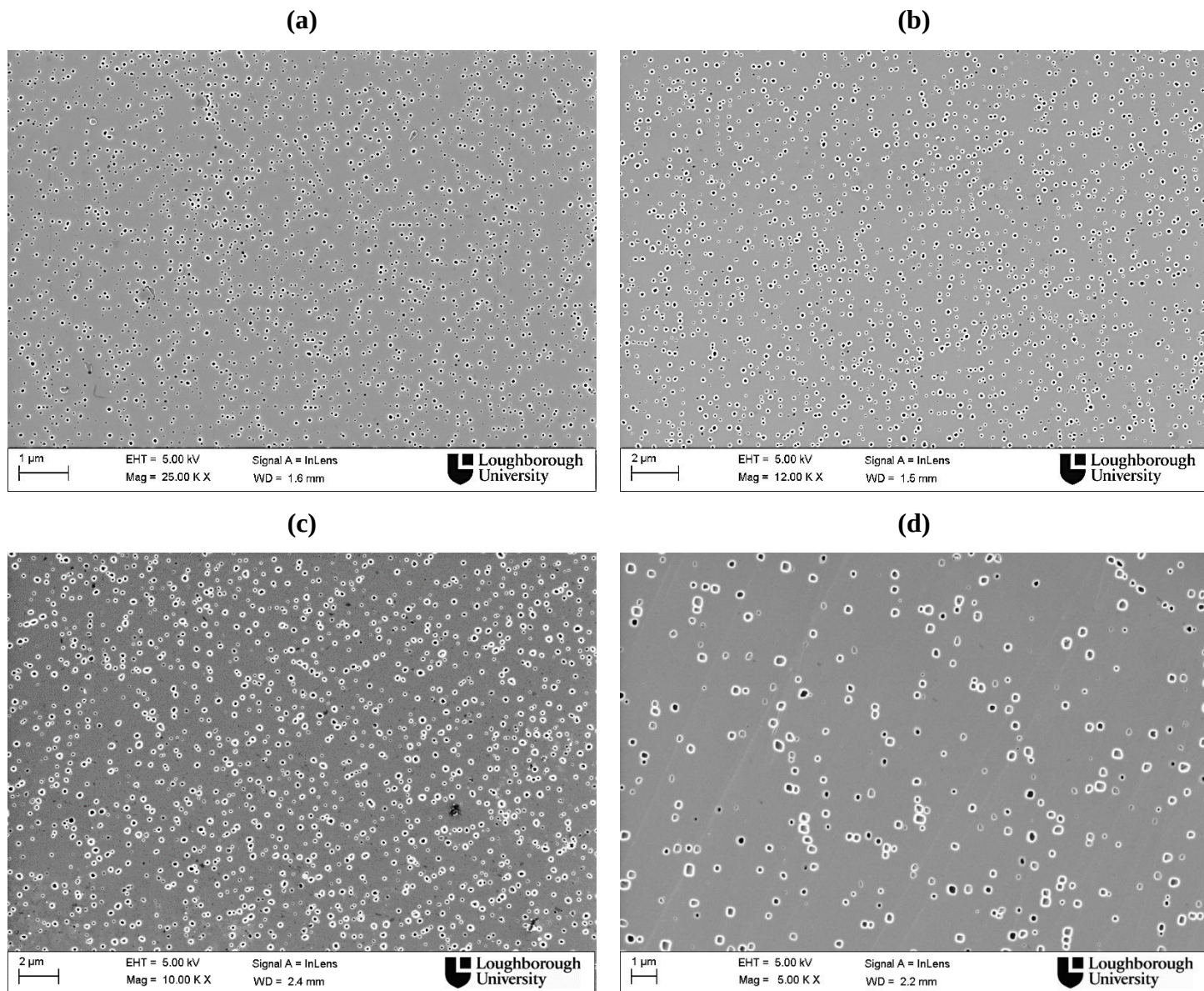


Figure 6.19: Electron micrographs showing γ' evolution after ageing at 800°C for (a) 100 h, (b) 1000 h, (c) 2000 h and (d) 5000 h

The coarsening rate of the 800°C sample set can be seen to be much higher when compared to that of the 700°C as would be expected. This is clearly shown in Figure 6.20 (a, b) in which the average γ' particle size has been plotted against ageing time for both the 700 and 800°C sample sets. The area fraction of the γ' precipitates for the 700 °C ageing sets is 0.06 with a standard deviation of 0.007, showing again the precipitation trends of γ' phase to be relatively homogeneous. Analysis of the 800°C ageing set provided the following result; an area fraction of 0.04 was recorded with a standard deviation of 0.01. This increase is attributed to the presence of the Eta phase and sensitivity of thresholding during image analysis. As the γ' phases coarsens the contrast between precipitates and the matrix lessen. It was for this reason that SE images were used during analysis instead of the in-lens mode. To ensure that the results using the SE mode are accurate, a contrast optimised electron

micrograph was taken using both modes and individually processed resulting in little difference in the average particle size calculated.

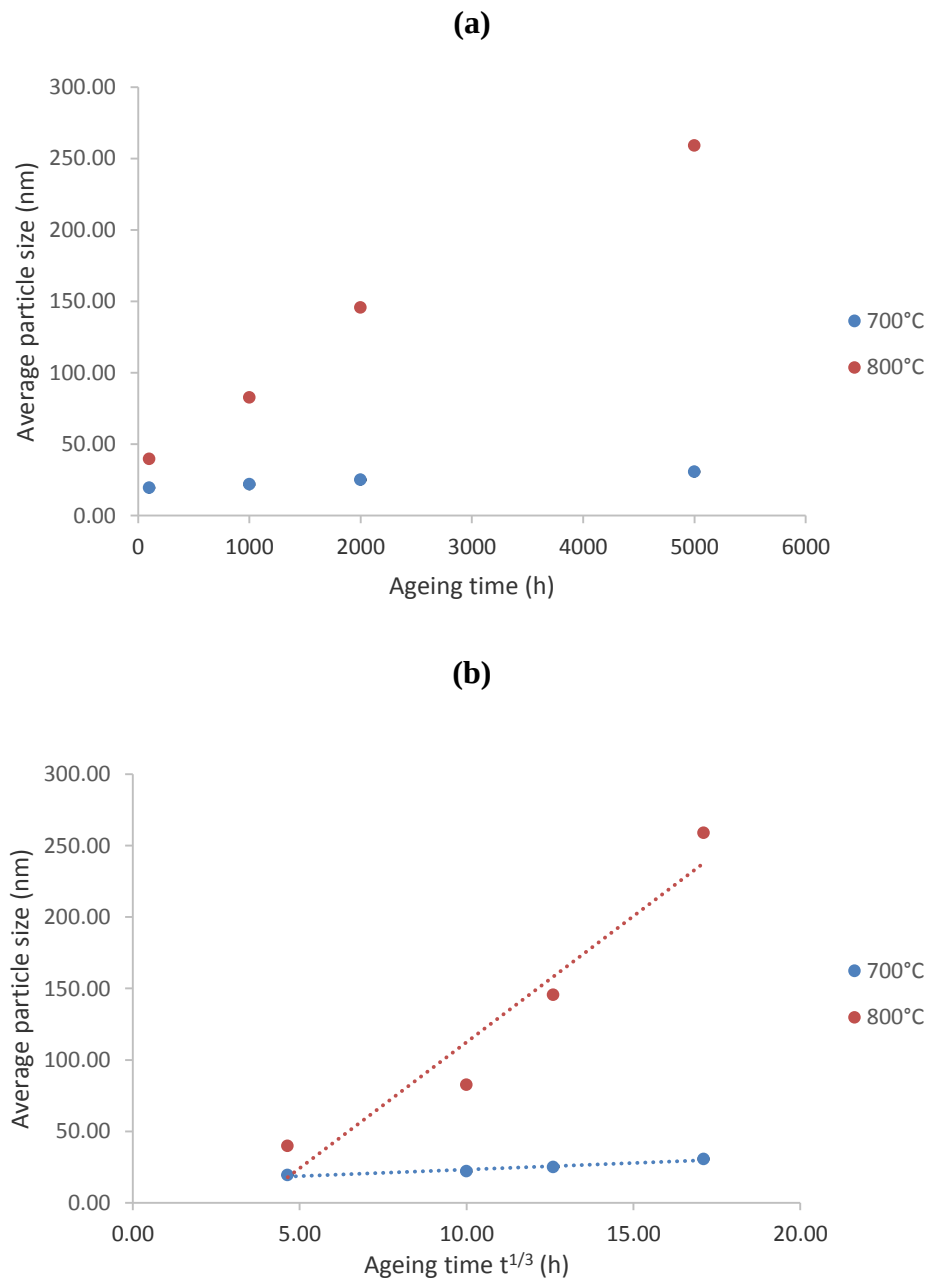


Figure 6.20: Graph showing (a) average particle size against ageing time and (b) average particle size against ageing time $t^{1/3}$

Figure 6.21 (a – f) presents electron micrographs for the microstructure of the 800°C ageing set. Linear clusters of the γ' phase were observed in the sample aged for 100 h; these clusters were elongated areas densely populated with γ' precipitates. They were found to exist in one area of the sample and were up to 10 μm long, and examples of these features can be seen in Figure 6.21 (a) and (b). The origin of these clusters is likely as a result of chemical segregation or preferential orientation relationships.

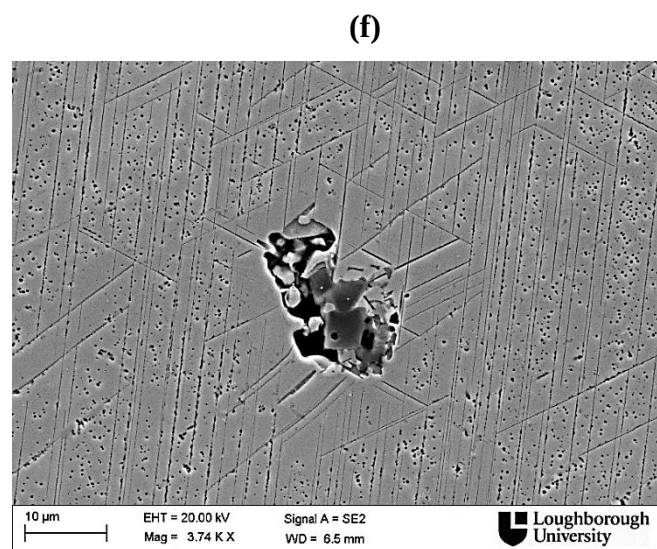
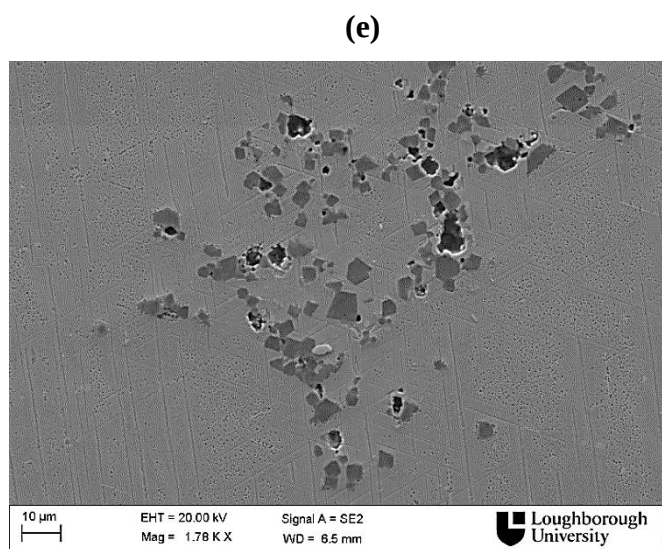
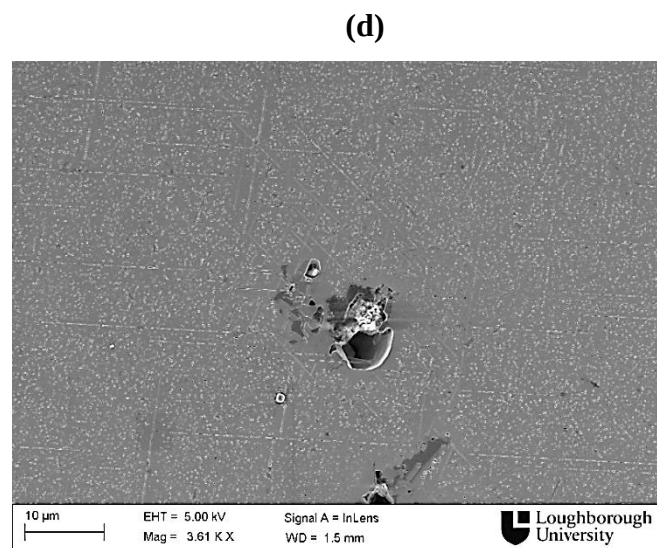
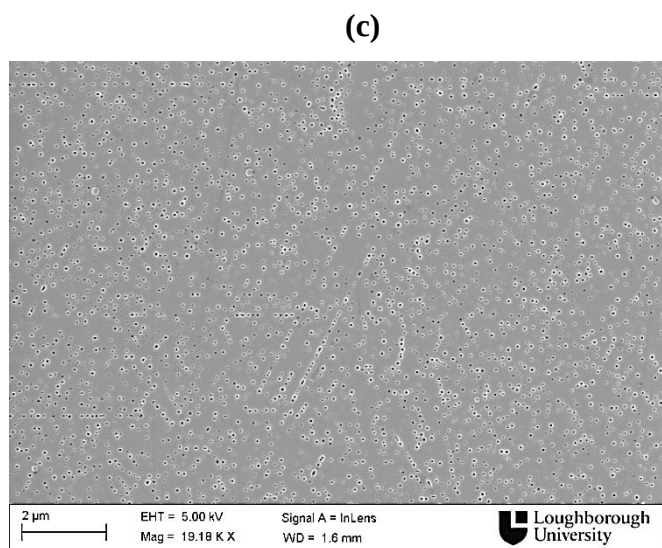
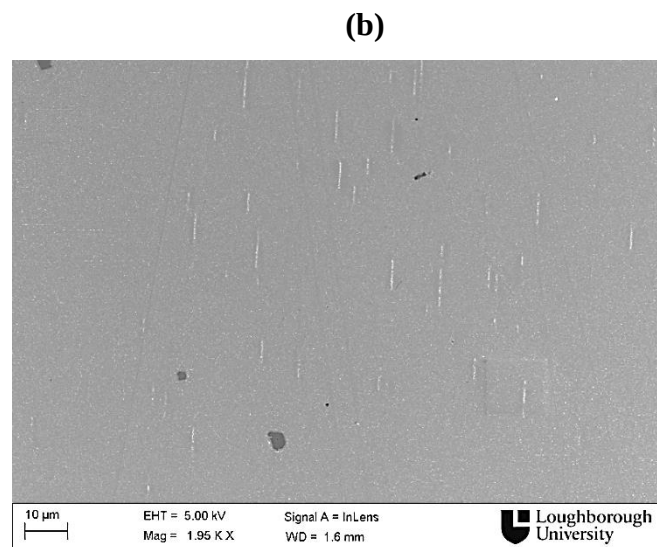
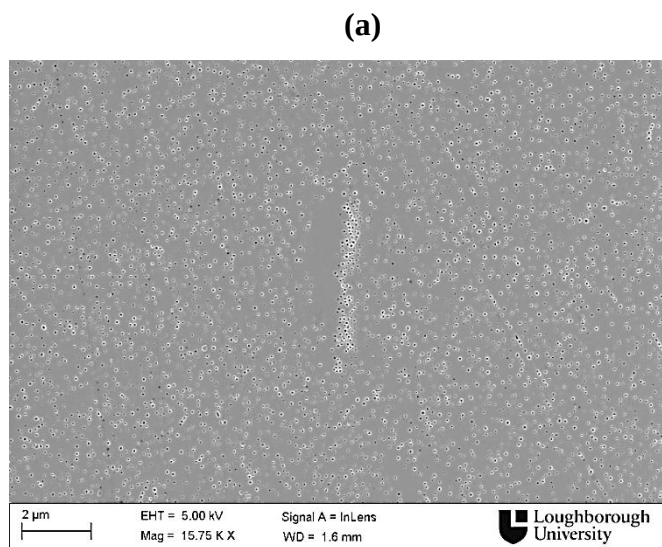


Figure 6.21: Electron micrographs showing (a) cluster of γ' precipitates in 800°C 100 h sample (b) distribution of γ' clustering, (c) Early Eta transformation in 800°C 100 h, (d) evidence of Eta transformation in 800°C 1000 h sample, (e) Cluster of MX precipitates and Eta phase in 800°C 5000 h (f) Eta precipitates surrounding MX precipitates in 800°C 5000 h sample

Alignment of the γ' phase was again observed, although at much shorter ageing times than the 700°C ageing set, shown in Figure 6.21(c). The Eta phase is widespread throughout the alloy and is significant in the alloy after only 1000 h, as can be seen in Figure 6.21 (d). Further evidence of segregation was observed with the clustering of Ti-rich MX precipitates, as seen in Figure 6.21 (e). There is an increased amount of Eta phase present in these regions although the γ' distribution remained consistent with the rest of the sample. The titanium rich Eta phase is clearly highlighted through the chemical mapping of an area around a defect in the long term aged sample from the 800°C sample set shown in Figure 6.22.

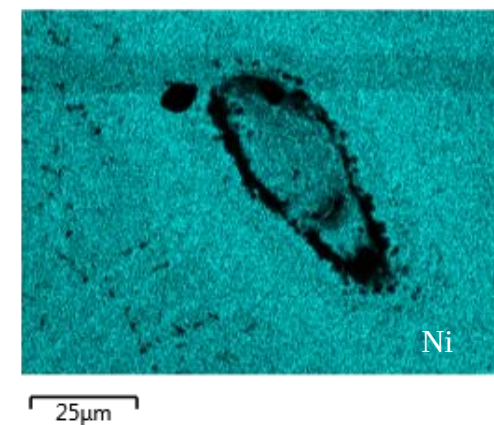
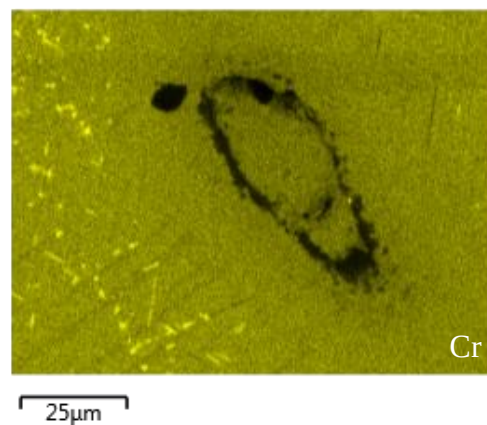
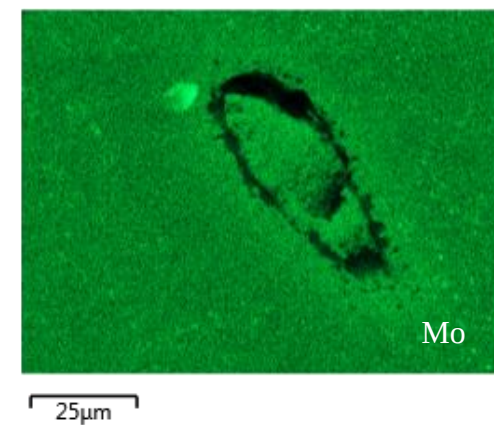
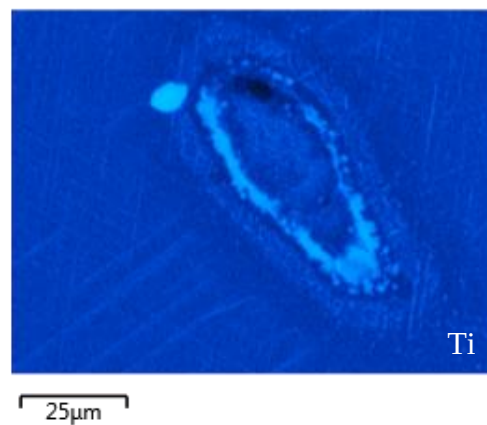
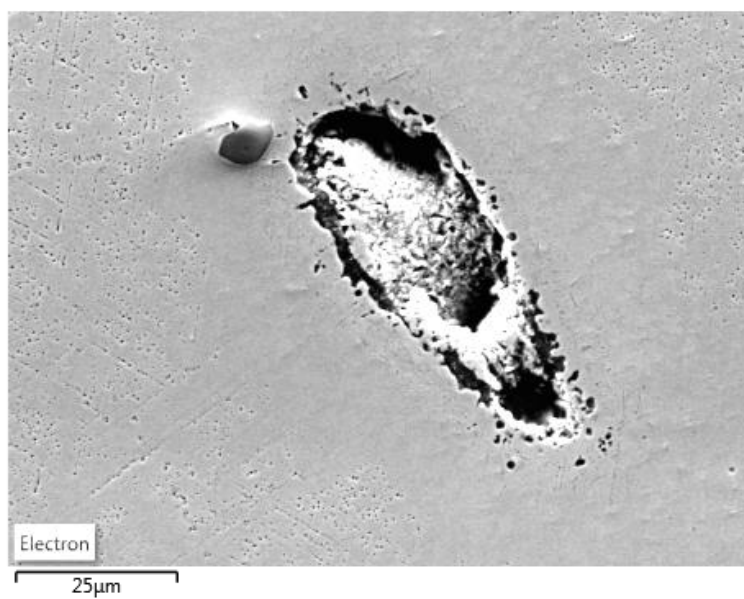


Figure 6.22: Chemical map of area around a defect in sample aged at 800°C for 5000 h

The grain boundary precipitates were fully assessed in the same way as those described in Chapters 4 and 5 using the carbon extraction replica technique. The Ti-Mo rich precipitates were found to be present along grain boundaries although not as a continuous film. This is probably due to the difficulty in extracting the long precipitates when producing the samples. Some smaller or broken up Ti-Mo rich precipitates were observed. The composition of the grain boundary phase can be seen both graphically in Figure 6.23 and numerically in Table 6.6.

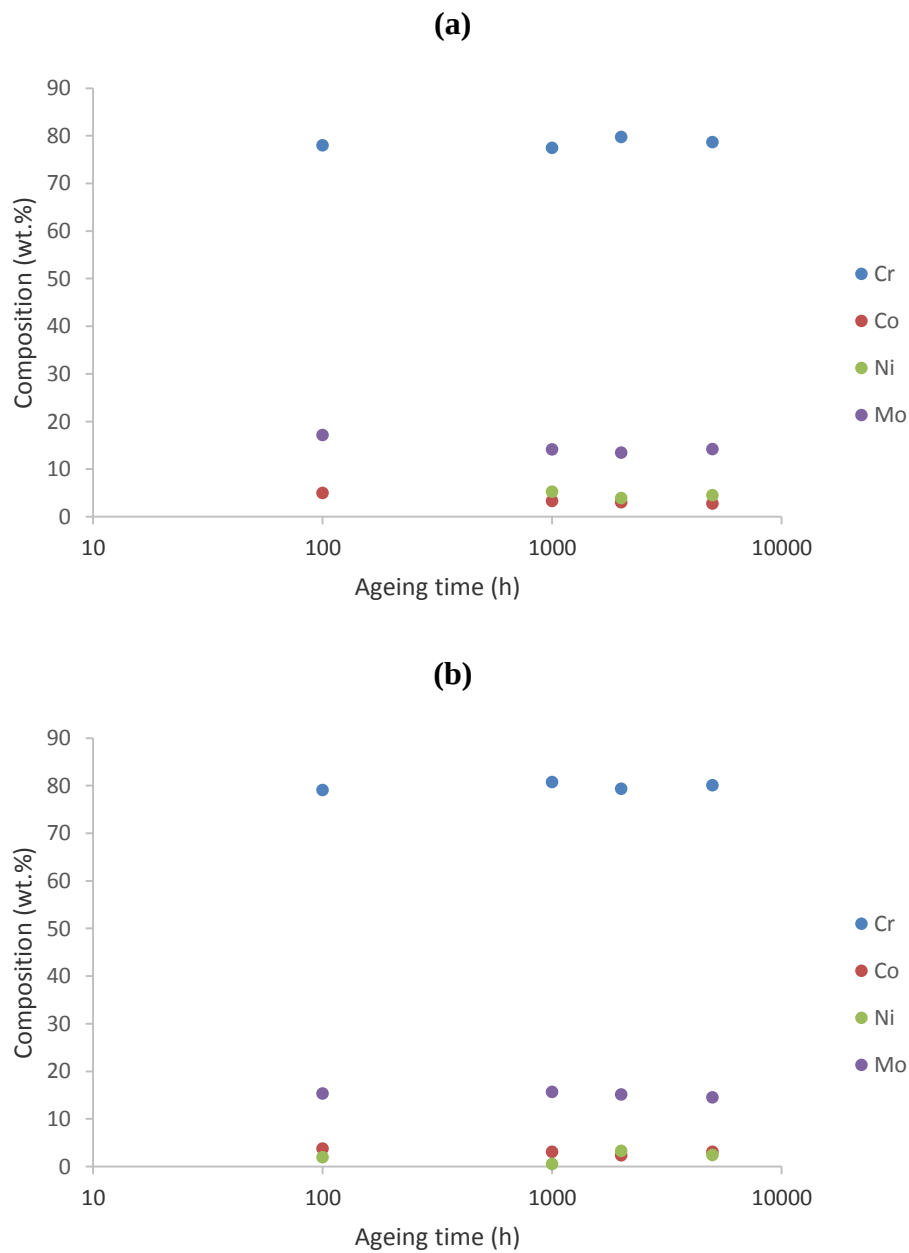


Fig 6.23: Graph showing $M_{23}C_6$ composition of (a) 700°C aged sample set and (b) 800°C aged sample set.

Table 6.6: Chemical composition of grain boundary $M_{23}C_6$

Ageing temperature (°C)	Ageing time (h)	Cr	Co	Ni	Mo
700	100	78.0	5.0	-	17.1
700	1000	77.5	3.2	5.2	14.1
700	2000	79.7	3.0	3.8	13.4
700	5000	78.7	2.7	4.4	14.2
800	100	79.1	3.7	1.9	15.3
800	1000	80.7	3.1	0.5	15.6
800	2000	79.3	2.3	3.2	15.1
800	5000	80.1	3.1	2.4	14.5

The chromium rich $M_{23}C_6$ carbide can be seen to be chemically stable across both ageing temperatures with very similar chemistry recorded across all exposure times and temperatures. Grain boundary precipitates were observed to be on average between 100 – 200 nm in size across both sample sets. Evidence of Mo rich precipitates which were the same size and morphology as the $M_{23}C_6$ carbide were detected across both the 700°C and 800°C samples. The average chemistry of these precipitates was approximately 80 wt.% Mo and 14 wt.% Cr with the remainder comprising Ni and Co. There were no predicted phases from thermodynamic calculations with similar chemistry, further work is recommended to identify this phase.

6.6 Summary of Cast Nimonic 263 work

In conclusion, the microstructure of cast Nimonic 263 was predicted to be similar to the samples manufactured by different routes studied in earlier chapters. Experimental results showed these predictions to be accurate in all conditions other than as-cast. The as-cast condition was observed to contain a continuous grain boundary phase, which was determined to be the Ti-Mo rich MX phase. After solution heat treatment the amount of this continuous phase was visibly reduced.

The effects of the segregated cast microstructure are less pronounced than would have been expected, with a homogeneous distribution of the γ' phase present throughout the alloy. Some areas of the microstructure were heavily populated with the Ti-rich MX phase suggesting local concentrations of titanium, although these regions were not widespread throughout the alloy.

In agreement with previous work on other product forms, the γ' phase was observed to coarsen, align and eventually transform in the Eta phase. The rate at which this process occurred was again demonstrated to be temperature dependent, being observed to happen more quickly at the higher ageing temperature of 800°C. The precipitation trends in segregated areas of the casting were less extreme than predicted, with a homogenous microstructure observed throughout the microstructure.

It is believed that Nimonic 263 would perform well if used as a cast alloy for valve bodies and other components. When used to produce larger castings, as demonstrated by the step block, the alloy is less sensitive to segregation than first thought. Results also showed that the current pre-service heat treatments were fit for purpose, ensuring a near-homogenous and stable microstructure both pre-service and at the intended operating temperature of 700°C. Ageing at 800°C showed a significant reduction in the hardness properties of the cast alloy. The decrease in hardness properties, along with significant Eta precipitation suggest that the alloy should not be installed in plant when operating temperatures are likely to exceed 750°C. This recommendation is not unique to the cast product form, with research into the isothermally aged forged pipe and welded samples presenting similar findings.

Chapter 7

Conclusions

7.1 Overview

The aim of this research was to gain a fundamental understanding regarding the microstructural evolution in the candidate next generation power plant alloy Nimonic 263. The microstructural evolution has been studied as a function of time and temperature in three main conditions; isothermally aged, welded and also as a cast alloy. Understanding the evolution of the alloy microstructure in these different conditions relating to potential product applications is essential for accurate predictions regarding the life assessment of this alloy in power plant applications and therefore determining its potential for use. Experimental data have also been used in conjunction with thermodynamic predictions to assess the effectiveness of current thermodynamic calculation software and existing databases for this type of alloy.

7.2 Isothermally Aged Nimonic 263

Nimonic 263 was studied in a several pre-service and aged conditions. The samples were taken from one of two forged thick section Nimonic 263 pipes produced in dimensions representative of a steam header pipe; 310 mm outside diameter, 70 mm wall thickness and over 3 metres in length. The pipe was produced predominantly to provide research material but also to help develop the forging process, which was a new production route for the material. The alloy was initially studied in its pre service conditions, specifically after solution and precipitation hardening heat treatments. A comprehensive set of aged samples was also studied at ageing times ranging from 1 – 20,000 hours at exposure temperatures from 700 – 800°C in laboratory furnaces. An initial investigation was also subsequently performed to investigate the potential rejuvenation to the original microstructural condition of the long term aged 800°C sample.

Results indicated that thermodynamic predictions carried out using the MTDATA software programme in conjunction with a nickel thermodynamic parameter database provided an accurate prediction of the alloy's microstructural condition. Equilibrium calculations predicted the phase composition of the alloy to consist of a gamma matrix (γ) strengthened by the gamma prime phase (γ'). The grain boundary phase, $M_{23}C_6$, was predicted to be present in addition to the inter/intragranular MX precipitate. Eta phase, which is known to occur only after very long times at temperature, was predicted to be present, although this phase was

suspended in some calculations to give a prediction more representative of the alloy's early microstructural condition. The presence of the Mu phase (μ) was predicted in all calculations but was not observed in this research or any other published works. The absence of the Mu phase can be explained by its prediction is being incorrect or it takes a long time to precipitate.

Experimental work subsequently found that thermodynamic predictions were on the whole accurate, although evidence of the presence of Mu phase was never detected. Thermodynamic calculations only predicted one composition of the MX precipitate, a Ti rich carbide, whilst a Ti-Mo rich carbide was observed and detected to be present throughout the alloy. Chemical analysis of the experimentally observed $M_{23}C_6$ phase was also in agreement with thermodynamic predictions. Due to the relatively small amount of the precipitates MX and $M_{23}C_6$ that were both predicted and observed to be present, it was difficult to assess either predictions accuracy in terms of the absolute amount of the phases present.

The precipitation strengthening gamma prime phase was found to coarsen in accordance with standard particle coarsening theory. Alignment of the gamma prime phase was also observed after long term ageing. It is thought this alignment is due to preferred orientation relationships within the alloy. An increase in ageing temperature under the precipitates dissolution temperature resulted in a higher coarsening rate and earlier transformation into the Eta phase. Ageing at elevated temperatures and long term ageing resulted in the transformation of the gamma prime precipitate into the Eta phase. The area fraction and length of the Eta phase was found to increase with ageing time, although this is at the expense of the gamma prime phase due to the transformation.

The potential for rejuvenation of Nimonic 263 was investigated with two heat treatments evaluated; a 2 h heat treatment at 1150°C and a 3 h heat treatment at 980°C. The high temperature rejuvenation heat treatment was found to successfully take the η and γ' phases back into solution before their reprecipitation during subsequent lower temperature heat treatments.

7.3 Welded Nimonic 263

Welded Nimonic 263 specimens were studied to determine the alloys microstructure as an effect of the welding process and the differing weld metal chemistry. The study initially looked at the effect of the different pre-service conditions on the weld and parent microstructures. Two sample sets were studied; IP (I) a modified Nimonic 263 composition and IP (II), a weld metal composition within the alloy limits set by Special Metals. The

microstructural constituents predicted to exist in the weld and parent metal were similar to those predicted and observed in the isothermally aged samples, however, the distribution of these constituents was found to vary due to the segregation brought about through the welding process. The effect of this segregation was modelled using the Scheil method in conjunction with equilibrium phase calculations, which predicted the phase composition of the segregated areas. Predictions showed an increased amount of Eta precipitation within interdendritic regions where the aluminium content was predicted to be lower. Experimental observations showed the concentrated presence of the Eta phase within the interdendritic regions, confirming the accuracy of thermodynamic predictions. Links can be drawn with work carried out in the isothermally aged chapter which calculated the effect of aluminium content on the precipitation of the γ' and η phase, and the observations made in the interdendritic regions of the weld metal.

The effect of four different pre-service heat treatments used in the IP (I) sample set was thoroughly investigated. The microstructural evolution of these four conditions was also studied as a function of time and temperature with subsequent ageing trials. The bulk microstructure of the weld metal was found to be similar to that previously observed in other conditions; a γ matrix strengthened by the γ' phase, grain boundary $M_{23}C_6$ and MX were present throughout. Ageing of the IP (I) sample set showed an increased γ' coarsening rate when compared to the parent pipe material studied in the isothermally aged chapter. The grain boundary precipitate phase $M_{23}C_6$ was present in all four conditions and found to be chemically stable even after ageing at 750°C.

Examination of the welded samples showed a heavily segregated microstructure in the stress relieved sample set which was heat treated at 980°C for 3 hours. The precipitation products and their evolution in segregated areas were significantly different from the other pre-service conditions. The stress relieved weld metal from IP (I) sample set was also shown to have a bimodal γ' distribution, with regular and large γ' observed in the dendritic and interdendritic areas respectively. Trials were conducted to investigate relationships between cooling rate and the resultant microstructures, and the results showed distinct differences in coarsening rate, however, the bimodal size distribution of the precipitates could not be replicated.

There was evidence which suggested the presence of the high molybdenum containing grain boundary M_6C precipitate in the stress relieved condition. Ageing at 750°C across all four pre-service conditions showed little to no variation in the alloy hardness even after long term ageing at 5000 h. The weld metal in the stress relieved condition was aged at 800°C with the

aim to observe the Eta transformation within the interdendritic regions. The Eta phase was observed along grain boundaries and the interdendritic areas after 1000 h ageing at 800°C.

The IP (II) sample set comprised a weld metal with a chemistry much closer to that of the nominal Nimonic 263 composition. Due to this, there was little difference in microstructure observed between parent and weld material. The IP (II) sample set was subsequently aged at two temperatures of 700 and 725°C in the precipitation hardened condition. The γ' phase was observed to coarsen as a function of ageing time and temperature as expected, however, little difference was observed between the welded and parent material in this case. The similarity in microstructure between parent and weld metal is therefore due to their similar composition and minimal effect of segregation in this case.

The difference in hardness between the parent and weld material was also less pronounced when compared to the IP(I) sample set, which can again be explained by the difference in weld metal chemistry between the two. It is recommended from a microstructural viewpoint that, where possible, similar composition welding consumables are chosen, although this recommendation does not take into account issues concerning weldability. Weldability covers a number of factors, chiefly how difficult it is to produce a defect free weld which is both mechanically and chemically suitable for an intended application. Weldability also describes the complexity of precautions that may be employed to provide a suitable weld such as; heat input, preheat and susceptibility to solidification cracking.

7.4 Cast Nimonic 263

An additional detailed microstructural investigation was carried out on cast Nimonic 263 in both pre-service conditions and isothermally aged cast samples. The cast microstructure was modelled using the supplied cast composition as was the case for the isothermally aged wrought and welded materials. The thermodynamic calculations showed the predicted microstructure as a function of temperature in addition to the chemical composition of included phases. The calculated microstructure was similar to that predicted in both the isothermally aged and welded chapters; this result was expected due to the similar composition of the product forms. Segregation, which is expected to be a significant factor in a thick section cast alloy, was also modelled using the Scheil method, which presented similar results to those observed when considering weld metal behaviour. However, the observed as-cast microstructure was markedly different to that observed in previous chapters with a continuous grain boundary phase observed throughout the microstructure. Cracking of these grain boundary precipitates was observed in the alloy and was confirmed not to be

present as a result of the etching process. This phase was confirmed to be the Ti-Mo rich MX phase, through both chemical analysis and crystallographic analysis. After a two step solution heat treatment the amount of the continuous grain boundary MX was visibly reduced. After precipitation heat treatment evidence of the $M_{23}C_6$ phase was found, with a composition consistent with that observed in the case of the isothermally aged and welded samples.

The cast alloy was subsequently aged in the fully processed condition at 700 and 800°C to study the effect of ageing on the alloy microstructure. Predictably the γ' phase was observed to coarsen and eventually align, a potential pre cursor to the Eta phase transformation. The higher ageing temperature of 800°C showed significant Eta precipitation, especially in areas of MX clustering. Finally, the precipitation trends upon ageing in the segregated areas were less pronounced than initially expected, with the cast microstructure found to be fairly homogenous following isothermal ageing.

Chapter 8

Further Work

The thesis has considered the potential origins and forms that Nimonic 263 might take in next generation plant. The microstructure of the alloy has been fully assessed in each of the conditions likely to be used in power plant, resulting in a good understanding of how the microstructure will enter, evolve and leave service. Using the findings from this work, a relatively simple life assessment method could be created using the evolution in the gamma prime phases as a basis enabling plant metallurgists to assess the thermal degradation of plant components manufactured from this alloy. The experimental data generated in this research could also be used to inform a model which could ultimately predict the alloy microstructure based on its thermal history.

In order to build on these studies and potentially increase confidence in the candidacy of Nimonic 263 for next generation power plant, further research could be carried out. Significant creep data exist for the alloy and are an integral part of its candidacy and certification for use in next generation plant. Long term creep exposed Nimonic 263 is likely to show signs of ‘rafting’, that is the alignment of the γ' phase due to creep. The gamma prime coarsening rate may also be affected as a result of creep deformation. Although some assumptions can be made, it is not known exactly what effect creep will have on the microstructure of the alloy.

The predicted future energy mix of different generation technologies demonstrates the importance of next generation plant being able to cycle due to the introduction of renewables. It will therefore be extremely important to understand how the alloy will behave when operating in creep-fatigue conditions.

This research has demonstrated that partial rejuvenation of the alloy microstructure and mechanical properties is possible, and further work could be carried out to understand how these rejuvenated samples subsequently evolve when reintroduced to service. An important step is to understand where Nimonic 263 ranks alongside other possible candidate materials for use in next generation plant. At the beginning of the research programme Nimonic 263 was one of three candidate alloys, including Inconel 740 and Inconel 617. The list of candidate alloys now includes Inconel 740H, which is a compositionally modified version of Inconel 740 primarily for enhanced weldability and castability, in which an increase in aluminium, a decrease in niobium, silicon and titanium and a complete absence of carbon results in a more stable microstructure. Haynes 282, another precipitation strengthened alloy,

is also being investigated as a potential power plant material. It appears likely that one of these three materials will be chosen for future operation should the implementation of these alloys prove necessary and economically viable.

Chapter 9

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