

CRANFIELD UNIVERSITY

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Hot Corrosion in Industrial Gas Turbines

School of Water, Energy and Environment

PhD

Academic Year: 2012 - 2018

Supervisor: Prof. N. J. Simms  
Associate Supervisor: Dr. J. Sumner  
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## Abstract

Future gas fired power stations are likely to use gas turbines operating both at higher temperatures to improve thermal efficiency, and fire cheaper fuels containing more deleterious contaminants. Additional changes relate to potential new methods of CO<sub>2</sub> reduction including pre-combustion capture. These developments in industrial gas turbine technologies present new materials challenges that must be understood. This research aims to further scientific understanding of type II hot corrosion and its effect on a range of candidate alloys for use in industrial gas turbines under novel exposure conditions. Selected parameters have been isolated under those conditions and their effects investigated.

Laboratory-based hot corrosion tests using the “deposit recoat” technique were used to evaluate the following variables on candidate materials (GTD 111, Rene 80, PWA 1483, MarM 509, RT22 and SC2464): exposure atmospheres including SO<sub>2</sub> (3.6 to 300 ppm) and water vapour content (0 to 20 vol.%); deposit flux (1.5 and 5 µg/cm<sup>2</sup>/h of 80% Na<sub>2</sub>SO<sub>4</sub> 20% K<sub>2</sub>SO<sub>4</sub>); and the addition of molybdenum particles to deposits. Qualitative assessment of hot corrosion morphologies used a scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectroscopy capabilities.

The effect of water vapour was found to be dependent on SO<sub>2</sub> concentration. Increasing water content increased hot corrosion in low (3.6 ppm) SO<sub>2</sub> atmospheres, but was found to reduce it at higher (300 ppm) SO<sub>2</sub> concentrations. Mixed mode corrosion features have been identified by SEM/EDX analysis, on all samples that progressed from hot corrosion incubation to propagation. These features are attributed to changes in the deposit melt’s chemistry allowing for both acidic and basic fluxing to occur.

Refractory metal carbide precipitates were found to exacerbate degradation and acted as nucleation points for hot corrosion damage. It is proposed that this is, at least in part, alloy induced acidic fluxing occurring concurrently with gas phase induced hot corrosion.

Keywords:

Type II hot corrosion, mixed mode corrosion, superalloys, water vapour, refractory metal carbides, acidic fluxing, basic fluxing.

## **Acknowledgments**

The Author would like to acknowledge the support and help of the supervisors Nigel Simms and Joy Sumner and for providing the opportunities to present research at multiple conferences around Europe. In addition, thanks must be given to Cranfield University for funding this research and allowing studies to be done on a part time basis.

Thanks go to my family for their support and enthusiasm which has always been a motivating factor to finish this thesis.

Finally, as tradition dictates, thanks go to the technician that worked on the project; you are the real hero!

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## List of Abbreviations

|      |                                                        |
|------|--------------------------------------------------------|
| BSE  | Backscattered electron                                 |
| EDX  | Energy dispersive X-ray                                |
| ESEM | Environmental scanning electron microscope             |
| IGCC | Integrated gasification combined cycle                 |
| OECD | Organisation for Economic Co-operation and Development |
| SEM  | Scanning electron microscope                           |



# 1. Introduction

In the modern age, the consumption of energy has become a fundamental foundation on which society is built. Almost every aspect of daily life in the developed world has become reliant on the use of energy generated, including essentials such as heating, food and health care, commerce and entertainment [1]. Through a combination of global population growth and the development of nations, the worldwide demand for power is increasing rapidly despite power efficiency becoming a more important design criterion. Figure 1.1 shows a comparison of world population and the demand for power [2], [3]. Between 1992 and 2017 the world population increased by approximately 40% while the energy production increased by approximately 69%.

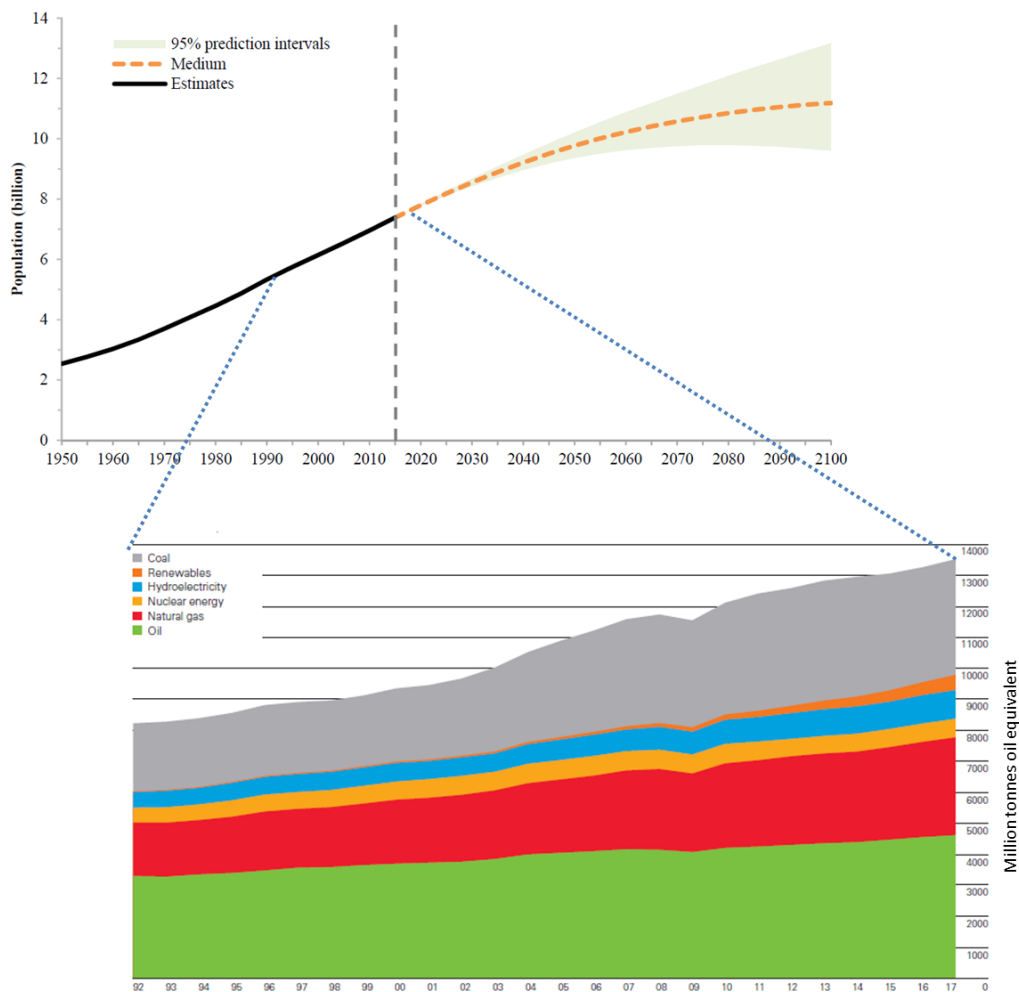
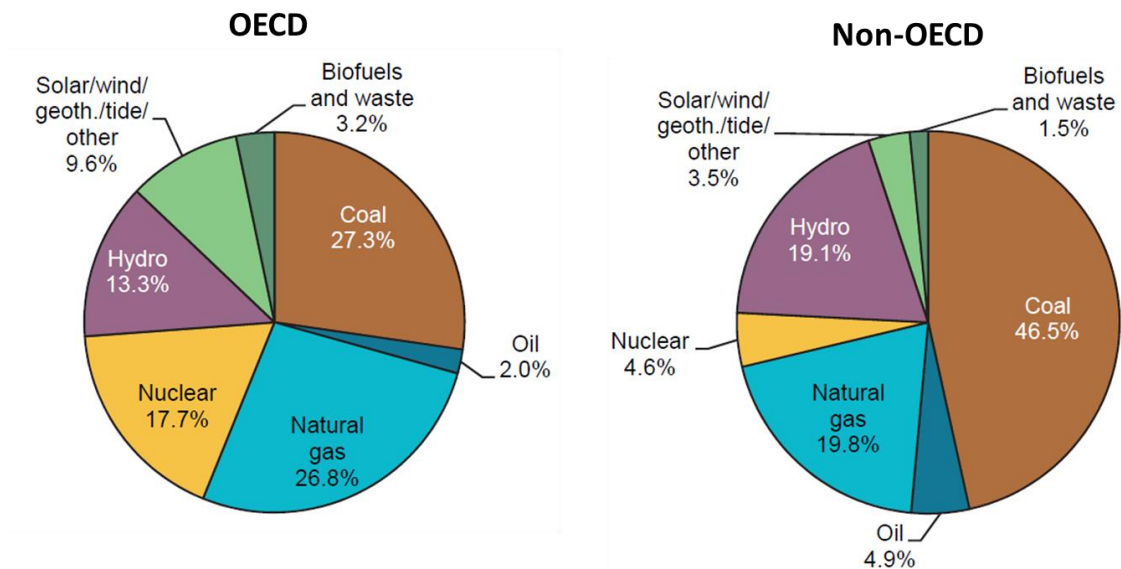


Figure 1.1: Graphs showing a comparison between population growth (2015 data, upper graph) [2] and energy production by resource (2018 data, lower graph) [3].

Despite an increasing awareness of environmental issues, the combustion of solid fossil fuels and natural gas as sources of power generation is increasing in real terms. While there is a drive towards the use of renewable sources of energy, the cost efficiency, reliability and versatility of supply associated with the combustion of fossil fuels ensures its position in the marketplace [4]. This is reflected in the comparison of energy production by source data between OECD and non-OECD countries that may not be able to afford the cleaner sources of energy production (Figure 1.2).

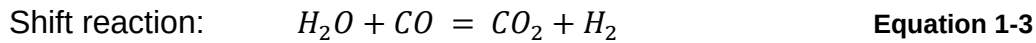
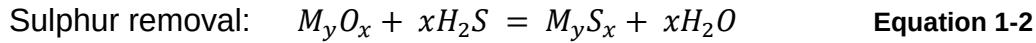
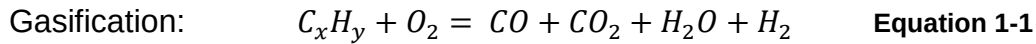


**Figure 1.2: Gross energy production by source (2016) for OECD (left) and non-OECD (right) countries [4].**

Increasing levels of CO<sub>2</sub> in the atmosphere have been identified as a cause of climate change otherwise known as the enhanced greenhouse effect [5]. The European Union set its members a target of reducing CO<sub>2</sub> emissions firstly by 20% by 2020 and then increasingly up to 80% by 2050 [6]. As the sector responsible for greatest level of CO<sub>2</sub> pollution, some of the responsibility for reducing emissions falls on the power generating industry.

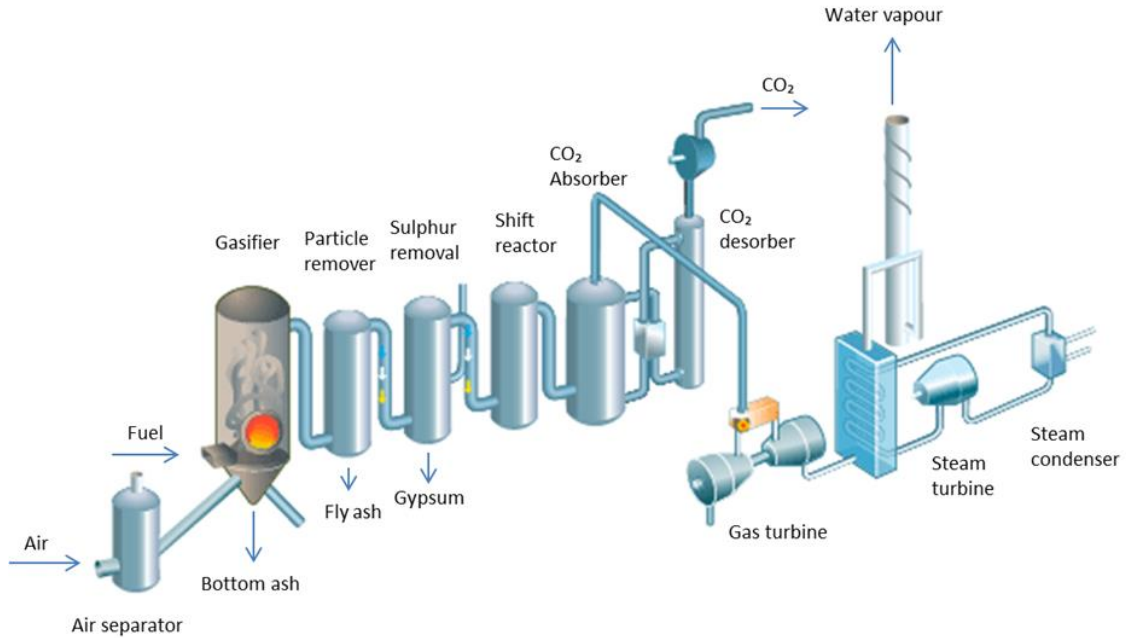
One technology being developed to reduce CO<sub>2</sub> emissions involves an integrated gasification combined cycle (IGCC) power plant utilizing pre-combustion CO<sub>2</sub> removal systems [7], [8]. This will incorporate an advanced gas turbine designed to combust a H<sub>2</sub> rich syngas while maintaining the capability of fuel flexibility and an ability to withstand the different possible operating atmospheres generated in the hot gas pathway of the gas turbine.

A proposed schematic of a H<sub>2</sub>-IGCC power plant is shown in Figure 1.3 [9]. In the early stages of the power plant, solid fuel is heated in an environment containing a low partial pressure of O<sub>2</sub> to generate a fuel rich gas stream (Equation 1-1). This then goes through particle and S removal stages (Equation 1-2). The shift reactor converts both CO into CO<sub>2</sub> (which can subsequently be captured) and H<sub>2</sub>O to H<sub>2</sub> which goes on to fuel the turbine (Equation 1-3). The reactions for these stages are shown in Equations 1-1 to 1-3 [10], [11], [12].



Emerging technologies, such as the proposed H<sub>2</sub>-IGCC system, present new materials challenges for gas turbines [13]. Higher combustion temperatures offer greater thermal efficiencies; consequently components in the turbine section may be required to endure higher operating temperatures or need additional cooling. The option of fuel flexibility and potential failures in the gas clean up system may produce novel atmospheres with variable concentrations of potentially corrosive species and water vapour. These variations may affect the hot corrosion rates of

exposed materials and/or alter the hot corrosion mechanisms occurring in the gas turbine section of a power plant.



**Figure 1.3: Conceptual schematic of a possible new generation IGCC power plant with the facility for carbon capture [9].**

Hot corrosion reactions are a form of accelerated degradation of materials brought about by the deposition of deleterious species onto material surfaces which may then be modified through the gas phase [14]. Hot corrosion has been recognised as potentially limiting the working lifetime of certain gas turbine components [15].

This thesis investigates the degradation of candidate materials under novel exposure conditions in terms of both hot corrosion kinetics and mechanisms. While components in the gas turbine section may experience a wide range of temperatures, the literature suggests that the corrosion rate of type II hot corrosion usually peaks around 700 °C [14]. This parameter is therefore kept as a constant throughout this study.

## **1.1 Aim**

To investigate and further scientific understanding of type II hot corrosion and its effect on a range of candidate alloys for use in industrial gas turbines under novel exposure conditions, by isolating selected parameters in those conditions and investigating their effects.

## **1.2 Objectives**

- To quantify the effects of variables such as atmosphere, deposit flux and materials on type II hot corrosion through a series of laboratory corrosion tests.
- To investigate the effects of between 0 and 20% atmospheric concentrations of water vapour on type II hot corrosion rates and mechanisms.
- To confirm and further explore the mechanisms for alloy induced acid fluxing as given in the literature.
- To determine the role alloy precipitates play during the type II hot corrosion process and how that may affect possible hot corrosion mechanisms.

## **1.3 Thesis structure**

Chapter 2 contains the literature review of topics associated with this thesis including an outline of the operation of gas turbines and materials challenges faced in their development before discussing the superalloys that are used for selected gas turbine components. The topics of oxidation in the presence of water vapour and hot corrosion are less mature areas of research than the other topics of the literature review and therefore focused on to a greater extent. The

methodology section (Chapter 3) describes both the experimental procedure and provides the details of candidate materials and the test matrix.

The results of the first three corrosion tests (A to C) with variables including deposit flux, test atmosphere and materials are presented and discussed in Chapter 4. The variable of atmospheric water content is isolated in tests D to F with the results given and discussed in Chapter 5. Chapter 6 investigates the effects of Mo additions to the deposit in test G. The findings of all hot corrosion exposures are brought together and discussed in Chapter 7. Chapter 8 presents the conclusions of this research, while recommendations for future work offered in Chapter 9. References are listed in Chapter 10.

Appendix A provides weight change data for tests A to G while Appendix B presents the full dimensional good metal loss data for tests A to C. A calculation of the error inherent in the methodology is given in Appendix C.

## **1.4 Presentations and publications**

Presentations of this work have been made at the following conferences:

- A. Potter, oral presentation “Hot corrosion in the next generation of industrial gas turbines” Eurocorr 2014, Pisa, 8-12 September 2014
- A. Potter, oral presentation “Type II hot corrosion of environmentally resistant coatings in the next generation of industrial gas turbines” Eurocorr 2015, Gratz, 6-10 September 2015
- Potter, A. oral presentation “The role of superalloy precipitates on the early stages of oxidation and type II hot corrosion” Microscopy of Oxidation 10, Loughborough, 3-5 April 2017

The following journal articles have been published:

- A. Potter, J. Sumner, N.J. Simms, J.E. Oakey, “Type II hot corrosion of environmentally resistant coatings in the next generation of industrial gas

turbines” European Corrosion Congress, EUROCORR 2015, vol. 1, pp 227-236, 2015 [16]

- A. Potter, J. Sumner, N.J. Simms, “The role of superalloy precipitates on the early stages of oxidation and type II hot corrosion” Mater. High Temp., vol. 35, pp. 236–242, 2018 [17]
- J. Sumner, A. Potter, N. J. Simms, and J. E. Oakey, “Modelling gas turbine materials ’ hot corrosion degradation in combustion environments from H<sub>2</sub>-rich syngas,” Mater. Corros. Vol. 68 no. 2, pp. 205–214, 2017 [18]
- J. Sumner, A. Potter, N. J. Simms, and J. E. Oakey, “Hot corrosion resistance of gas turbine materials in combusted syngas environments,” Mater. High Temp., vol. 32, no. 1–2, pp. 177–187, 2015. [19]



## 2. Literature review

This chapter reviews, critiques and identifies gaps in the current literature pertaining to the phenomena of hot corrosion in industrial gas turbines. This includes the topics of the principles of gas turbine operation, materials selection, superalloys, oxidation and hot corrosion. Of these topics, the operation and materials selection and the mechanics of oxidation in air are mature areas of research. In comparison, the oxidation of alloys in atmospheres containing water vapour and hot corrosion are less well understood.

### 2.1 Gas turbines: principles of operation

A gas turbine can be broken down into three essential parts; the compressor, combustion chamber and the power turbine [13], [20] (Figure 2.1). The principle of operation is simple; air is ingested into the compressor (1) where the pressure, and consequently the temperature, are increased to typically 15-20 bar and 500 °C [21]. The pressurised air then enters the combustion chamber (2) where it is mixed with fuel and combusted. The expansion of gas that occurs pushes through the turbine section (3) where a series of blades and vanes drive the turbine to do work. Usually, over 50% of the work generated by the power turbine is used to drive the compressor part of the gas turbine with the remainder operating a generator [22].

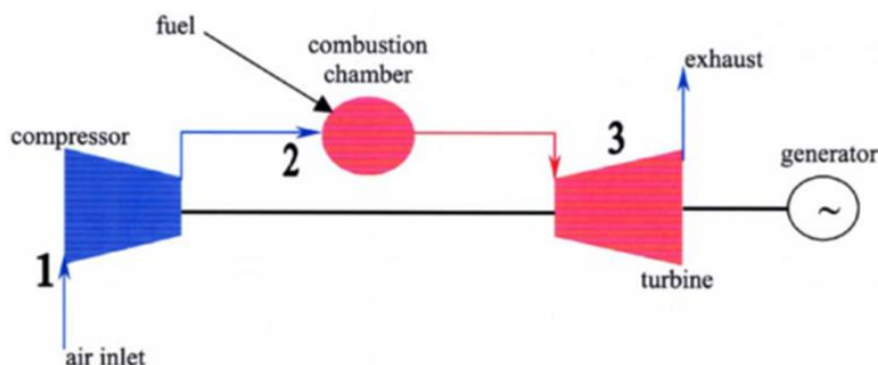


Figure 2.1: Principles of operation of an industrial gas turbine [13].

### 2.1.1 The Brayton cycle

The thermodynamic cycle occurring during the operation of a gas turbine is known as the Brayton cycle [23]. Two Brayton cycle diagrams are shown in Figure 2.2, which plot (a) pressure against volume and (b) temperature against entropy. Moving from point 1 to 2 in both images of Figure 2.2 represents the compression of the gas in the compressor. From 2 to 3 is the combustion stage with the pressure remaining constant as gas expands into the turbine at point 4. The cycle completes by moving back to point 1 by a constant pressure cooling process [24].

The efficiency of the gas turbine is largely dependent on the pressure ratio and the firing temperature of the engine. The pressure ratio of the engine is the pressure at which the gas leaves the compressor and enters the combustor (point 2 in Figure 2.2) divided by the compressor inlet pressure (point 1 in Figure 2.2). The firing temperature is the highest temperature achieved during the cycle. Having a higher pressure ratio increases the benefits gained from increasing the firing temperature [24], [25].

The inlet pressure and temperature are related to the ambient conditions; therefore the geographical siting of the gas turbine is important. Ideally the turbine should be at low altitude in a cold, dry climate. Where this is not possible, solutions can be engineered such as air inlet cooling [13].

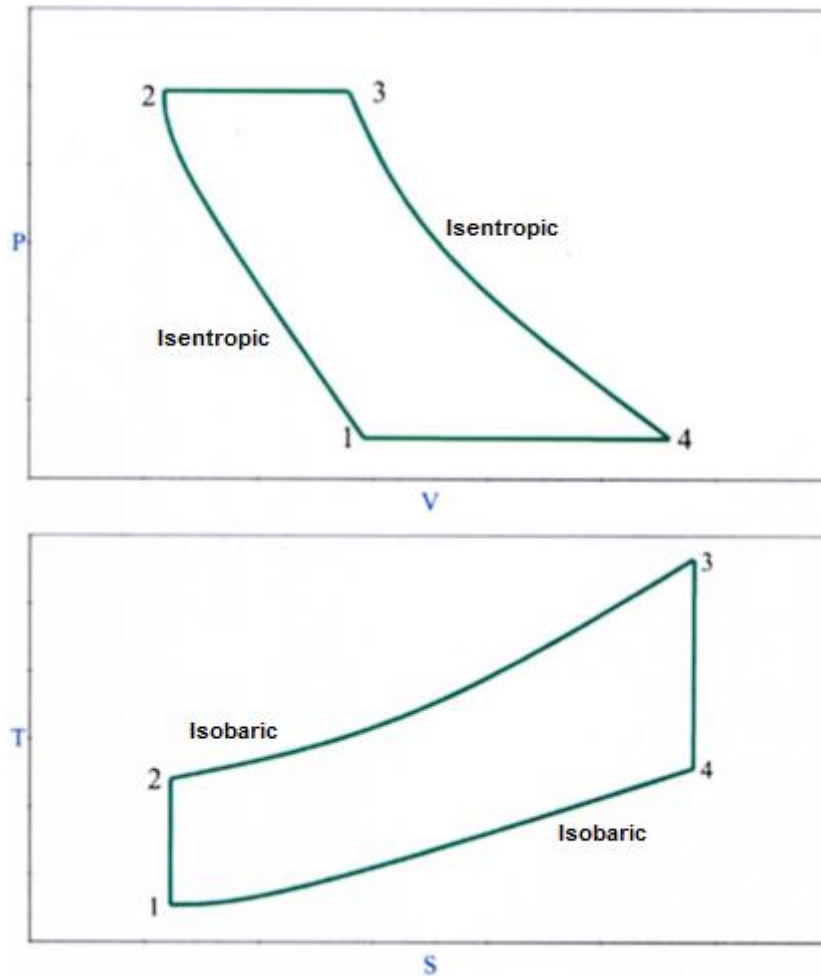
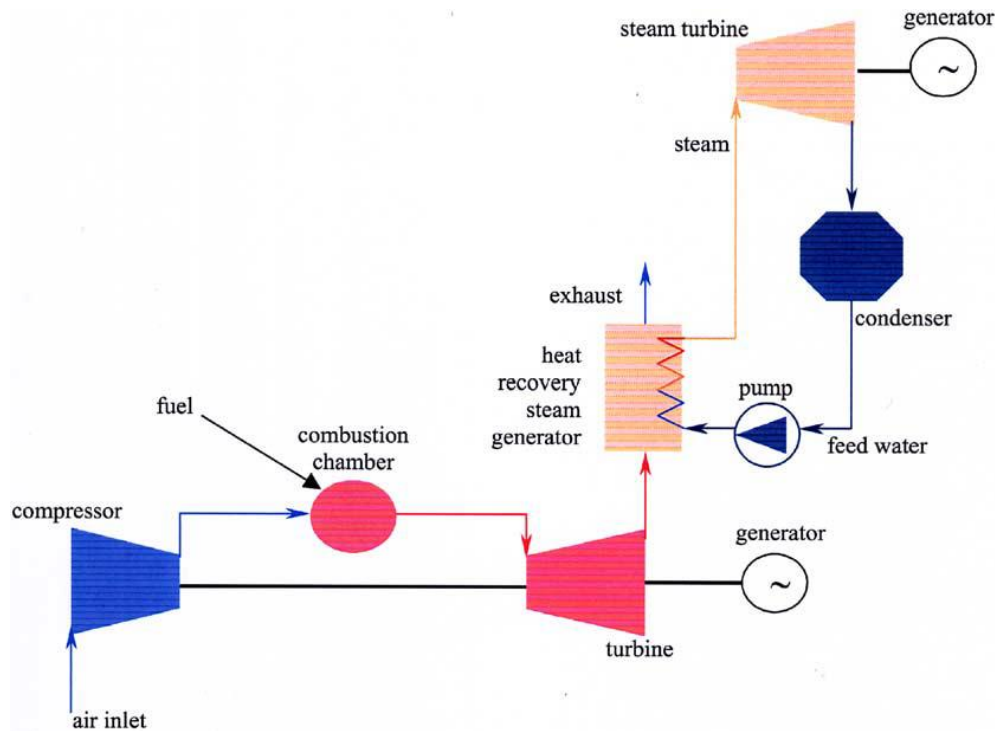


Figure 2.2: The Brayton cycle showing pressure against volume (upper image) and temperature against entropy (lower image) [13].

### 2.1.2 The combined cycle

The combined cycle, also known as the Brayton-Rankine cycle, uses the heat of the gas exiting the turbine exhaust (this can be between 400 and 600 °C) to operate a steam turbine [13]. Figure 2.3 shows a schematic of a simple combined cycle system with the heat from the turbine exhaust used to generate steam to power the steam turbine. Up to 70% of the fuel input energy can leave the system as exhaust heat, by utilising that energy, thermal efficiencies of close to 60% have been reported [13], [25] compared to up to 45% efficiencies reported for conventional coal and oil fired plants [22].



**Figure 2.3: Combined cycle operation [13].**

As well as improved thermal efficiency, the combined cycle system provides several other advantages over typical simple-cycle power systems. These include lower  $\text{SO}_x$ ,  $\text{NO}_x$  and  $\text{CO}_2$  emissions; lower capital investment costs and build times; and smaller site size requirements [25]. Energy demand is not constant and output from certain renewable energy sources can be variable, therefore the fast start up time of a gas turbine is also an important feature [22].

Over the lifetime of turbine components such as blade and vanes, there is a decline in their efficiency [13]. This performance degradation can be categorised as either recoverable or non-recoverable. Recoverable losses are typically caused by fouling in the compressor section and can be treated by washing or mechanical cleaning. Non-recoverable degradation is often associated with damage to component surfaces and changes to compressor and turbine clearances. Such damage cannot be rectified and ultimately requires the replacement of affected components. Oxidation and hot corrosion are both major

sources of non-recoverable degradation that limit component lifetimes in the turbine.

## 2.2 Turbine materials

Historically, the materials development for industrial gas turbines has lagged behind the aircraft technology by between 10 and 20 years [26]. However, in recent years increasing demands for improved efficiencies have accelerated the development of materials to comparable levels. Figure 2.4 shows some of these major developments in turbine materials along with selected superalloys in terms of creep rupture life.

The power industry requires gas turbine components to serve for over 50000 hours at operating temperature [26]. This is in contrast with the aviation industry where the turbines are exposed to higher peak temperatures but with significantly lower required cycle times [27].

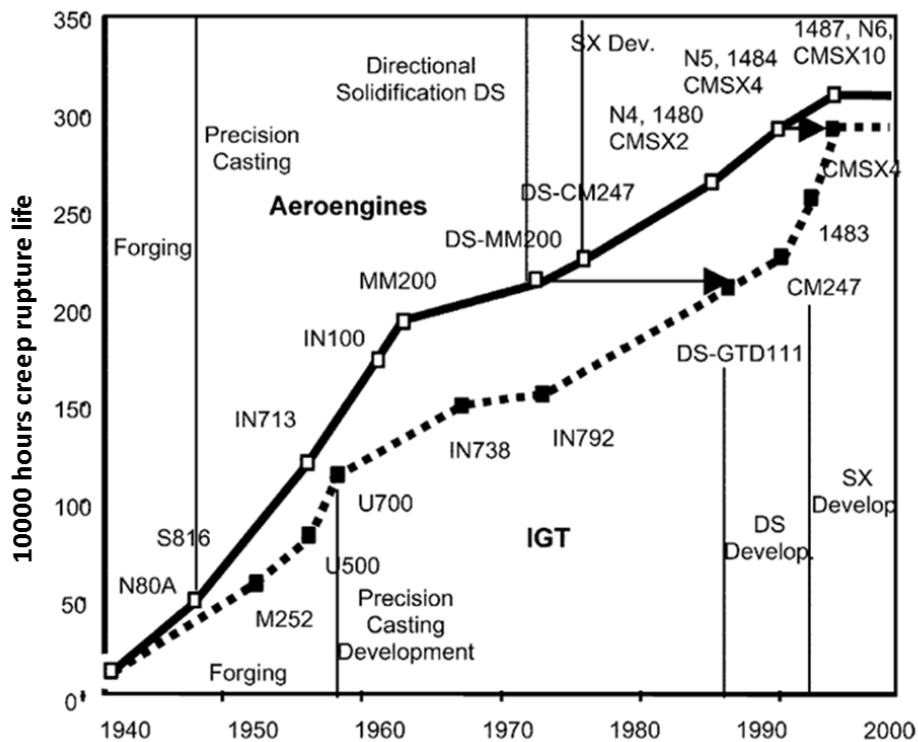


Figure 2.4: Historical development of turbine materials in terms of creep rupture life at 870 °C [26].

### **2.2.1 Combustor materials and conditions**

The combustor can's inner liner is typically made from a Ni-based superalloy with a suitable thin film bond coat and plasma sprayed thermal barrier coating [21]. In industrial gas turbines, the combustor can experience gas pressures of up to 20 bar and gas temperatures exceeding 1400 °C [21]. To reduce NO<sub>x</sub> and CO emissions, steam is injected directly into the combustion chamber [28]. In addition to degradation brought about by oxidation and hot corrosion mechanisms, the process of combustion can also cause a pulsation effect that exposes the materials to high cycle fatigue [21]. Current materials used for the combustion chamber include Hastelloy X and Haynes 230.

As gas turbine development pushes turbine firing temperatures higher, further demands are being put upon the materials' creep load and oxidation resistance [21], [26]. In addition, as the combustion of alternative fuels is explored, the atmosphere within the combustor is subject to change.

### **2.2.2 Turbine materials and conditions**

The power turbine section of the engine is the most demanding from a materials perspective [21]. The blades and vanes of the first stage may see gas temperatures above 1200 °C [7] while the blades also experience centrifugal forces inflicting creep and fatigue. In addition to this, foreign objects may be carried through the gas stream causing erosion and air cooling ducts can cause the deposition of various contaminants on the components.

The most advanced turbine blades tend to be Ni-based superalloys cast as a single crystal [29]; these are discussed in more detail in Section 2.3. Turbine components can have protective coatings such as MCrAlYs or platinum aluminides applied which improve oxidation and corrosion resistances while thermal barrier coatings may be used for the hottest parts of both blades and vanes.

The turbine blades are locked in place around the circumference of a turbine disc that is not exposed directly to the hot gas pathway. Nevertheless, the discs in the early stages of the turbine can see temperatures in excess of 600 °C [7] and have the radial force of the rotating disc and attached blades acting upon them. Turbine discs may also receive contamination through air cooling making them susceptible to hot corrosion mechanisms (discussed in chapter 2.6).

Because there is a temperature and pressure gradient through the power turbine section with gas entering at over 1200 °C and exhausting at approximately 500 °C [21], the materials used for the later stages do not have the same demands put upon them.

## **2.3 Superalloys**

As discussed in the previous section, the materials used within power turbine sections have seen continuous improvement to meet the increasingly demanding conditions of use [29], [15]. Indeed, materials' development and availabilities have often been the limiting factor in the improvement of gas turbine engines. Somewhere along the evolutionary path from steels to modern single crystal and precipitation strengthened Ni-based superalloys, it was noticed that the properties had improved to such an extent that such alloys should be categorised separately to more conventional alloys. For this reason, the exact definition of a superalloy can be ambiguous and vary between publications. In general, it is safe to define a superalloy as a material designed to offer good creep resistance, mechanical strength and oxidation resistance at elevated temperatures [30].

Superalloys can be broadly categorised depending on the base metal used; iron-based, Ni-based and Co-based. The scope of this study includes both Co and Ni based superalloys [15].

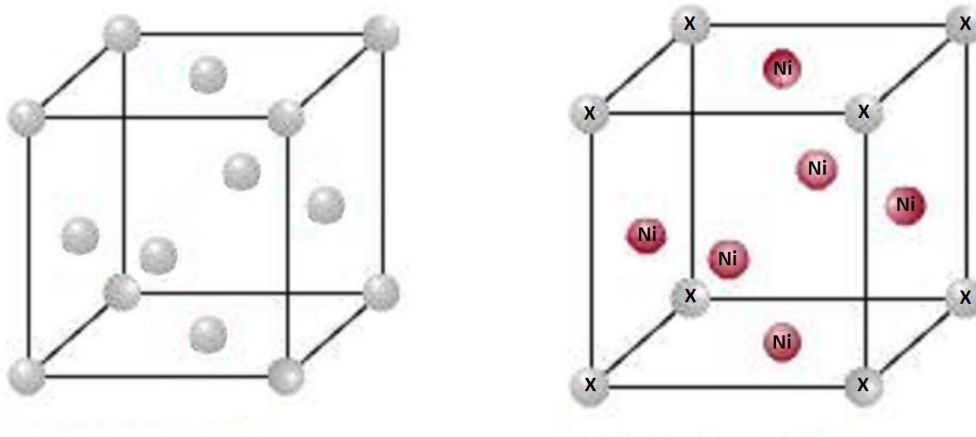
Co-based

- High melting temperature
- Superior hot corrosion resistance at the time of development.
- Surpassed by  $\gamma'$  strengthened Ni alloys

#### Ni-based

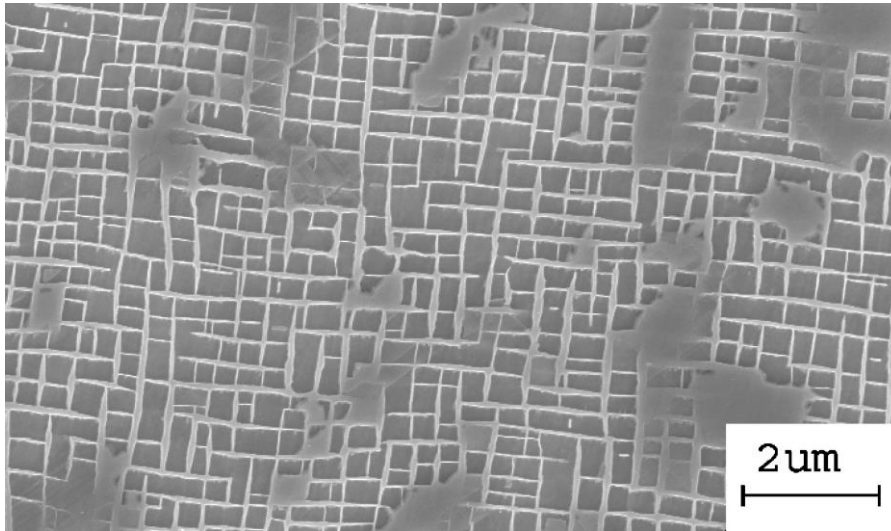
- Good tolerance for alloying without phase instability
- Able to form  $\text{Cr}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$ -rich protective scales dependant on additions.
- Can be precipitation hardened for superior strength at high temperatures
- Most expensive

As the amount of Al added to  $\gamma$ -Ni increases, a second phase precipitates within the matrix termed  $\gamma'$ . The  $\gamma'$  phase has an ordered  $\text{Ni}_3\text{Al}$  face centred cubic crystal structure, shown in Figure 2.5. The formation of the  $\gamma'$  phase occurs as the alloy's solid solution cools past its equilibrium solvus temperature. For this reason, the rate of cooling has a great effect on the formation of the  $\gamma'$  phase and is carefully controlled. Faster cooling rates (in excess of 40 k/min) give rise to a unimodal distribution of small (300–500 nm)  $\gamma'$  precipitates whereas a slower cooling rate is found to create a less even distribution of the  $\gamma'$  phase forming in multiple populations [31].



**Figure 2.5: (Left) FCC  $\gamma$  structure where the element distribution is random. (Right) FCC ordered structure of  $\gamma'$  where X is other alloyed elements [32].**

Since the formation of the  $\gamma'$  phase greatly enhances the strength of the alloy, a high  $\gamma'$  ratio is desired and heat treatment processes focus on improving the  $\gamma'$  yield [31]. The  $\gamma$ - $\gamma'$  binary phase microstructure for a high  $\gamma'$  yield Ni base superalloy is shown in Figure 2.6.



**Figure 2.6: Microstructure showing the  $\gamma$  (lighter) and  $\gamma'$  (darker) phases of a nickel base superalloy [31].**

A common feature of most superalloys is the relatively large number of alloying elements in their composition [31]. In general, additions such as W, Mo and Re, are added to enhance the strength of the  $\gamma$  phase through solid solution strengthening, whereas the elements Ti, and Ta assist in the formation and strength of the  $\gamma'$  phase. The addition of Nb is found to enhance both the  $\gamma$  and  $\gamma'$  phases [31]. Minor additions of elements such as C, B, Hf and Zr can be made to control the grain size of the intermetallic structure with these elements partitioning to the grain boundaries where possible. Finally, to improve the oxidation and corrosion resistance of the resulting alloy via the promotion of a protective oxide scale Cr, Al and Y could be added [31]. The properties brought by these alloying elements are related to their atomic radius and electronic structure [15]. This can be seen in the periodic table shown in Figure 2.7.

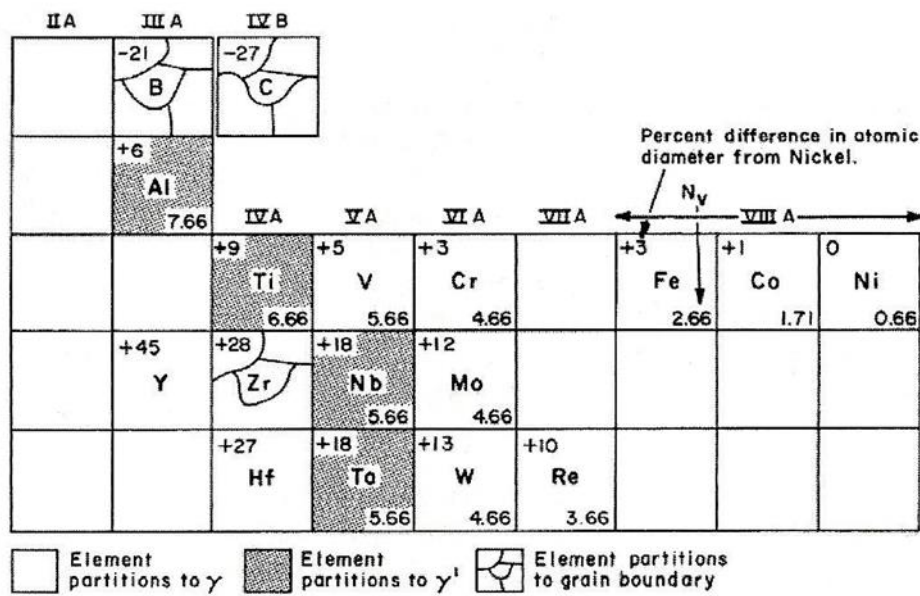


Figure 2.7: Elements commonly used in the composition of superalloys [15].

## 2.4 Oxidation

In chemistry the term “oxidation” refers to the loss of electrons and consequent increase in valence of a reactant during a chemical reaction. The word oxidation is used because, historically, the first reactions where this process was recognised involved the donation of electrons from metal reactants to O. The definition was later changed when reactants other than O were found to be able to accept electrons, however they are still referred to as oxidants [33].

The oxidation state refers to the ability of a reactant to either donate or receive electrons. The International Union of Pure and Applied Chemistry describes it in the following manner [33]:

“A measure of the degree of oxidation of an atom in a substance. It is defined as the charge an atom might be imagined to have when electrons are counted according to an agreed-upon set of rules:

- (1) The oxidation state of a free element (uncombined element) is zero.

(2) For a simple (monoatomic) ion, the oxidation state is equal to the net charge on the ion.

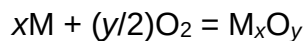
(3) Hydrogen has an oxidation state of 1 and O has an oxidation state of –2 when they are present in most compounds. (Exceptions to this are that hydrogen has an oxidation state of –1 in hydrides of active metals, e.g. LiH, and O has an oxidation state of –1 in peroxides, e.g. H<sub>2</sub>O<sub>2</sub>.)

(4) The algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion.”

Because metals have a positive oxidation state and the oxidation state of O is -2, metals will fundamentally be oxidised in air to form a metal oxide [14], [34]. In other atmospheres, nitrides, carbides, sulphides, etc. may form depending on the oxidant species present. In a non-aqueous low temperature environment, the rate of this reaction may be low enough to prove negligible. In high temperature environments, such as those found in certain sections of a gas turbine, the oxidation reaction rates may be much quicker and consequently becomes a key issue in materials selection [21].

#### **2.4.1 Thermodynamics of oxidation**

The chemical reaction for a truly pure metal (M) with O (O<sub>2</sub>) forming metal oxide (M<sub>x</sub>O<sub>y</sub>) may be written in the following manner [35]:



**Equation 2-1**

The energy available to drive a reaction is known as Gibbs free energy and is given the symbol G [36]. The change in Gibbs free energy ( $\Delta G$ ) undergone during a reaction can show if the reaction is thermodynamically favourable. If  $\Delta G$  is positive then energy must be provided for the reaction to take place and is thus

thermodynamically unfavourable. On the other hand, if  $\Delta G$  is negative the products have less free energy than they reactants and are therefore more stable, and the reaction is thermodynamically favourable.

For the reaction shown in Equation 1, the change in Gibbs free energy can be calculated with the following equation [14], [34], [36]:

$$\Delta G^o = -RT \ln \left( \frac{a_{M_xO_y}}{a_M P_{O_2}} \right)$$

**Equation 2-2**

Where R is the universal gas constant, T is the temperature,  $a_M$  is the activity of the metal,  $a_{M_xO_y}$  is the activity of the oxide and  $p_{O_2}$  is the partial pressure of  $O_2$ .

If the activities of the metal and the oxide are assumed to be 1 then they can be removed and the equation becomes:

$$\Delta G^o = RT \ln(p_{O_2})$$

**Equation 2-3**

A plot of the change in Gibbs free energy as a function of temperature is known as an Ellingham diagram [34]. Figure 2.8 shows such a diagram for the formation of certain oxides and has several noteworthy features:

- A more negative value of  $\Delta G^o$  indicates a more stable oxide. Therefore the most stable oxides are located towards of bottom of the diagram and the least stable at the top. The less stable oxides can be reduced by those that are more stable although the speed of this reaction is not reflected in the diagram and may be very slow.
- Changes in the gradient of an individual line show a phase change (either state or structure) in either the metal or oxides. This gradient change reflects changes in entropy.
- Using the nomographic scale later added to the Ellingham diagram, the equilibrium dissociation pressure of the oxides can be determined. This can show the partial pressure of  $O_2$  required for the oxide reaction to take place.

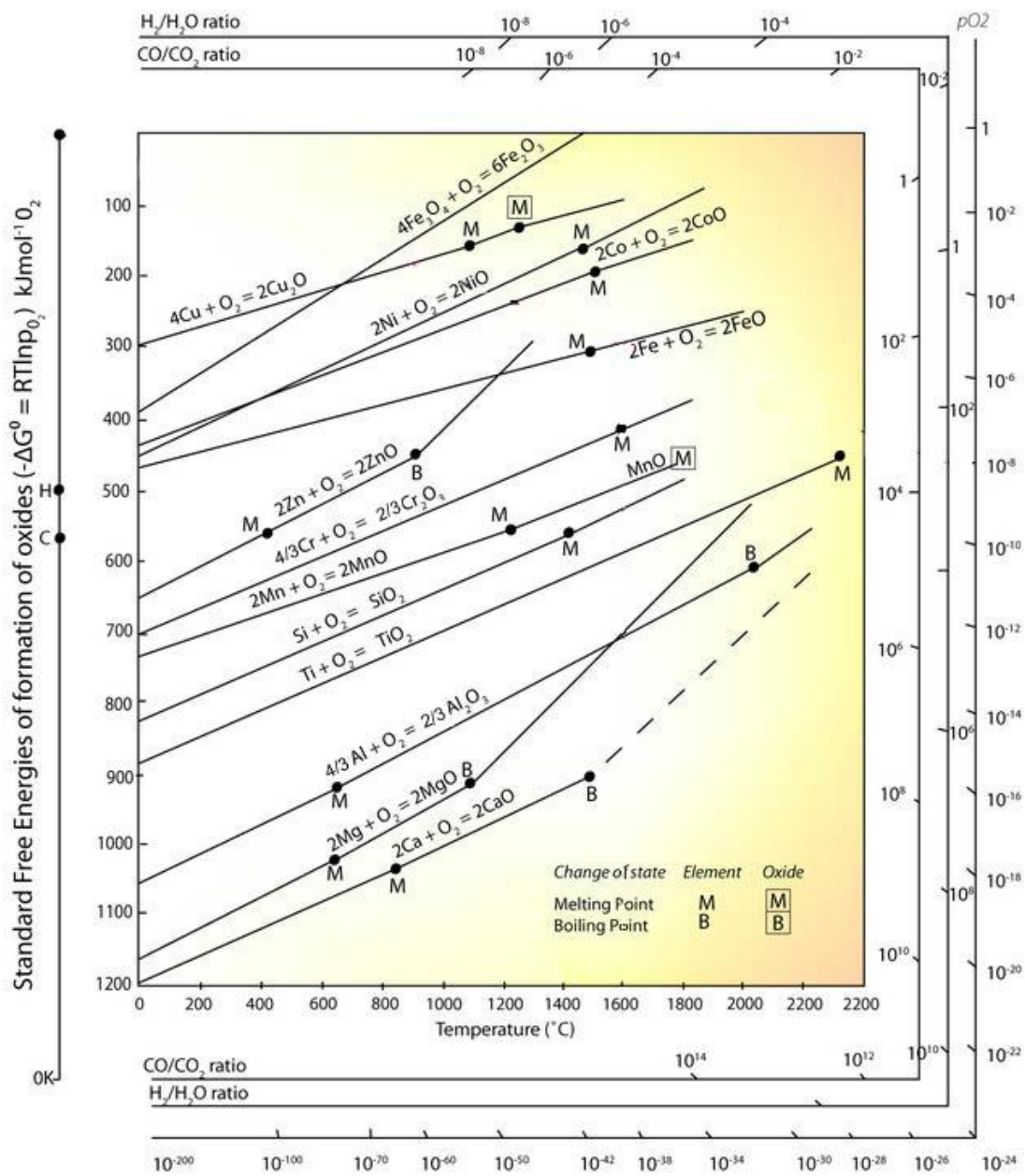


Figure 2.8: Ellingham diagram for the formation of various metal oxides [37].

Since the metal oxide is fundamentally more stable than the parent metal, it plays an important role in the corrosion resistance of a system by protecting the underlying metal from aggressive forms of attack [38]. To fulfil the role of a protective scale, the oxide layer should meet certain criteria:

- Continuous: The oxide scale should entirely cover the whole surface in a single phase.
- Free from defects.
- Of adequate thickness.

#### 2.4.2 Oxidation mechanisms

The Ellingham diagram shows that metals react with  $O_2$  (at a great enough partial pressure) to form an oxide. It does not however show how fast these reactions are. Such reaction rates are often governed by the ability of O to access unreacted metal [36].

If a flawless oxide layer has initially been formed, it is apparent that for the oxidation reaction to continue either metal cations must migrate through the metal oxide scale to react with  $O_2$  or  $O^{2-}$  anions must migrate across the scale to react with the metal. This is illustrated in Figure 2.9. Previous research has shown that the formation of  $Cr_2O_3$  (which is most relevant to this study) is propagated almost entirely by the outward migration of Cr cations across the oxide scale [39].

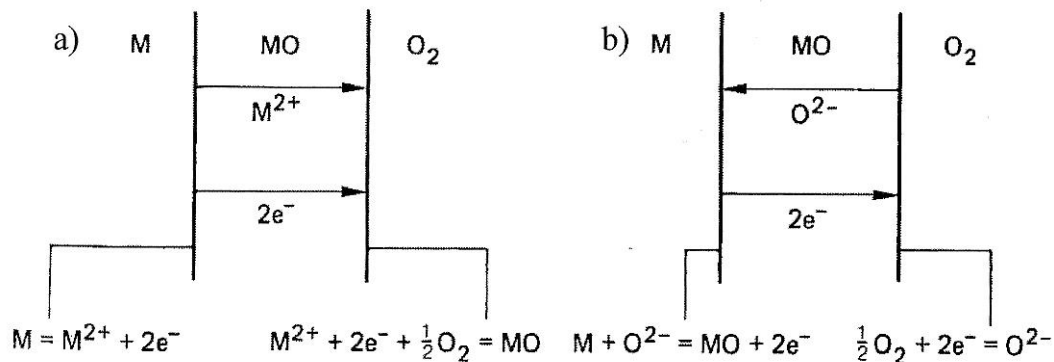


Figure 2.9: Interfacial reactions for (a) cation migration and (b) anion migration [14].

Oxidation rates may vary as a function of time due to a number of factors. Three main kinetic trends have been observed; linear, logarithmic and parabolic. An idealised schematic of these trends is shown in Figure 2.10.

- Linear: with this trend, the reaction kinetics remains constant and are governed by the rate of the metal-oxygen reaction. The oxide scale is non protective and its thickness does not affect the reaction rate [14].
- Logarithmic: this rate law is usually associated with the formation of thin oxide films at relatively low temperatures and therefore has little bearing on high temperature applications [40].
- Parabolic: metals that form a continuous protective oxide scale at high temperatures follow this rate law. The transportation of cations or anions across the scale governs the rate of oxidation. As the scale grows thicker the transportation distance increases and the rate is therefore slower. Oxides on components intended for use in high temperature applications ideally follow a parabolic rate law [14].

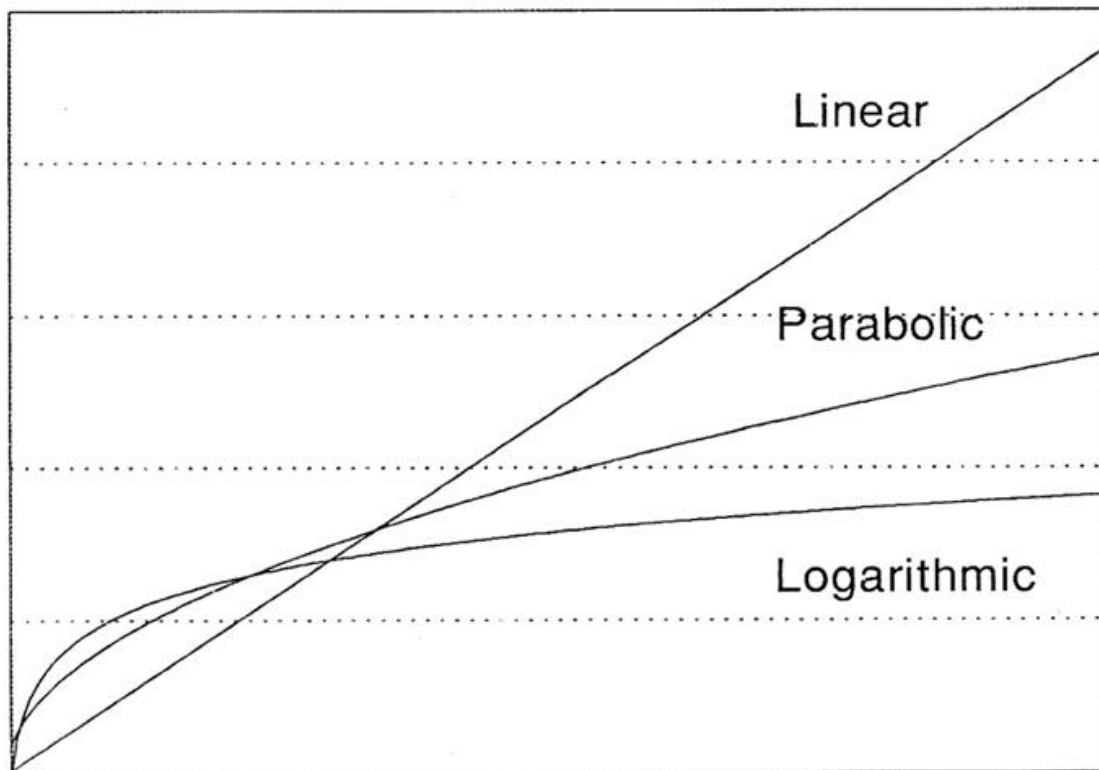
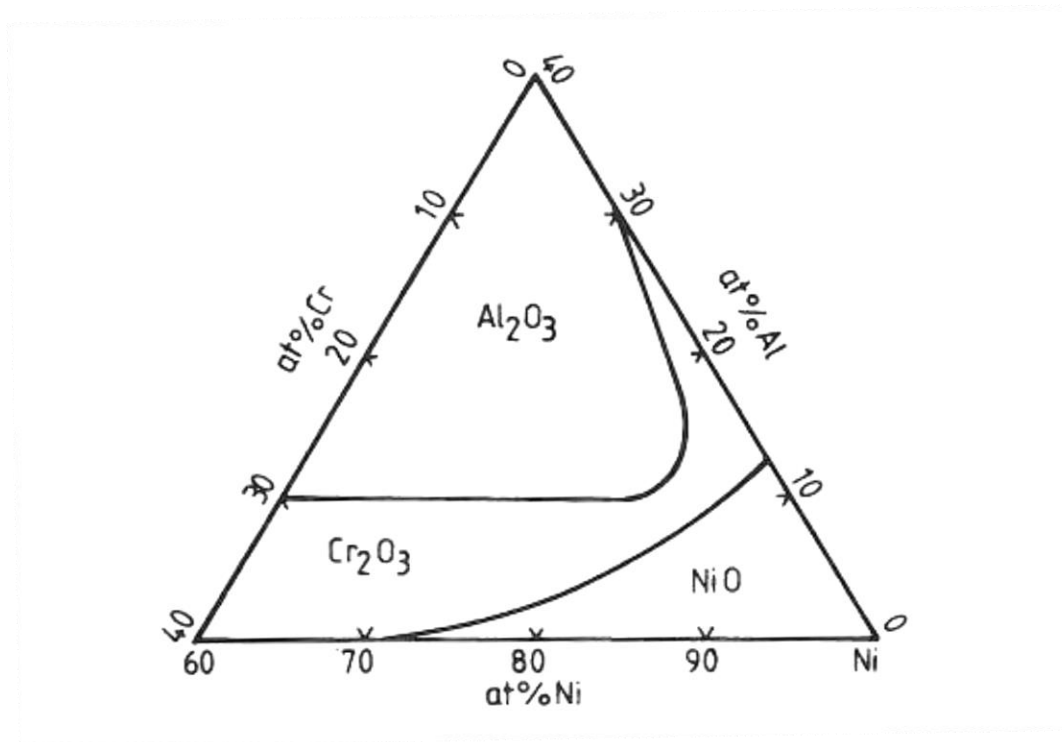


Figure 2.10: Schematic of the oxidation rate laws [41].

### 2.4.3 Oxidation of alloys

If a fresh alloy surface is exposed to an environment conducive to oxidation, each element for which it is thermodynamically favourable to do so may initially oxidise forming an oxide nucleus. Over time and depending on a number of factors including affinity for  $O_2$ , abundance, and oxide thickening and lateral spread rates, one metal oxide may become dominant and form a continuous oxide scale [42]. This is illustrated by the ternary phase diagram for a Ni-Cr-Al system at 1100 °C shown in Figure 2.11.



**Figure 2.11:** Ternary phase diagram showing the dominant oxide scale of a Ni-Cr-Al system at 1100 °C [43].

The oxide nuclei that may have formed during the initial stages of the oxidation sequence can potentially remain either on the surface of or within the continuous oxide scale [44]. These species are known as transient oxides. The oxidation sequence showing the formation of transient oxides is presented schematically in Figure 2.12 for a Cr-rich alloy (A) and a Cr-lean alloy (B).

Chen et al. [45] was one study that confirmed the presence of transient oxides. X-ray diffraction was used to detect the oxides  $\text{NiCr}_2\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  in the external scale of the alloys Udimet 720 and Waspaloy after exposure at  $750^\circ\text{C}$  in air.

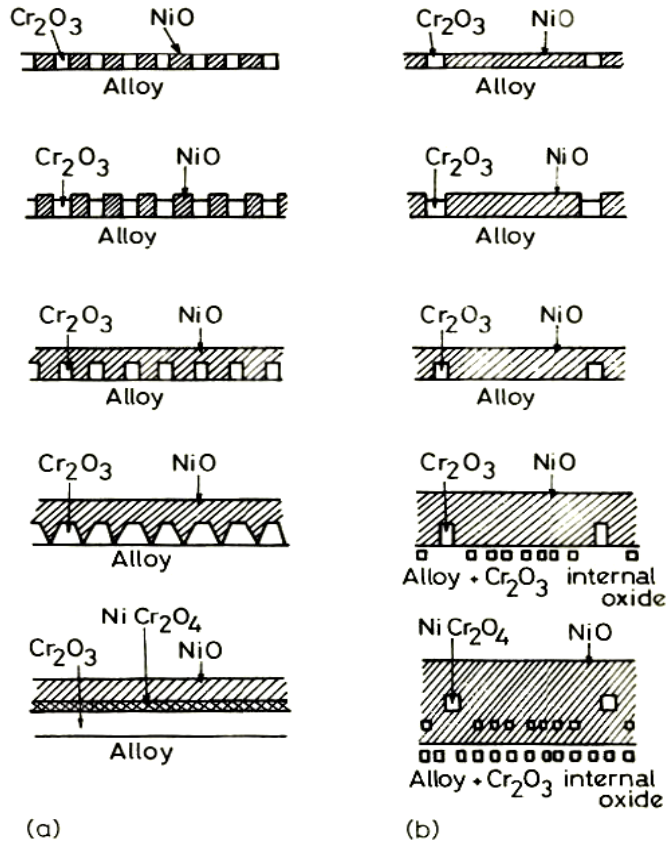


Figure 2.12: Schematic showing the formation of transient oxides for Ni-Cr alloys that are (a) Cr-rich and (b) Cr-lean [42].

## 2.5 Oxidation in the presence of water vapour

The act of combustion can generate a water vapour rich gas stream with the volume of water vapour dependent on the fuel being combusted. Coal will typically form an atmosphere of approximately 7 vol.% water vapour, whereas biomass could potentially produce up to 30 vol.%. In addition, in a gas turbine steam can be injected into the combustor to lower the flame temperature as a method to control  $\text{NO}_x$  emissions. It therefore follows that components along the

post-combustion hot gas pathway of industrial gas turbines operate in an environment containing a certain amount of water vapour [19].

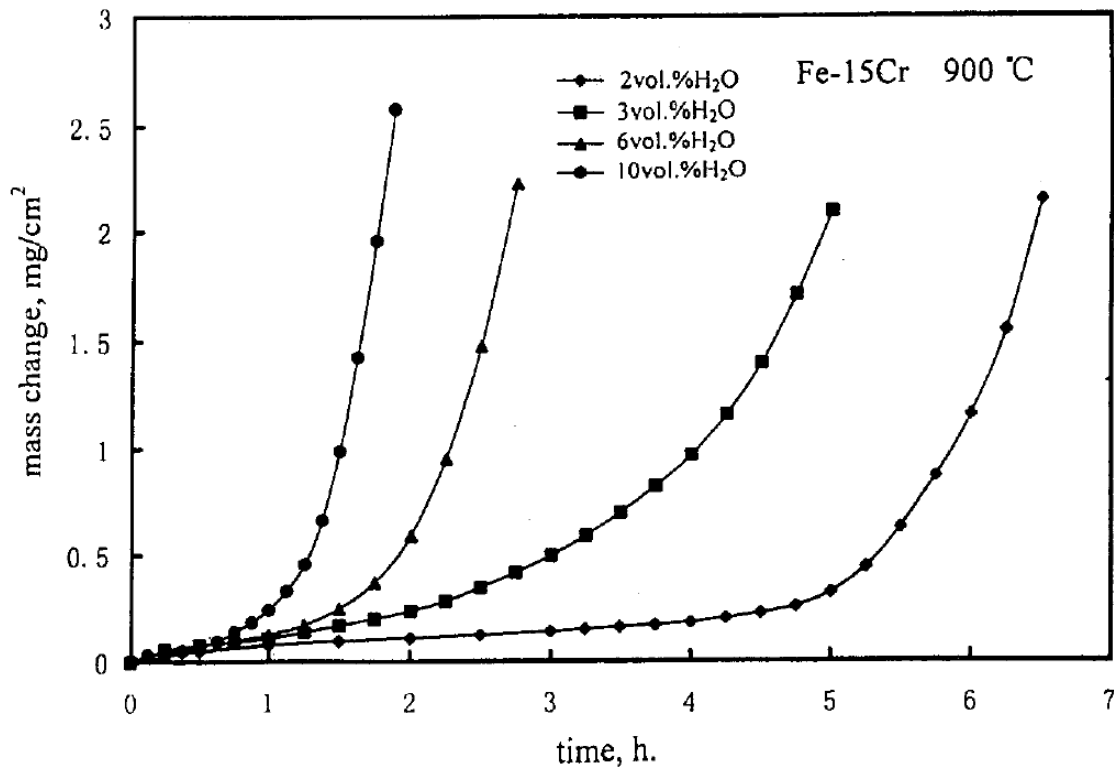
As a result of the presence of water vapour in the practical environments, there is a wide body [46]–[62] of research investigating the effects water vapour has on the oxidation of metals and alloys at elevated temperatures. The majority of this work is based on the oxidation of steels with relatively few studies investigating superalloys [46].

In this section, the results of and inference from studies involving the oxidation of both chromia forming and alumina forming alloys in the presence of water vapour are presented. Unless otherwise stated, these studies all used coupon samples of either circular or rectangular geometry with a surface area of between 1 and 1.5 cm<sup>2</sup> and a thickness between 1 and 3 mm.

### **2.5.1 Chromia formers**

The majority of research into the effect of water vapour on iron-based chromia forming alloys at elevated temperatures find that rates of oxidation are increased in environments containing water vapour compared to dry air [46], [47], [55]–[60], [62]. It is commonly observed that, after an initial period of slow oxidation, the system goes into rapid breakaway oxidation. This corresponds to degradation of the protective chromia scale leading to oxidation rates governed by the base alloy. The rapid transition to breakaway oxidation is widely attributed to the formation of volatile  $\text{CrO}_2(\text{OH})_2$  and  $\text{Cr}(\text{OH})_3$  species which may subsequently be vaporised [59], [60], [62], [63].

Research by Jianian et al. [47] investigating the oxidation kinetics of Fe-Cr alloys in  $\text{O}_2$  with differing amounts of water vapour is an example of this trend. Some of the data from this study is presented in Figure 2.13. This shows that the amount of time before the onset of breakaway oxidation decreases with increasing water vapour up to the maximum tested concentration of 10 vol.%. The paper proposes these differences in kinetics are a consequence of the formation of voids and microcracks caused by the outward transportation of Cr.



**Figure 2.13:** Oxidation rates of Fe-15Cr at 900 °C in oxygen with increasing quantities of water vapour [47].

An alternative mechanism has been proposed by Ehlers et al. [60] for 9% Cr steel in environments with a relatively low partial pressure of O<sub>2</sub> (vol. 1%). Volatile Fe(OH)<sub>2</sub> could form in the inner layers of the scale at sufficiently low partial pressures of O<sub>2</sub>. In the outer layers of the scale, this was then converted to magnetite or haematite therefore accelerating rates of oxidation through the disruption of the protective scale.

The corrosion behaviour of ferritic steel boiler tubes has been studied by Nakagawa et al. [58]. The steam side permeation of hydrogen through the tubes was measured electrochemically using a proton conductive solid electrode. Hydrogen was observed to diffuse through the boiler tube from the steam side and exacerbate corrosion rates at the air side. These increases in corrosion rates are thought to be caused by dissociation mechanisms that allow the continuation of redox reactions inside the voids. Two mechanisms for the diffusion of hydrogen

were proposed: in the first, hydrogen formed from the dissociation of water vapours may diffuse through the scale as protons. These protons may react with electrons in the steel to form hydrogen before permeating through the tube. Alternatively defects in the scale may allow water vapour to react with the alloy to form hydrogen that can permeate into the tube.

Relative to the widespread use of chromia forming nickel-based alloys in high temperature turbines and combustion systems, there is only limited information available [46]. There is currently no common consensus of the findings with most data observing increased rates of oxidation, while a lesser but significant amount of data does not. It should be noted that these studies have greatly differing parameters and in no way aim to replicate each other.

Research by Onal et al. [61] compared the cyclic exposure of both chromia forming superalloys (IN 738 and X-40) in dry air to air saturated with 0.3 atm water vapour at 700, 900 and 1000 °C. At 700 °C these alloys proved resistant to cyclic oxidation in both wet and dry conditions with a relatively small increase in weight change for only one of the alloys (IN 738) when exposed in wet air. Both alloys were more severely degraded during the 900 °C exposures with the wet air thought to be exacerbating the weight change through cracking and spallation of the scale.

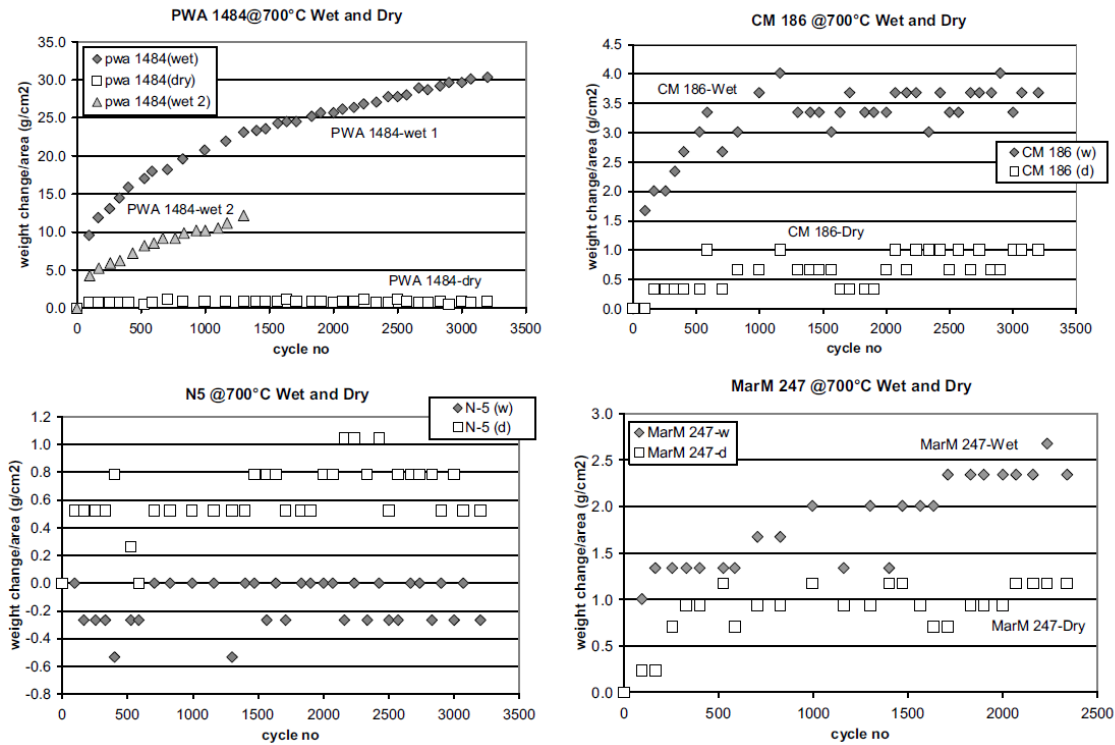
In contrast to the majority of research on this topic, a comparison of two studies by Hussain et al. [50], [49] looking at the oxidation of Hastaloy C-4 in air and steam respectively show lower oxidation rates in steam. During the exposures in steam, a dense, compact and adherent chromia scale was able to form and consequently reduced oxidation rates. In air, the inability to form a protective scale and higher oxidation rates was attributed to a greater diffusion rate of Mo through the chromia scale. The sample preparation involved in Hussain's studies differs significantly from other research described in this section. Here, specimens with a surface area of between 15 and 20 cm<sup>2</sup> were cut from 1 mm sheet before undergoing electrochemical polishing in a solution of H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O.

Xie et al. [51] studied the effects of water vapour on the oxidation of Ni-Cr binary alloys in environments rich in CO<sub>2</sub>. Such atmospheres are relevant to the oxyfuel process that involves combusting pulverised coal in a mixture of recirculated flue gas and O<sub>2</sub>. In dry atmospheres a NiO scale formed a uniform layer with some porosity. In comparison, in wet atmospheres the NiO scale produced was thinner and more dense. This density was attributed to improved inward transport of O<sup>2-</sup> through NiO and, for alloys with a sufficiently high Cr content, resulted in buckling in the internal oxidation zone of the sample.

Relative to the study by Xie et al. [51], Rouaix-Vande Put et al. [52] investigated the effects of water vapour in atmospheres with a higher activity of carbon (CO and CO<sub>2</sub>) conducive to metal dusting (a form of corrosion brought about by the formation of metal carbides on the metal surface). The presence of water vapour was found to reduce the activity of carbon and therefore suppress the effects of metal dusting. Over a 500 hour exposure time the oxide scales for both alumina and chromia formers remained intact (with the exception of one Ni/Al binary alloy). The authors suggest that cracks in the scale did not form under these conditions.

### **2.5.2 Alumina formers**

K. Onal et al. [62] report on the oxidation kinetics and changes in morphology for the alumina forming alloys PWA 1484, CM 186, N5 and MarM 247 cyclically exposed in either wet (0.3 atm H<sub>2</sub>O) or dry air at temperatures between 700 and 1100 °C for up to approximately 3250 hours of exposure. Some of the data for exposures at 700 °C are shown in Figure 2.14. In most cases greater weight change was observed in wet air although N5 exhibited a slightly greater weight change in dry air. These results were attributed to two main effects of water vapour: the selective oxidation of Al was adversely affected causing more transient oxides to form on the alloy surface. Additionally, a decrease in the toughness of the alumina scale interface can cause the scale to crack and spall. These effects were observed to be more pronounced at 700 °C compared to 900 °C.



**Figure 2.14: weight change data for several alumina forming alloys exposed in 45 minute cycles at 700 °C in either dry or wet (0.3 atm H<sub>2</sub>O) [62].**

A study by Janakiraman et al. [53] investigated the cyclic oxidation of CMSX 4, PWA 1480, PWA 1484 at 1100 °C in both dry and wet (0.1 atm H<sub>2</sub>O) air. All three of these alloys showed greater weight changes in the wet air condition, with a lesser difference in weight change being observed for CMSX 4. The authors attribute the lower weight change of CMSX 4 to a lower naturally occurring S content (3 ppm compared to between 5 and 8 ppm). To determine the impact of this, PWA 1484 was desuphurised to less than 1 ppm by annealing in hydrogen at 1200 °C. This specimen showed relatively little weight change in both the dry and wet conditions. Despite this finding, practical combustion environments normally involve S as a contaminant which may render attempts to remove S from the alloy futile. It may also be possible that the hydrogen annealment process had effects other than just the removal of S that affected the oxidation characteristics.

Research by Liu and Narita [54] studied the oxidation of alumina forming TiAl alloys with additions of 0, 2 and 3 at. % Ag. These alloys were exposed in both dry air and in the presence of water vapour (30.8 vol. %) at 900 °C over up to 350 hours. The alloy variant without any Ag had significant mass change in both wet and dry air. The variants with additions of 2 and 3 at. % Ag only exhibited significant mass change in the wet air condition. This mass change was attributed to water vapour promoting the formation of  $\text{TiO}_2$  through the dissolution of  $\text{H}_2$  in  $\text{TiO}_2$  increasing the concentration of crystal defects. It is suggested that effect of Ag additions may be to broaden  $\gamma$ -phase grain boundaries although this is not shown graphically in their paper.

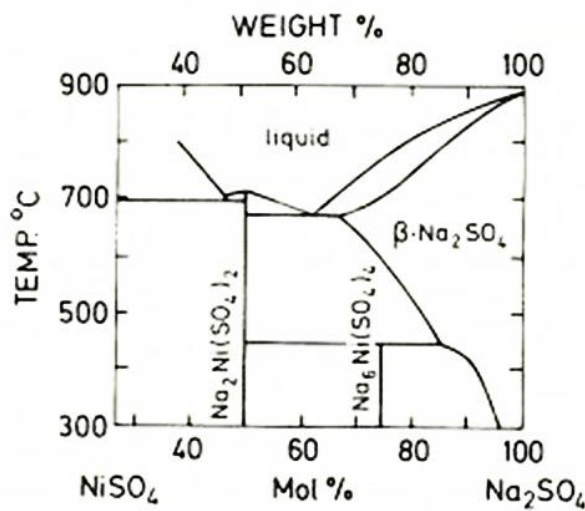
## **2.6 Hot Corrosion**

The working lifetime of certain components in gas turbines can be limited by an aggressive form of degradation known as hot corrosion [38]. This phenomenon was first observed in boilers, combustion systems and turbines in the 1940s [30]. Initial analysis of affected components observed that Ni and Cr sulphides had formed internally adjacent to the remaining good metal surface. For this reason, the process was initially known as sulphidation, until further research revealed that the sulphides had formed through reaction between the metal and a thin film of fused molten salt on the component surface [64], [65]. A second form of hot corrosion, consisting of pit features, was observed in the 1970s in marine propulsion turbines [66], consequently the terms type I and type II hot corrosion were coined based on their chronological discovery. Over the last 50 years, design developments of gas turbine in the power generation and aerospace industries have exposed component materials to higher temperatures and harsher operating conditions of use causing the phenomenon to become more of a problem.

Type I hot corrosion, sometimes known as high temperature hot corrosion, is typically observed to occur in the 850-950 °C temperature range. The mechanism is dominated by basic dissolution and features a uniform distribution of damage

and the formation of sulphides beneath the metal surface [66]. Corrosion rates decrease with decreasing temperature until peaking again between 650 and 750 °C in the regime of type II hot corrosion [67]. The lower temperature range of type II hot corrosion means it is sometimes referred to as low temperature hot corrosion and features an uneven distribution of damage in the form of corrosion pits [68].

Since it has been established that a molten deposit is a requirement for hot corrosion mechanisms, and that the melting point of pure  $\text{Na}_2\text{SO}_4$  for example is 884 °C [69] while the temperature regime of type II hot corrosion is between 650 and 750 °C, it is apparent that something must happen to allow the deposit to become molten. Several mechanisms have been proposed that involve the formation of low melting point compounds [68], [70]. An example of this is shown in Figure 2.15 where  $\text{NiSO}_4$  may have formed through sulphidation of  $\text{NiO}$  using  $\text{SO}_3$  in the gas phase. In practice the salt chemistry of the deposit may be extremely complex given the potential contaminants that may be encountered[71].



**Figure 2.15: Phase diagram of a  $\text{NiSO}_4$ - $\text{Na}_2\text{SO}_4$  system showing eutectic composition with a melting point below 700 °C [66].**

Once the molten deposit has established itself on the metal surface, for the corrosion reaction to continue, either reactants from the gas phase diffuse

through the deposit to reach the metal interface or reactive elements from the metal must dissolve into the deposit to reach the gas interface [14]. This can be achieved by either basic or acidic fluxing [72].

$\text{Na}_2\text{SO}_4$ , as an example, in a molten state can exhibit amphoteric behaviour in that it can be broken down into basic ( $\text{Na}_2\text{O}$ ) and acidic ( $\text{SO}_3$ ) components [72]. Figure 2.16 shows how the partial pressure of S in the gas phase is able to influence the deposit acidity by contributing  $\text{SO}_3$  to the melt.

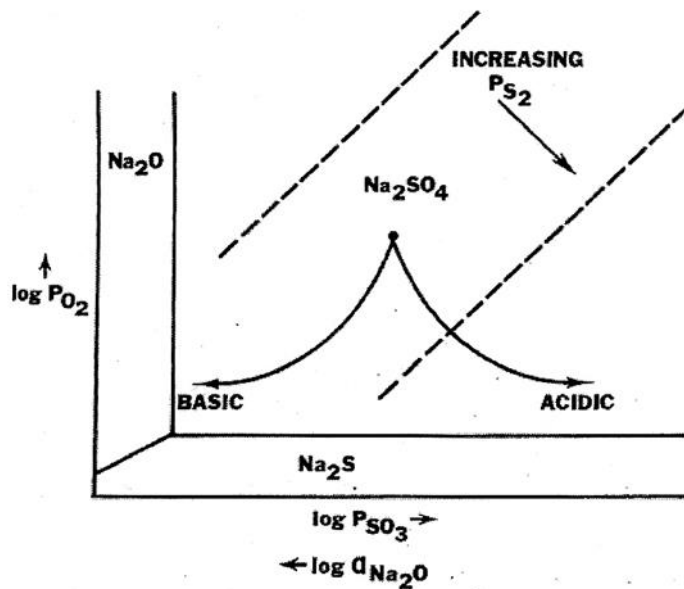
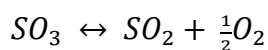


Figure 2.16: Thermodynamic stability diagram at constant temperature for a Na-O-S system [15].

In the gas phase,  $\text{SO}_3$  exists in equilibrium with  $\text{SO}_2$  (Equation 2-4) dependent on temperature with the right hand side being favoured with increasing temperature.



Equation 2-4

This has been demonstrated by Hussain et al. [73] using MT Data modelling software to plot  $\text{SO}_2/\text{SO}_3$  against temperature for two different gas compositions

(Figure 2.17). When Equation 2-4 is applied to Figure 2.16, it is apparent that temperature is able to influence the acidity of the melt through the partial pressure of  $\text{SO}_3$  (x axis in Figure 2.16). Thus basic fluxing tends to be observed at higher temperatures (in practice between 850 and 950 °C) and acidic fluxing occurs at a lower temperature (650 °C to 750 °C).

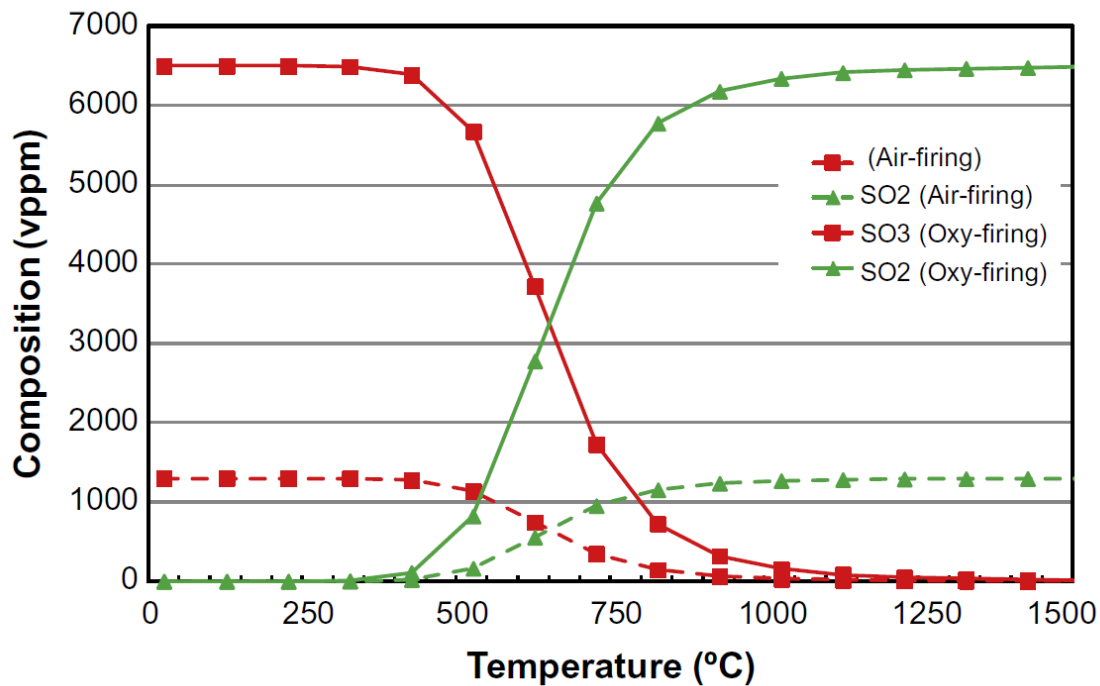


Figure 2.17: Modelled data showing the relationship between temperature and  $\text{SO}_2/\text{SO}_3$  composition [73].

### 2.6.1 Hot corrosion degradation sequence

As described in section 2.3, alloys designed for high temperature applications tend to form a protective oxide scale that is more inert than its parent material. For such alloys, the hot corrosion degradation sequence has been observed to occur in two stages [74]: an initial incubation period characterized by a low corrosion rate where the protective scale is attacked. This is followed by a propagation stage with a much higher corrosion rate where the protective scale has been compromised exposing the base alloy to reactive species in the melt.

Data demonstrating the incubation and propagation stages are presented in Figure 2.18 [66]. The rapid metal loss accompanying propagation usually heralds the imminent failure of a system component. For this reason, the corrosion lifetime of a component can be proportional to the length of the incubation period and efforts to extend component lifetimes often focus on the extension of the incubation period.

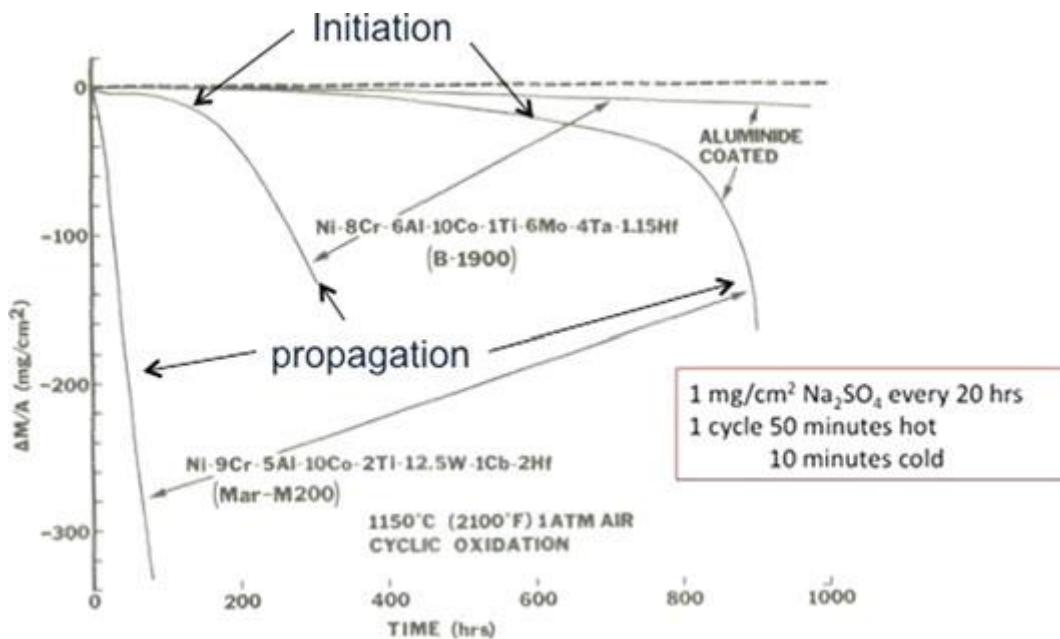


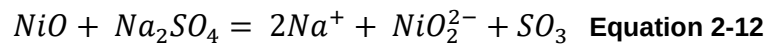
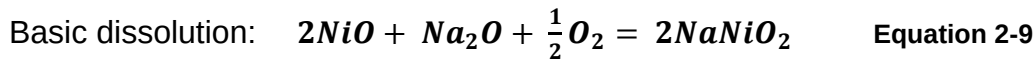
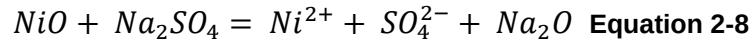
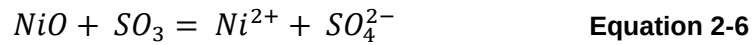
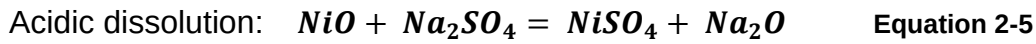
Figure 2.18: Data demonstrating the change in corrosion rate associated with the transition from incubation to propagation in the hot corrosion mechanism [66].

## 2.6.2 The fluxing mechanism

Early studies by Bornstein et al. [64][75] into the phenomena that became categorised as type I hot corrosion determined the requirement for a deposit rather than having corrosive species present only in the gas phase. This was achieved through comparing high temperature exposures using a  $\text{Na}_2\text{SO}_4$  deposit and exposures with the same quantity of S added to the gas phase [64]. In contrast, a review paper by Pettit describes a test comparing Ni-25Cr-6Al specimens exposed with a  $\text{Na}_2\text{SO}_4$  deposit and specimens presulphidised in a

H<sub>2</sub>S/H<sub>2</sub> gas mixture [66]. Similar weight change measurements and internal sulphide formation were observed for both kinds of exposure. Some authors [41] have defined hot corrosion as specifically involving a deposit and separate from gas phase sulphidation despite some similarities in the morphology.

Rapp et al proposed that for the hot corrosion mechanisms to proceed there needs to be a negative solubility gradient across a molten salt deposit [76]. A schematic of this is shown in Figure 2.19, here the dominant solute (either acidic or basic) has greater activity adjacent to the metal/salt interface. Species from the metal or its protective interface dissolve through either acidic or basic dissolution before precipitating out at the salt/gas phase interface [72].



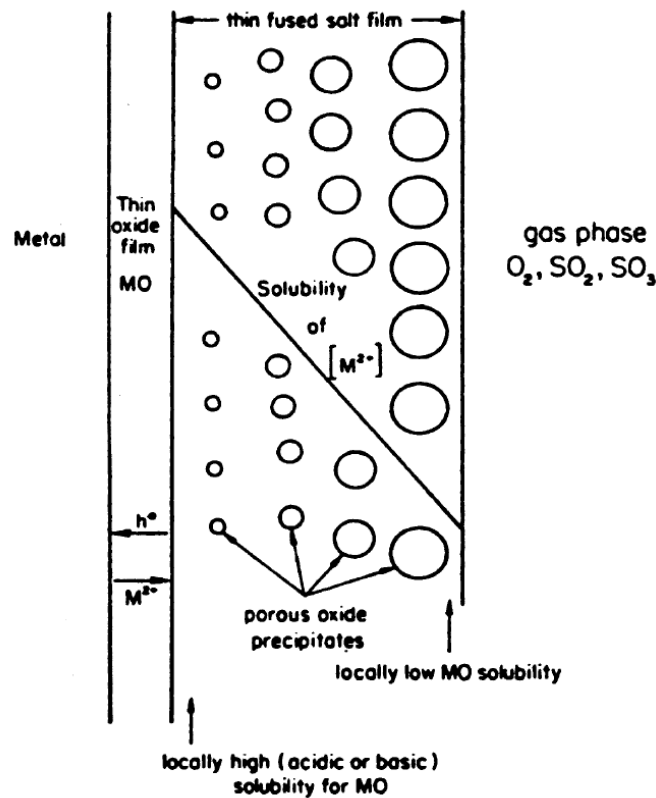
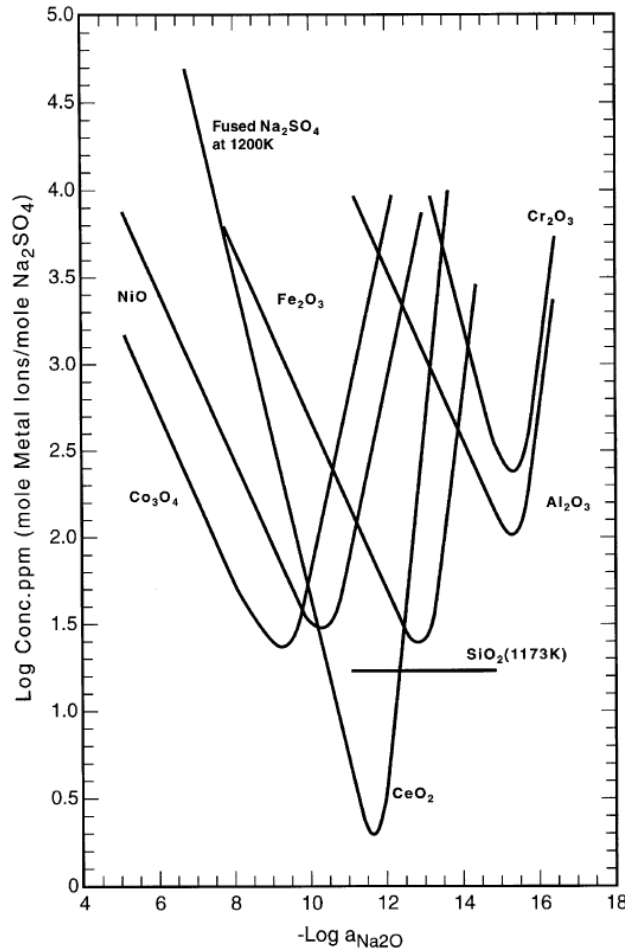


Figure 2.19: Schematic of the negative solubility gradient in a fused salt film on a metal surface in an environment conducive to hot corrosion [76].

The solubility of various metal oxides important to alloys for high temperature applications were determined as a function of melt basicity and O activity of molten  $Na_2SO_4$  at 1200 K in a series of experiments by Rapp et al. [77]–[82]. Data from this body of research is presented in Figure 2.20. Each solubility curve could be described as having three segments: the left side leg of the curve favours basic dissolution at the oxide/salt interface (Equation 2-9). The right side leg of the curve favours acidic dissolution (Equation 2-5). The trough of the curve represents a minimum solubility value; at this point a negative solubility gradient can only be established if local conditions straddle the minimum.

It can be seen in Figure 2.20 that it is possible for one metal oxide to dissolve through basic dissolution while another metal oxide dissolves through acidic dissolution. For superalloys the solubility curves of base element oxides such as

$\text{Co}_3\text{O}_4$  and  $\text{NiO}$  compared to protective oxides such as  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  are particularly relevant where the former metal oxides could be in a regime of acidic fluxing while the latter oxides undergo basic dissolution.



**Figure 2.20: Measured solubility curves for various metal oxides in fused  $\text{Na}_2\text{SO}_4$  at  $927^\circ\text{C}$  [72].**

Rapp and Otuska [83] measured the  $\text{Na}_2\text{O}$  activity and  $\text{O}_2$  partial pressure at the interface between the metal and deposit of pre-oxidised  $\text{NiO}$  at  $900^\circ\text{C}$  in an  $\text{O}_2/\text{SO}_2$  gas mixture with a thin film of  $\text{Na}_2\text{SO}_4$  applied to the surface. The results, shown in Figure 2.21, are presented superimposed on a  $\text{Ni-O-S}$  thermodynamic stability diagram. The melt starts off favouring acidic dissolution before entering a regime where  $\text{NiS}_2$  becomes favourable. As  $\text{S}$  from the melt is used to form  $\text{NiS}_2$ , the activity of  $\text{Na}_2\text{O}$  and partial pressure of  $\text{O}_2$  increases until a regime of

basic dissolution is achieved and NiO is once again thermodynamically favoured. After 10 hours, the results show that the activity of Na<sub>2</sub>O has decreased back to a point where acidic dissolution is once again favoured. This body of research shows that the basicity of the melt may change over time allowing different mechanisms to come into play. It therefore maybe somewhat erroneous to define type I hot corrosion as basic fluxing and type II hot corrosion as (gas phase induced) acidic fluxing even if these mechanisms are typically more dominant in their respective temperature regimes. Further research, using the methodology described by Rapp and Otuska, showing how the salt chemistry changes over time could be used to explore variables that may prove insightful and verify proposed mechanisms. Such variables could include the composition of the alloy (especially refractory metals that may induce acidic fluxing, Figure 2.22), temperature, gas phase composition and deposit compositions.

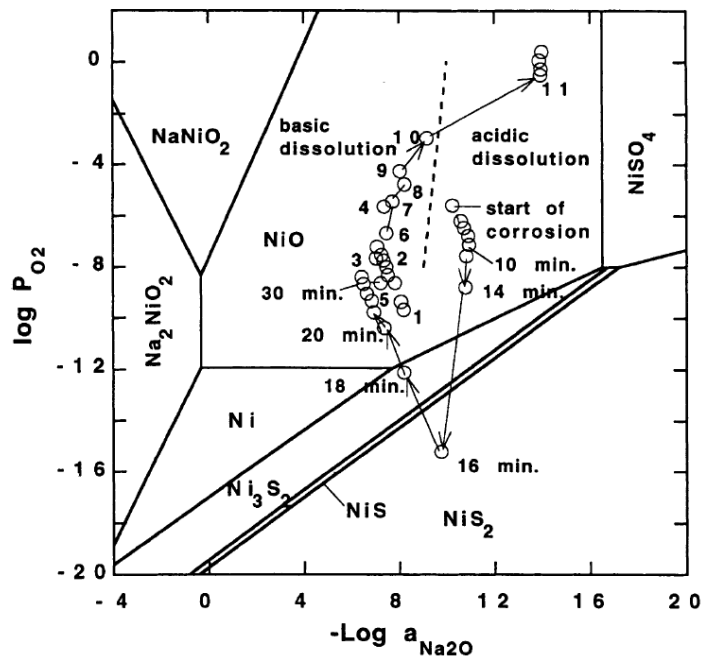
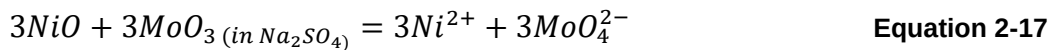
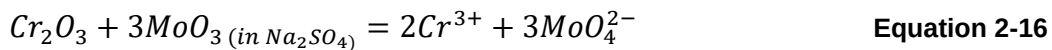
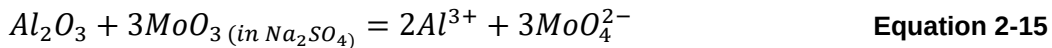


Figure 2.21: Basicity and oxygen activity plot measured on a peroxidised Ni coupon with a molten Na<sub>2</sub>SO<sub>4</sub> deposit in an O<sub>2</sub>, 0.1% SO<sub>2</sub> atmosphere at 900 °C. The time stamps are in hours or minutes where indicated, the dashed line represents the minimum in NiO solubility [83].

### 2.6.3 Alloy induced acidic fluxing

The mechanism of alloy induced acidic fluxing describes a method by which certain elements within the alloy may locally increase the acidity of the molten salt deposit [14]. As discussed in Section 2.2, elements such as Mo, vanadium and W are common additions to superalloys adding strength to the alloy matrix [31]. At the surface of the alloy, these refractory metals can form an oxide with a relatively high activity. This oxide reacts with the basic constituent of the molten salt and may form an acid species (for example  $\text{Na}_2\text{MoO}_4$  shown in Equation 2-8) or subsequently precipitate out away from the metal/deposit interface. This leaves a local area with a higher concentration of the acidic constituent of the melt [84]. This process is shown schematically in Figure 2.22.

Investigations identifying alloy induced hot corrosion were carried out between 900 and 975°C in atmospheres containing only air [85][86]. Alloy induced acidic fluxing has also been observed to occur at 700 °C in the presence of a  $\text{Na}_2\text{SO}_4$  deposit and an air atmosphere [87]. It is not clear from the existing literature to what extent the increased corrosion rate is caused by the acidic fluxing mechanism or if particles of refractory metal oxides at the surface disrupt the formation of a fully protective scale. Using Mo as an example, the reactions associated with alloy induced acidic fluxing are shown below [14].



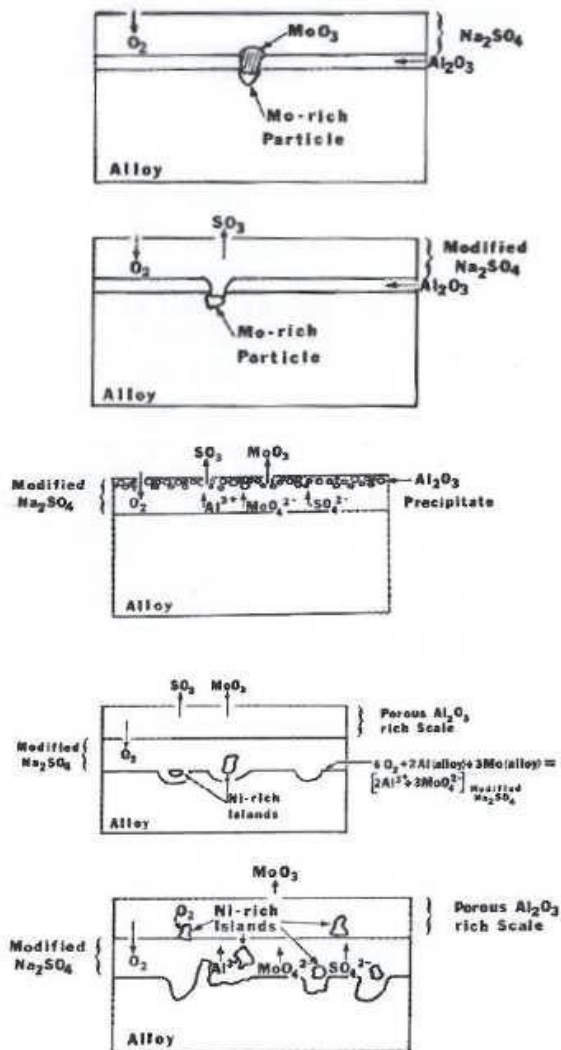


Figure 2.22: Schematic showing the alloy induced acidic fluxing mechanism for a Ni-Al-Mo system [84].

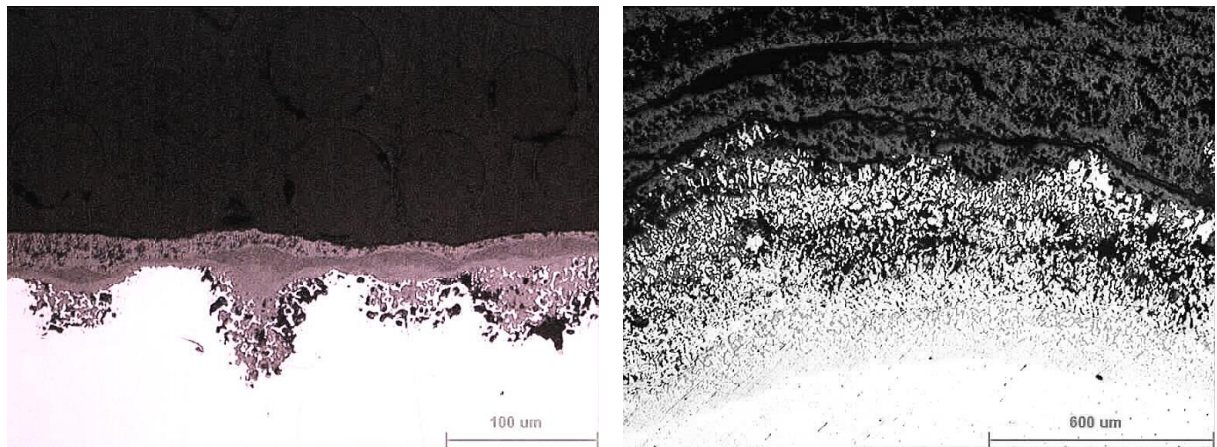
#### 2.6.4 Corrosion morphology

Visual inspection of a corroded alloy can only provide limited information as to the nature of the corrosion attack [32]. Observations can vary greatly depending on composition of the alloy, the formation of adhered corrosion product, the spalling of oxide scale and corrosion product, and changes to the colouration of the alloy surface are all common. Microscopic analysis of specimen cross-sections can reveal the differing features of the corrosion mechanisms.

Micrographs showing typical features of type I and type II hot corrosion are shown in Figure 2.23 [88].

Type I corrosion hot corrosion most commonly features a honeycomb structure at the alloy surface with sulphide precipitates formed internally below the alloy surface. This is accompanied by the depletion of alloying elements through the internal sulphidation zone. The distribution of type I hot corrosion damage is typically uniform over the affected areas of the specimen [14], [34], [38].

In contrast, type II hot corrosion is associated with the formation of pit features extending into the alloy. These features are typically unevenly distributed around the affected surface. As a consequence of the solubility gradient described by Rapp et al. [76] alloy elements dissolved in the deposit melt precipitate out at the interface between the deposit melt and the gas phase in order of their affinity for  $O_2$ . In concurrence with the Ellingham diagram (Figure 2.8), oxides of Cr and Al form a corrosion product inner layer whereas oxides of Ni and Co form a corrosion product outer layer. Type II hot corrosion does not typically feature the depletion of elements below the alloy surface [14], [34], [38].



**Figure 2.23: Typical morphological feature of type II (left) and type I (right) hot corrosion [88].**

### 2.6.5 Investigations into the type II hot corrosion of superalloys

This section reviews other studies that have investigated the type II hot corrosion of superalloys similar to those used in this thesis. Of these alloys, were selected as for having compositions similar to the Ni-based alloys used in the experimental section of this thesis. CMSX-4 is included here to provide a comparison between  $\text{Al}_2\text{O}_3$  forming alloys and the  $\text{Cr}_2\text{O}_3$  used in this thesis.

The type II hot corrosion of IN738 (a precipitation hardened Ni-based  $\text{Cr}_2\text{O}_3$  forming superalloy commonly used in gas turbine blades and discs) has been studied by a number of authors [87], [89]–[93]. Features associated with both type I (internal sulphidation) and type II (pits and corrosion products layered based on the elements affinity for  $\text{O}_2$ ) hot corrosion were commonly observed at exposure temperatures of 700 and 900 °C. Quantative data is most often presented in terms of weight change, an example of this is shown in Figure 2.24. Some studies present quantative data in terms of dimensional metal loss. Data from these studies show the progression of hot corrosion from incubation to propagation. The kinetics of this progression are shown to vary depending on factors such as temperature, deposit flux, and atmospheric  $\text{SO}_2$  concentration.

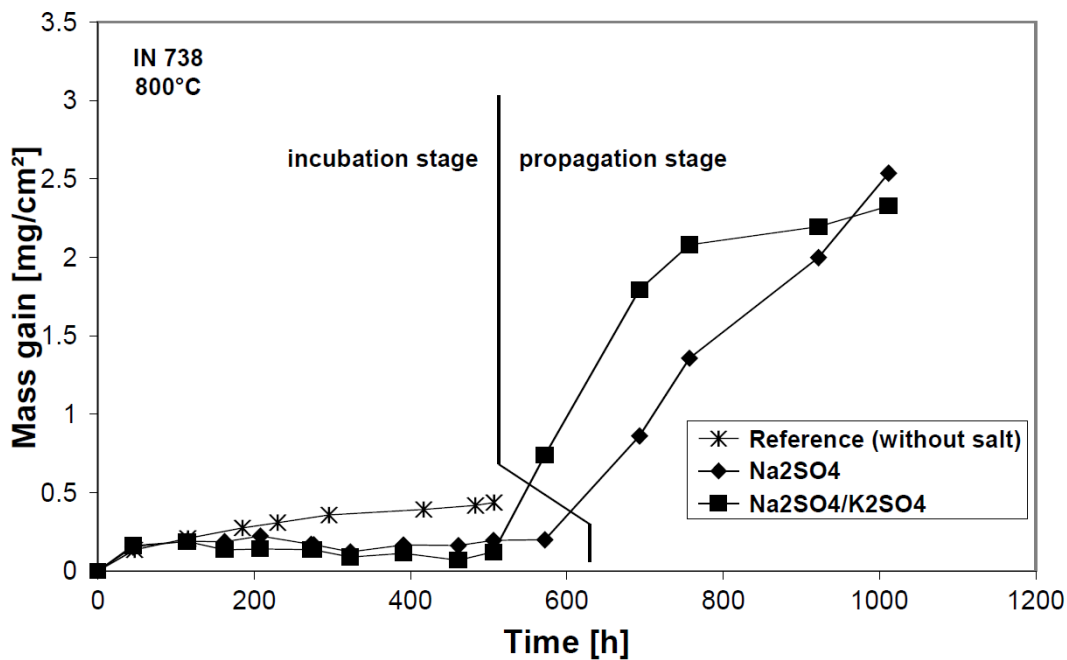


Figure 2.24: Specific mass gain of IN738 in air + 300ppm  $\text{SO}_2$  at 800°C. The deposit was applied at the start of the test with a quantity of  $1 \text{ mg}/\text{cm}^2$ .

RR1000 is a Ni-based  $\text{Cr}_2\text{O}_3$  forming disc alloy developed for use in aeronautical gas turbines. The type II hot corrosion performance of RR1000 has been studied by several authors [32], [87], [94]. The damage morphology observed consists of broad pit features that resemble a broad front attack, internal sulphidation is not shown in any of the presented micrographs.

CMSX is a an  $\text{Al}_2\text{O}_3$  forming Ni-based single crystal superalloy commonly used in turbine blades and combustors. As an alumina forming alloy, it's hot corrosion resistance has been observed to be better under temperatures associated with type I hot corrosion (900 °C) than temperatures associated with type II hot corrosion (700 °C). Studies carried out at 700 °C report relatively short (below 100 hours), incubation periods [93], [95]–[99]. Micrographs of corrosion morphology show broad pit features with no internal sulphides in the presented micrographs.

#### **2.6.6 Hot corrosion recent developments and research gaps**

In a series of studies, Chang et al. [100], [101], [102] have investigated the effect on type I hot corrosion of differing quantities of Ta additions to superalloy compositions. Increasing the Ta quantity was observed to allow the formation of a relatively continuous (Cr, Ti) $\text{TaO}_4$  sub layer that the authors believe acts as a second protective scale. The data produced suggests that, for the alloy compositions tested, the hot corrosion resistance depends on the ratio between Cr and Ta. With a Cr/Ta wt.% ratio less than about 0.5, a doping effect promoted the Cr oxidation rate consequently improving hot corrosion resistance. When the ratio is approximately 0.5 then the formation of Ta spinels may reduce ion diffusion and the corrosion rate is again reduced. When the ratio is above 0.5, the formations of Ta oxides compete with the formation of a  $\text{Cr}_2\text{O}_3$  scale to prevent any protective scale from forming.

This body of work is so far somewhat limited in scope, the subject alloys were chromia formers with Cr contents of up to 12 wt.%. The effects of Ta additions may be reduced in alloy systems with Cr content high enough to form a better protective scale. Furthermore these studies have so far only been carried out in lab air; so a  $\text{SO}_x$  containing atmosphere may alter the corrosion chemistry

especially given the thermodynamic favourability of  $\text{TaS}_2$ . The experimental procedure used by this research involved the removal of salt using boiling water between each 20 hour cycle. Such manipulation may have unintended consequences such as removing soluble species formed from reactions with the deposit or removing corrosion product. Finally, the corrosion rate kinetics were determined using weight change data rather than dimensional metal loss making predictions of the incubation period length unreliable.

Many environments that are conducive to hot corrosion attack, also involve mechanical stress and the fatiguing of components [21]. As discussed in section 2.1, this is particularly relevant to gas turbines. The interaction of hot corrosion attack and these mechanical effects are being investigated in on-going research (eg. [102], [103]). The pit features associated with type II hot corrosion have been observed to act as nucleation points for the formation of cracks induced by stress and fatigue. Currently these studies have only involved CMSX-4 and environments conducive to type II hot corrosion.

Despite the prevalence of water vapour in combustion systems and a number of studies investigating oxidation in the presence of water vapour, there is little research into its effects on hot corrosion. In her thesis [104], B. Bordenet, included water vapour in calculations of deposit dew points but did not include it in their experimental methodology. Since the majority of the literature suggests that water vapour can volatilise chromia, and the length of incubation is related to the quality of the chromia scale, one might expect water vapour to shorten the incubation stage of hot corrosion.

Studies by Gleeson and coworkers [105] have built upon the synergistic fluxing model proposed by Rapp [72]. These authors suggest that Al and Cr are the elements first removed from the alloy during type II hot corrosion. This is attributed to the position on the solubility curve of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  relative to  $\text{NiO}$  and  $\text{CoO}$  in Figure 2.20. Based on the hot corrosion of a Co-based alloy at  $700^\circ\text{C}$ , initial basic fluxing of  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  was observed to shift the salt composition in the acidic direction. As the salt melt becomes more acidic, the acidic dissolution of Co oxides returns the salt to a more basic state.

### 3. Methodology

This chapter describes the experimental methodology used for the hot corrosion test programme. The deposit re-coat technique employed in this research has been used in a number of other studies eg. [32], [88], [98], [97], [99]. The corrosion test procedure can be divided into four sections:

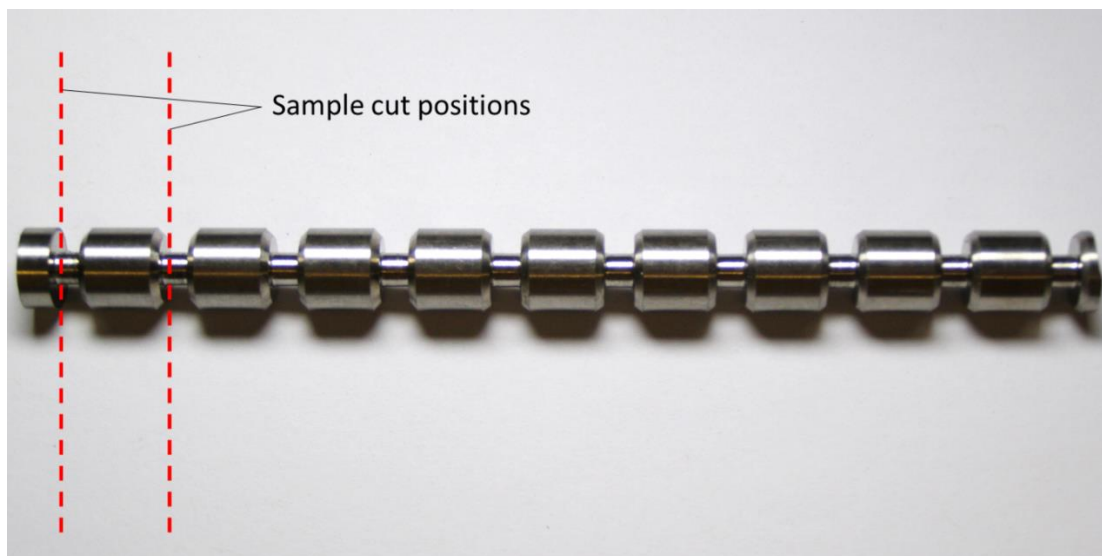
- Pre-test sample preparation and metrology
- Running and cycling the corrosion test using the deposit re-coat technique
- Post-test sample preparation
- Post-test metrology and analysis

These are described in different sections in this chapter, together with sections describing the materials selection and their characteristic, the hot corrosion test matrix and modifications to the methodology.

#### 3.1 Pre-test preparation

The purpose of this activity was to produce samples suitable for corrosion testing and to provide measurements of the sample dimensions before their exposure. Samples were provided in the form of bars made up of a series of “cotton reel” samples 10 mm in length. The bars were ground down using a grinding disc to produce an approximate diameter of 10 mm. The average surface roughness was measured using a Dektak profilometer to be approximately 0.4  $\mu\text{m}$ , a similar roughness to that achieved by grinding using P1200 grit (600 grit UK standard).

The samples were parted from these bars using a precision saw with a diamond impregnated cutting blade; an example of one sample material as provided is shown in Figure 3.1. The cuts were positioned to allow for a protrusion of material at the top of the sample (to aid handling with tweezers) and a smaller protrusion at the bottom (for the sample to sit on), these help to avoid unnecessary contact with the cylindrical surfaces of the sample (which is the one being tested).

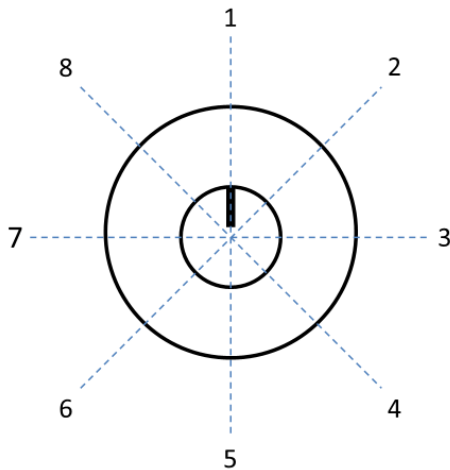


**Figure 3.1: Bar of GTD 111 cotton reel samples as supplied. Red dashed lines denote the cut positions for one sample.**

Once parted from the bar, the upper most protrusion was marked with a notch using a dremel. This mark acts as a reference point for orientation while measuring the sample.

Before measuring, each sample underwent a two-stage cleaning process. The first stage involved 10 minutes of ultrasonic cleaning in a beaker of acetone, the purpose of which was to remove oil-based contaminants. In the second stage, the samples were ultrasonically cleaned in propanol for 10 minutes to remove traces of acetone and any other contaminants.

Pre-exposure measurement of the sample dimensions was carried out using a Mitutoyo digital micrometer with a resolution of  $\pm 1 \mu\text{m}$ . Using the notch as an origin point, the diameter was measured at eight approximately equally spaced points around the circumference of each sample (shown in Figure 3.2). From these data, the surface area used in deposit flux calculations could be derived. These measurements were also used in determining the dimensional metal loss occurring during exposure.



**Figure 3.2: Plan view schematic showing sample dimensional measurement positions.**

In preparation for the sample exposures, the furnace was ramped up to the target test temperature and a temperature profile was measured using a calibrated thermocouple. From these measurements, the position of the furnace hot zone (defined as  $\pm 5\text{ }^{\circ}\text{C}$ ) was determined and the discrepancy between the furnace controller temperature and the actual temperature was factored.

The ceramic test furniture and crucibles were cleaned with water to remove any residual salt deposits from previous tests before washing with propanol and being given a 24-hour heat treatment at  $1000\text{ }^{\circ}\text{C}$  to remove other possible contaminants.

### **3.2 Corrosion tests**

The deposit re-coat corrosion test method involves the application of a deposit at a selected flux both initially and after exposure cycles of a specified length. Both initially and between each cycle, the test specimens went through a set procedure of weighing and salt spraying:

- Samples were removed from the corrosion vessel after the hot zone had cooled to below  $200\text{ }^{\circ}\text{C}$ .
- The samples were allowed to cool to room temperature and weighed.

- A hot plate was used to heat the samples to  $\geq 100^{\circ}\text{C}$ .
- Whilst hot each sample was sprayed evenly around its circumference with the correct flux of test deposit dissolved in an aqueous solution.
- The samples were cooled to room temperature before weighing and being re-inserted to the corrosion vessel.

Measurements of sample weight (removed from the crucible) were made using a calibrated balance with a resolution of 10  $\mu\text{g}$ . Changes in sample weights calculated by comparing the weights after cooling from a cycle to the weights measured immediately prior to the start of that cycle. This procedure prevents spallation caused by the salt spray process from affecting the results. The sum total of the cycle weight changes are referred to as cumulative weight change and are presented in Appendix A.

The test deposit was prepared as an aqueous solution of a concentration below the saturation limit of the medium. The spray gun used to apply the deposit was pneumatically operated with the samples rotated between sprays to ensure a more even distribution of deposit on the sample surface. The samples were heated during the deposit spray procedure to allow the instant evaporation of the aqueous medium upon contact with the sample.

The test exposures were carried out using a ceramic-lined reaction vessel within a vertically positioned tube furnace; a schematic of this is shown in Figure 3.3. The samples were held within the hot zone of the furnace using ceramic furniture suspended from the stainless-steel lid. Test gases and water were admitted through the central column of the furniture entering the vessel near the bottom and exhausting through a port in the lid. Exhaust gases then were passed through both a catch pot and a bubbler containing a NaOH scrubber solution to remove acidic gases such as  $\text{SO}_x$ . The flow of the gas into the furnace was controlled using a mass flow controller to provide the correct ratio of gas and water (that subsequently vaporised).

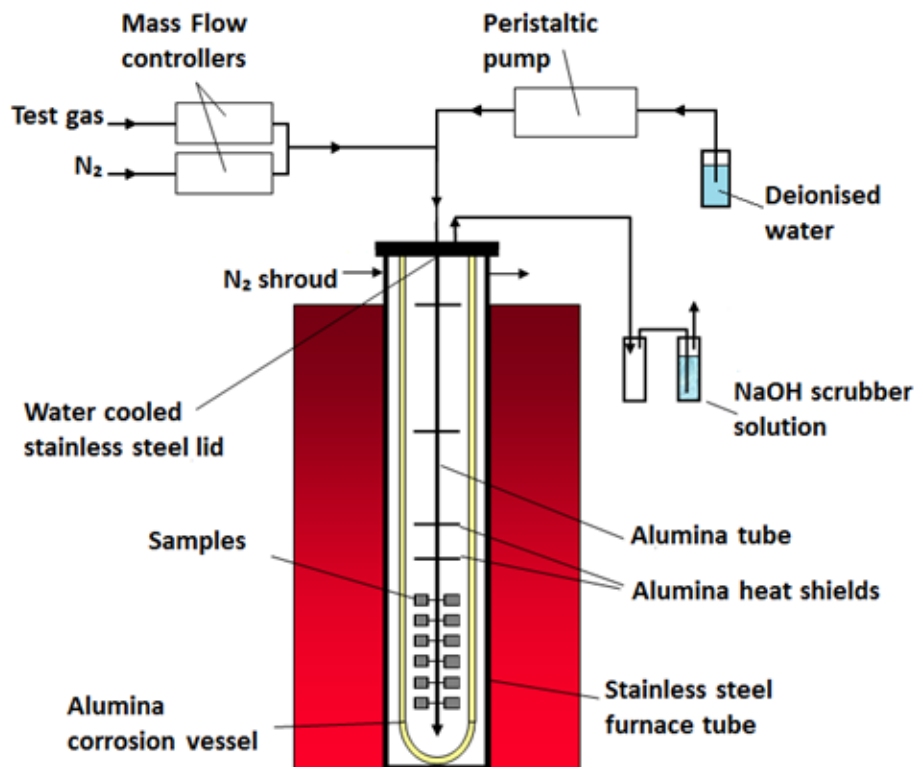


Figure 3.3: Schematic showing the test furnace and apparatus set up [107].

Water was supplied to the corrosion vessel using a peristaltic pump. With an rpm of 10 and a tube inner diameter of 0.27 mm, the flow was measured using a measuring cylinder to be 0.04 ml/min. The flow of test gas required to form the correct concentration for water vapour was calculated in the following manner (for 10% water vapour). The calculation assumes the expansion of water vapour and test gas with temperature is the same.

At 10 rpm, the measured flow of water was 0.04 g/min<sup>-1</sup>. The number of moles per minute can be calculated in the following manner:

$$\frac{m}{mr} = \frac{0.04}{18} = 0.0022 \text{ mol/min}^{-1} \quad \text{Equation 3-1}$$

Where m is mass and mr is the relative molar mass.

1 mole of water is known to make 22.4 litres of steam [106]. Therefore the volume flow of steam generated at 10 RPM can be calculated:

Volume flow =  $22.4 \text{ l} \times 0.0022 \text{ mol/min}^{-1} = 0.04928 \text{ L/min} = 49.28 \text{ cc/min}$

For 10 % water vapour, test gas flow =  $49.28 \times 9 = 443.52 \text{ cc/min}$

To allow a more suitable gas flow, the pump rpm can be reduced. At 2 rpm the test gas flow = 88.7 cc/min.

### 3.3 Post-test sample preparation procedure

For dimensional calculations of metal loss and microscopical analysis of the metal below any corrosion product, sample cross-sections are necessary. Initially the samples were mounted in resin using a custom-made jig (shown in Figure 3.4). This features two locating pins to keep the sample vertically oriented allowing for the generation of a perpendicular cross-section. A spring-loaded scalpel blade held the sample against the guiding pins and acted as a reference point (positioned in line with the reference notch on the top of the sample). The samples were encased in a specially prepared mixture of epoxy resin and ballotini (silica glass beads with a diameter of 0.04-0.07 mm). The addition of ballotini reduced the degree of shrinkage that could affect the sample surfaces as the resin set and helped retain the deposit and corrosion product on the sample surfaces. After the application of the resin mixture, the sample jigs were exposed to a low vacuum to remove any trapped pockets of air and ensure a good interface between the sample surfaces and resin.

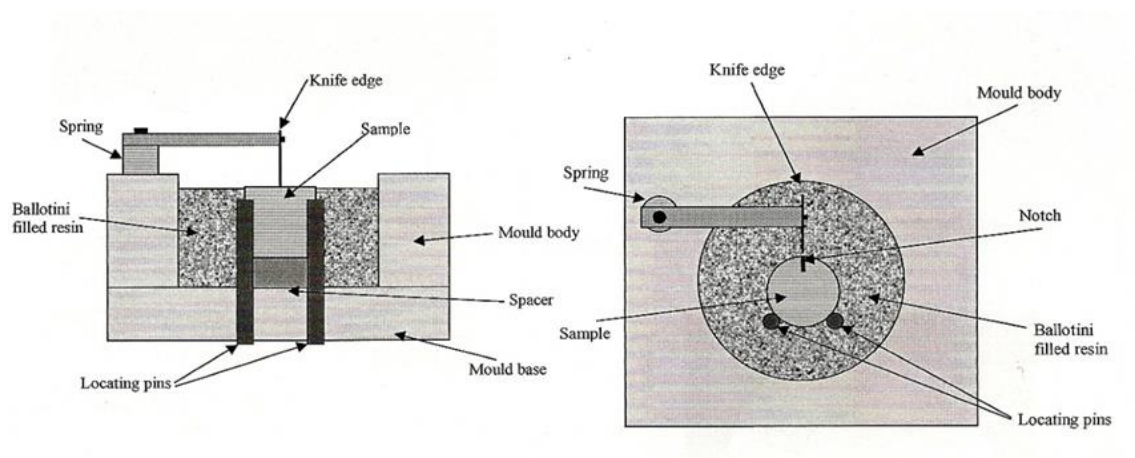


Figure 3.4: Post-test sample mounting jig schematic [88].

The samples were given a minimum of 24 hours setting time before being removed from the jig and a minimum total of 48 hours before cutting. The cut was made using a precision saw fitted with a diamond cutting blade. The samples were held in an aligned vice using the ends of the locating pins that protrude from the resin; this allowed for an accurate right angle between the cut and orientation of the sample. Lapping oil was used as the cutting lubricant in place of water to try to stop dissolution of deposits and corrosion products..

The cross-sectioned surfaces were prepared for analysis through a process of grinding using a series of silicon carbide papers followed by polishing to a 1  $\mu\text{m}$  finish using diamond abrasive polishing compound. The lubricants for grinding and the polishing medium were all oil based. The samples were subsequently stored in desiccators. Non-aqueous fluids were used throughout this procedure to ensure that soluble species on the sample surface were not lost.

### **3.4: Dimensional metal loss calculations**

Corrosion tests generate both mass change data and dimensional metal loss data. Mass change data has often been used as a quantitative tool to measure corrosion. In certain circumstances, where there is little or no spallation this data can be useful. In the types of accelerated hot corrosion tests used in this project, the erratic nature of spallation limits how useful mass change data can be. For this reason, the results are presented here in terms of dimensional metal loss with the mass change data available in Appendix A.

Dimensional metal loss measures the amount of metal lost from the surface of the sample plus damage incurred beneath the surface in terms of distance. These measurements were achieved using an optical microscope fitted with a calibrated x/y motorised stage and a 20X magnification lens. Custom developed software produced clusters of micrographs at 30 equally spaced points around the

circumference. The coordinates of the sample surface plus any internal damage were identified manually along an automatically selected radius from the centre of the sample.

The post-test measured sample coordinates were inputted to a spreadsheet and compared with the pre-test measurements of the original dimensions. Metal loss values are calculated by subtracting post-test sample radii from the pre-exposure radii. Some authors [19] distinguish between metal loss and internal damage (deleterious species within the alloy matrix adjacent to the surface) by defining good metal loss as the metal loss plus internal damage while defining metal loss as not including internal damage.

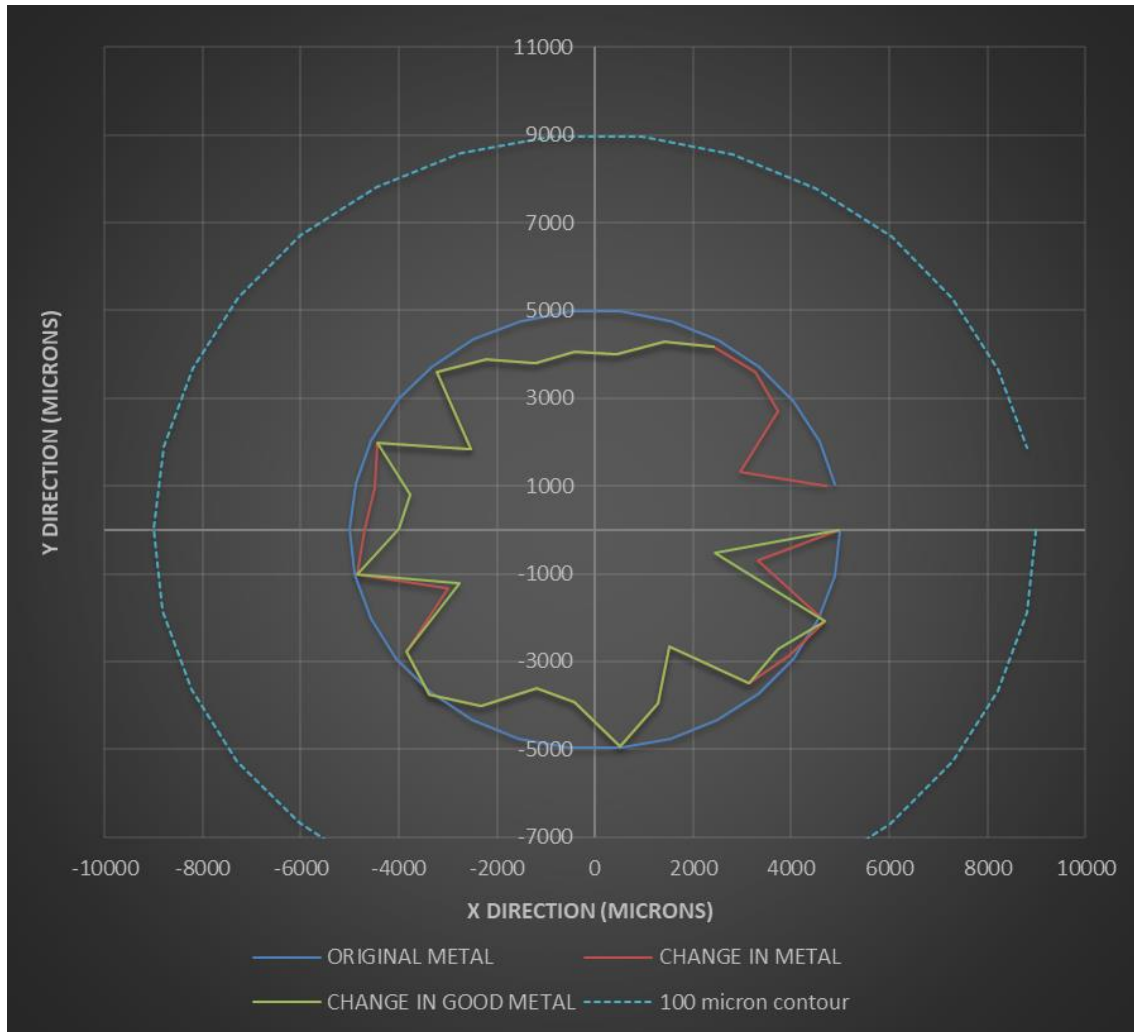
Data generated through measurements can be used to produce two concentric shapes denoting the original sample circumference and the post-test remaining good metal with the distance between these shapes being the dimensional metal loss. An example of the image produced by this technique is shown in Figure 3.5.

Dimensional metal loss data was calculated along the radii from the sample centre to each of the 30 measured post-test coordinates at the sample surface. Because this is a finite number of measurements, the data is presented in terms of the cumulative probability of metal loss exceedance. To calculate this, the calculated metal loss values are ranked in order of their magnitude and the following equation is used to determine the cumulative probability.

$$\text{cumulative probability (\%)} = \frac{n}{N+1} \times 100 \quad \text{Equation 3-2}$$

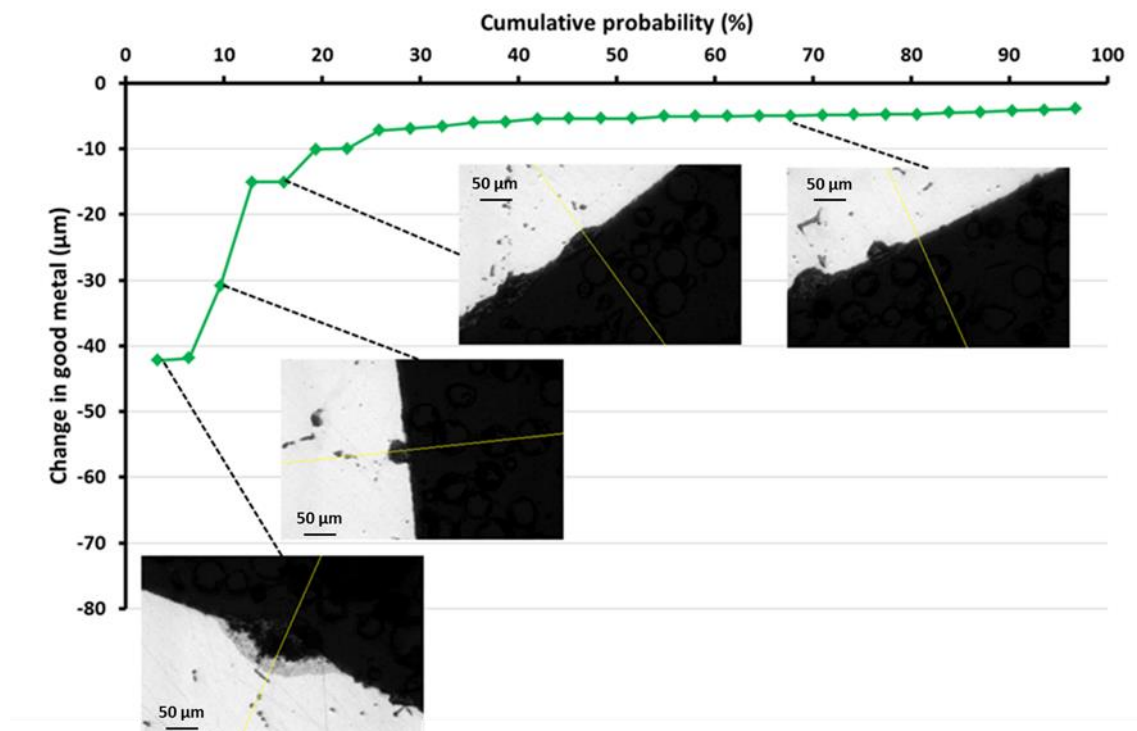
( $n$  is the rank number and  $N$  is the total number of points).

Uncorroded reference samples for each material underwent the full pre- and post-exposure measurement processes. Metal loss values calculated for the reference samples could be attributed to systematic and random errors in the measurement techniques and was therefore used as a correction factor to correct metal loss values for exposed samples.



**Figure 3.5: Example graphical plot of pre-test measurements (original metal) and post-test coordinates of remaining metal (change in metal) plus internal damage (change in good metal). The differences between the plots has been magnified by 10, a 100 micron contour from the original metal is included for reference.**

Figure 3.6 shows a montage of dimensional measurements and where the measurements place on a cumulative probability of metal loss exceedance plot. The yellow line passing through the centre of each micrograph is the axis along which the remaining metal and good metal coordinates was determined.



**Figure 3.6: Montage of micrographs showing the measurement axis and their corresponding positions on a cumulative probability of metal loss exceedance plot.**

Figure 3.7 shows an example graph of cumulative probability of metal loss exceedance showing example datasets typical of hot corrosion features observed. Data points on the graph denote the % probability of metal loss being greater than the value indicated. For this reason, the data point with the lowest level of probability of metal loss exceedance does not represent the greatest degree of metal loss on the sample, but one with 4% chance of being exceeded. The gradient of a data trend is proportional to the standard deviation of the data, this indicates how evenly distributed around the sample circumference the metal loss is.

Dataset A is typical of a sample that has remained entirely in incubation during exposure with no significant metal loss that would be associated with propagation. This degree of metal loss could be associated with scatter inherent in the methodology and could be described as negligible.

Data set B shows negligible metal loss over the majority of the sample but has a significant degree of metal loss at lower levels of probability. This trend indicates the formation of pit features with parts of the sample having entered into propagation while the majority remains in incubation. This is typical of type II hot corrosion damage described in the literature (Section 2.6).

Dataset C has significant metal loss at all levels of probability and relatively steep gradient. This shows that all the measured points on the sample have progressed into the propagation stage of the hot corrosion mechanism and the distribution of damage is uneven indicative of pit features. As for data set B, this indicates type II hot corrosion damage but in this case at a later stage of progression.

Dataset D has a significant degree of metal loss at all levels of probability but a relatively shallow gradient. All the measured points are in propagation but in this case the damage is distributed evenly around the circumference of the sample. This is typical of the internal damage that is associated with type I hot corrosion in the literature. This distribution of damage has also been observed in type II hot corrosion conditions with an alloy especially vulnerable to hot corrosion damage; in this case the rapid metal loss resulted in particularly broad pits that here linked together to allow a relatively even damage distribution.

When considering the performance of a material, several different measurements could be used to track progress. These include the mean or total area of metal loss, the median value or the maximum value. Selecting the appropriate measurement is dependent on what information is desired. The pits that form during type II corrosion have been shown to act as nucleation points for cracks in systems under stress or suffering fatigue. Thus from an engineering point of view, the depth of the deepest pit may be useful. However, when considering the advancement of the hot corrosion mechanism from incubation to propagation, the median value can indicate which stage of the mechanism the majority of the sample is in.

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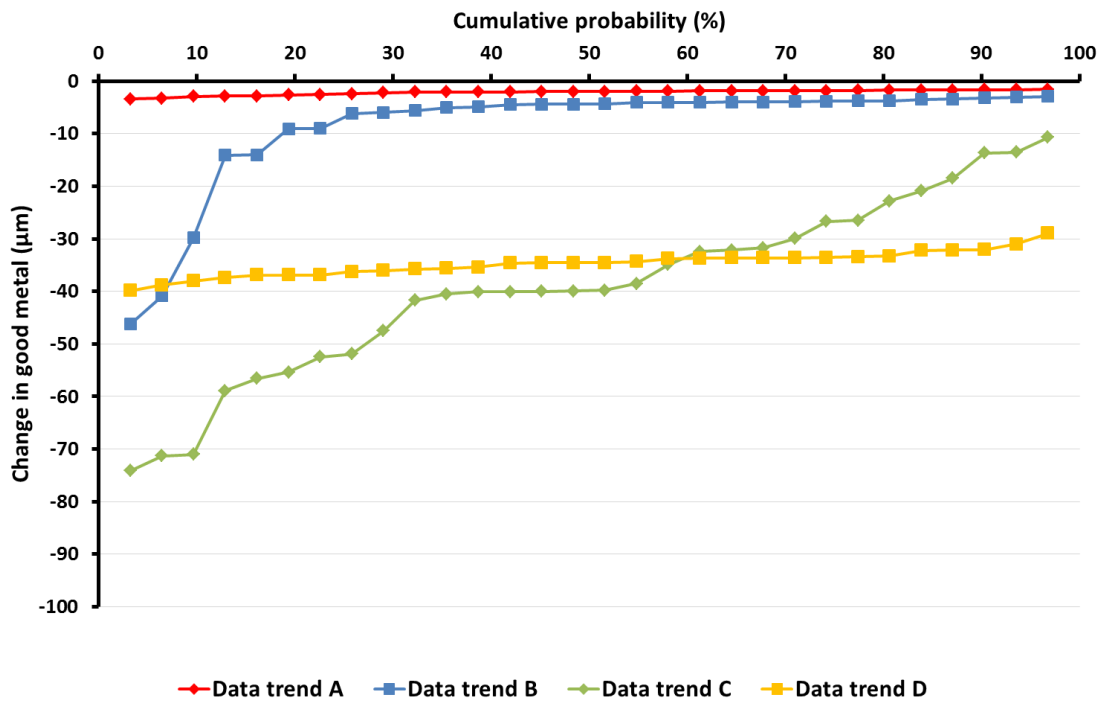


Figure 3.7: Cumulative probability of metal loss exceedance plots for four distinct datasets typical of different stages and types of hot corrosion.

### 3.5 Microscopical analysis

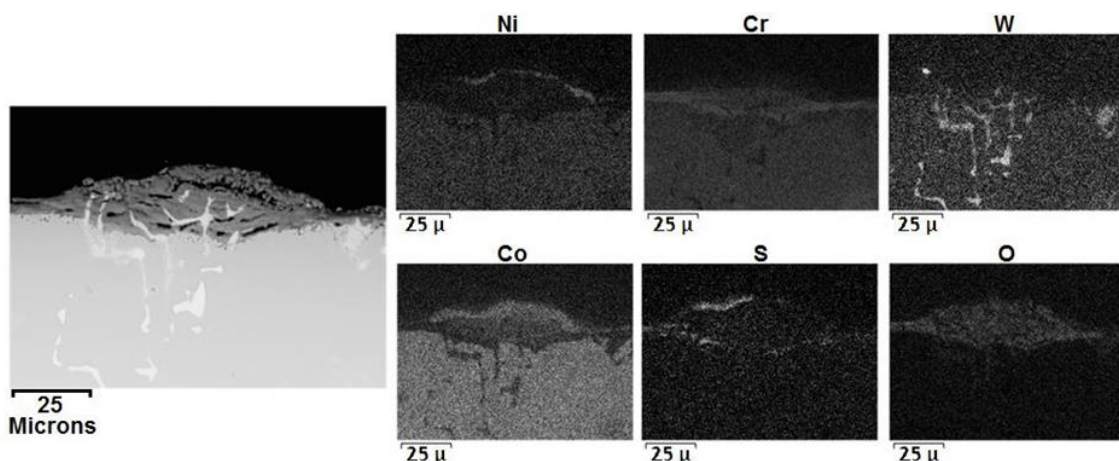
Post-test microscopy was carried out using a Philips XL30 environmental scanning electron microscope (ESEM) fitted with an energy dispersive X-ray (EDX) system from Oxford Instruments.

SEMs operate by scanning specimens with a focused beam of electrons. This excites the constituent atoms of the specimens to emit secondary electrons that can be detected to provide topographical information. The ESEM can also detect high-energy electrons originating from the beam that are reflected from the specimen after elastic scattering interactions with the constituent atoms; these are termed backscattered electrons. Heavier elements have a higher atomic number and reflect electrons more strongly than lighter elements and therefore appear brighter in the generated images [108]. Sample cross-sections produced in this research are polished flat; therefore topographical information is not as useful as the distribution of phases based on their atomic number. For this reason

sample cross-section micrographs have been generated using backscattered electron images in this thesis.

EDX analysis allows the identification of elements at points or in areas on sample surfaces. The technique involves the electron beam exciting electrons from within the inner shells of atoms. The electrons are ejected from the atoms creating vacancies that are immediately filled with electrons from outer shells. The differences in energy levels from the outer (higher energy) and inner shell (lower energy) are emitted in the form of x-rays that can be detected. Since an emitted x-ray has an energy that is generally specific to a particular element, that element can be identified [108]. There are some overlaps in emitted energy levels between certain elements that can cause a degree of ambiguity. An example of this relevant to this research is Mo (a common addition to superalloys) and S (present in the gas phase and salt deposits). It should be noted that although EDX analysis can identify the elements present in an area of a sample, it does not identify the chemical formula of any phases that may be present.

Figure 3.8 shows an example backscattered electron image (left side larger image) and EDX element maps (right side smaller images). The element maps can be used to identify the distribution of elements within the feature shown in the backscattered electron image. The brightest areas of the backscattered electron image are shown to be rich in W (atomic number 74) on the EDX map.



**Figure 3.8: Backscattered electron image and associated EDX element map of MarM 509 after exposure in an environment conducive to hot corrosion.**

### 3.6 Test matrix

Table 3.1 gives the parameters for the corrosion tests relating to this body of research. Tests A, B and C are accelerated simulations of novel atmospheric conditions based on possible operating conditions encountered in a new generation of industrial gas turbine that integrates gasification and carbon capture and storage technologies. Tests A to C make up part of the H<sub>2</sub>-IGCC project. Tests D to F investigate the effects of water vapour on hot corrosion in an atmosphere known to be inductive to type II hot corrosion. Test G used a deposit modified with Mo to investigate the mechanics of alloy induced hot corrosion.

**Table 3.1: Corrosion test matrix. \*The deposit of test G included an equal deposition of molybdenum between cycles.**

| Test | Materials                                                                     | Atmosphere                                                                                                                      | 80% Na <sub>2</sub> SO <sub>4</sub> ,<br>20% K <sub>2</sub> SO <sub>4</sub><br>(molar %) flux | Temperature<br>(°C) | Exposure<br>time<br>(hours) |
|------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|---------------------|-----------------------------|
| A    | GTD 111<br>Rene 80<br>PWA 1483<br>MarM 509<br>GTD 111+RT 22<br>Rene 80+SC2464 | 10 vol% CO <sub>2</sub><br>8 vol% O <sub>2</sub><br>86 ppm SO <sub>2</sub><br>5 vol% H <sub>2</sub> O<br>Balance N <sub>2</sub> | 0, 1.5 and 5<br>µg/cm <sup>2</sup> /h                                                         | 700                 | 100<br>200<br>500           |
| B    | GTD 111<br>Rene 80<br>PWA 1483<br>MarM 509                                    | 6 vol% CO <sub>2</sub><br>8 vol% O <sub>2</sub><br>3.6 ppm SO <sub>2</sub><br>10 vol% H <sub>2</sub> O                          | 0, 1.5 and 5<br>µg/cm <sup>2</sup> /h                                                         | 700                 | 100<br>200<br>500           |

|   |                                                                               |                                                                                                                                  |                                       |     |                         |
|---|-------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|---------------------------------------|-----|-------------------------|
|   | GTD 111+RT 22<br>Rene 80+SC2464                                               | Balance N <sub>2</sub>                                                                                                           |                                       |     |                         |
| C | GTD 111<br>Rene 80<br>PWA 1483<br>MarM 509<br>GTD 111+RT 22<br>Rene 80+SC2464 | 1 vol% CO <sub>2</sub><br>8 vol% O <sub>2</sub><br>3.6 ppm SO <sub>2</sub><br>20 vol% H <sub>2</sub> O<br>Balance N <sub>2</sub> | 0, 1.5 and 5<br>µg/cm <sup>2</sup> /h | 700 | 100<br>200<br>500       |
| D | PWA 1483<br>MarM 509                                                          | 300 ppm SO <sub>2</sub><br>Balance air<br>0 vol% H <sub>2</sub> O                                                                | 1.5 µg/cm <sup>2</sup> /h             | 700 | 50<br>100<br>200<br>500 |
| E | PWA 1483<br>MarM 509                                                          | 300 ppm SO <sub>2</sub><br>Balance air<br>10 vol% H <sub>2</sub> O                                                               | 1.5 µg/cm <sup>2</sup> /h             | 700 | 50<br>100<br>200<br>500 |
| F | PWA 1483<br>MarM 509                                                          | 300 ppm SO <sub>2</sub><br>Balance air<br>20 vol% H <sub>2</sub> O                                                               | 1.5 µg/cm <sup>2</sup> /h             | 700 | 50<br>100<br>200<br>500 |
| G | PWA 1483<br>MarM 509                                                          | 300 ppm SO <sub>2</sub><br>Balance air                                                                                           | 1.5 µg/cm <sup>2</sup> /h*            | 700 | 50<br>100<br>200<br>500 |

### 3.7 Materials

The materials selected for this research are based on those selected as candidate materials for the H<sub>2</sub>-IGCC project. These are GTD 111, Rene 80, PWA 1483, MarM 509, and the alloy coatings SC2464 and RT22. These material systems were chosen to allow like for like comparison in terms of materials between exposure based on H<sub>2</sub>-IGCC test environments and further derived test conditions targeted at investigating specific issues. The nominal alloy compositions for the alloys are given in Table 3.2.

GTD 111 is a Ni-based superalloy developed by General Electric in the 1990s [109]. GTD 111 was designed for use as a blade alloy in land-based gas turbines. Also developed by General Electric, Rene 80 is a Ni-based superalloy designed in the 1960s [110] for use as aeronautical jet turbine blades.

PWA 1483 is a Ni-based superalloy developed by Pratt and Whitney and patented in 1982 [111]. PWA 1483 was designed to have longer rupture lifetime than comparable prior art superalloys.

MarM 509 is a Co-based superalloy developed in the 1970s [112] for use as stationary turbine vanes [113]. The nominal elemental compositions of the four alloys in terms of % weight are presented in Table 3.2.

**Table 3.2: Nominal alloy elemental compositions (% weight) [114],[115]. Atomic % values given in Table D.1.**

| Alloy    | Ni  | Co  | Cr   | Ti   | W   | Al  | Ta  | Mo   | Fe   | C    | B    | Zr   |
|----------|-----|-----|------|------|-----|-----|-----|------|------|------|------|------|
| GTD 111  | Bal | 9.5 | 13.5 | 4.75 | 3.8 | 3.3 | 2.7 | 1.53 | 0.23 | 0.09 | 0.01 | ...  |
| Rene 80  | Bal | 9.5 | 14   | 5    | 4   | 3   | ... | 4    | ...  | 0.16 | 0.02 | 0.03 |
| PWA 1483 | Bal | 9   | 12.2 | 4.1  | 3.8 | 3.6 | 5   | 1.9  | ...  | 0.07 | ...  | ...  |
| MarM 509 | 10  | Bal | 23.5 | 0.2  | 7   | ... | 3.5 | ...  | ...  | 0.6  | ...  | 0.5  |

The literature describes the alloys as containing following phases [113], [116], [117], [118]:

- An austenitic  $\gamma$  face centred cubic (FCC) crystalline matrix.
- A  $\text{Ni}_3(\text{TiAl})$   $\gamma'$  phase precipitated into the  $\gamma$  matrix to form a  $\gamma$ - $\gamma'$  binary phase structure. In the case of MarM 509 the  $\gamma'$  phase is  $\text{Co}_3(\text{Al}, \text{W})$ .
- MC primary carbide phases where M can be Ti or Ta or W distributed within grains.
- $\text{M}_{23}\text{C}_6$  and  $\text{M}_6\text{C}$  secondary carbides where M can be Cr or Mo.

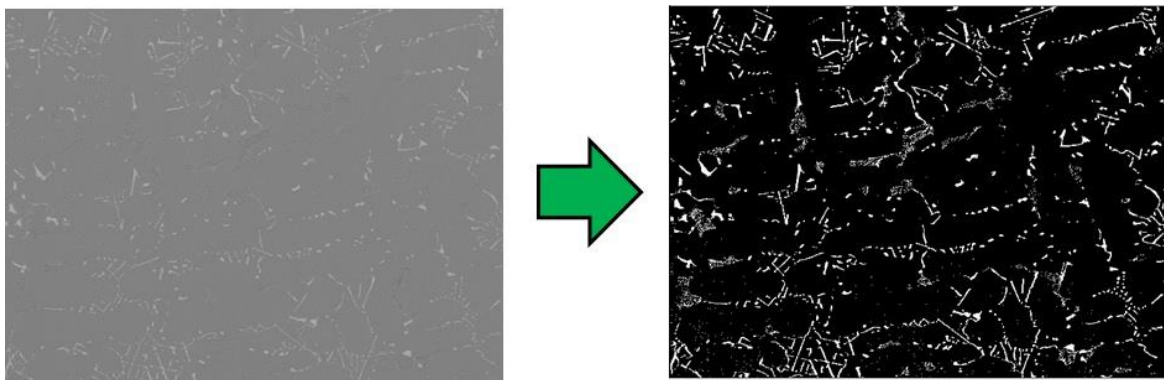
In this study, SEM backscattered electron micrographs of GTD 111, PWA 1483 and MarM 509 sample cross sections do not show the  $\gamma$ - $\gamma'$  binary phase. It is likely that the alloy was provided without having undergone the specific treatment required to form these phases. The  $\gamma$ - $\gamma'$  binary phase can be observed in Rene 80. The  $\text{M}_{23}\text{C}_6$  secondary carbides phase described in the literature was only observed in MarM 509.

Experimental work in conditions associated with the  $\text{H}_2$ -IGCC project also included the environmentally resistant coatings RT22 and SC2464 [119]. RT22

is a commercial Pt-Al coating applied in this study to GTD 111 by TSTL using Pt electroplating followed by an aluminising and standard heat treatment. SC2464 is a powder coating applied using high velocity oxy-fuel technique. SC2464 in this study was applied to Rene 80 by Flamespray. The nominal composition (% weight) of SC2464 is 71.2% Ni, 17% Cr, 10% Al, 1.5% Re, 0.3% Y [19].

### 3.7.1 Alloy precipitate area percentage

The approximate area percentages of the alloy precipitate phases were determined using Image J software to threshold the shades of grey in BSE images different from the bulk alloy. This method of analysis used the average precipitate percentage from 5 separate images for each alloy taken at sites chosen randomly deep within the alloy sample. The dimensions of each image were 633  $\mu\text{m}$  by 466  $\mu\text{m}$ . The technique is demonstrated in Figure 3.9 for a location towards the centre of a MarM 509 cross section. It should be noted that the secondary carbide phase in MarM 509 are known to be Cr rich show up darker than the primary phase in the BSE image. These secondary carbide phases are not recognised by the image J technique. While the secondary carbide phases of GTD 111, Rene 80 and PWA 1483 are recognised by image J, they have a low abundance and small sizes (approximately 1  $\mu\text{m}$ ). The average precipitate area percentages for the alloys are shown in Table 3.3.



**Figure 3.9: Technique using Image J software to shade threshold the metal carbide precipitates that show up lighter in back scattered electron SEM images.**

**Table 3.3: Approximate alloy precipitate area percentage.**

|         | 1   | 2   | 3   | 4   | 5   | Average |
|---------|-----|-----|-----|-----|-----|---------|
| GTD 111 | 1.2 | 0.9 | 1.3 | 1   | 1.6 | 1.2     |
| Rene 80 | 1.2 | 1.1 | 1.4 | 1.1 | 1.2 | 1.2     |
| PWA1483 | 0.6 | 1   | 1   | 1.4 | 0.7 | 0.9     |
| MarM    | 5.6 | 6   | 6.4 | 6.7 | 6.4 | 6.2     |

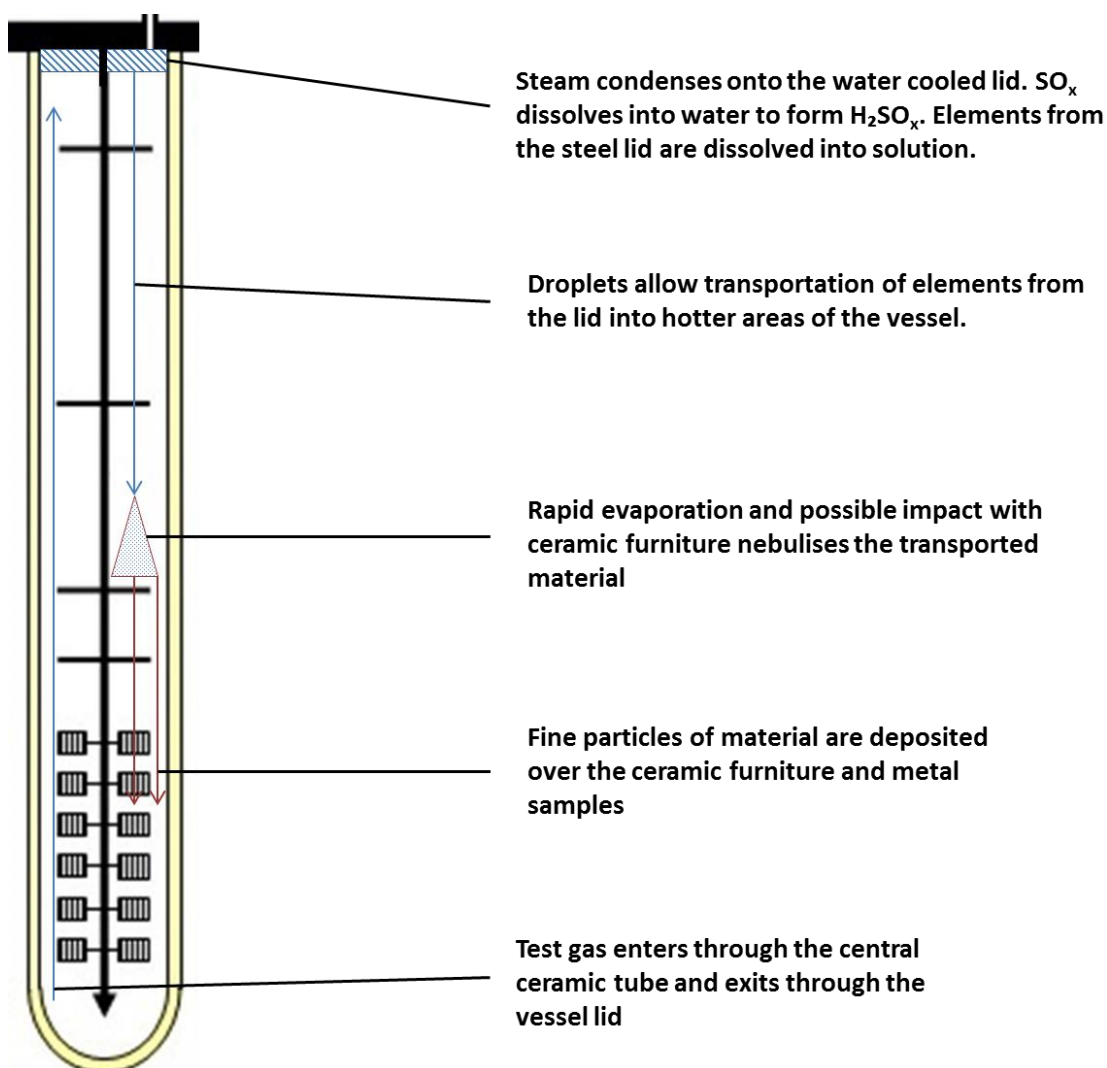
509

### 3.8 Modifications to the methodology

After exposures in atmospheres containing water vapour, brown coloured particles were observed to have been deposited on the ceramic furniture and samples. Upon energy dispersive x-ray analysis, this deposit was identified as containing iron. The samples used during these previous tests contain either no or very little iron (0.23 %wt. in GTD 111) therefore they could not be the source of this phenomenon. With the corrosion vessel tube and furniture being constructed of alumina, the only likely origin of the iron was the 316 stainless steel furnace lid.

It is possible that the cooled flange is able to lower the temperature of the lid to a point that steam is able to condense as water plus acidic species on the underside surface. Because  $\text{SO}_x$  is present in the gas phase, this condensate is likely to contain a certain concentration of  $\text{H}_2\text{SO}_4$ . Elements from the steel lid (specifically iron) are able to dissolve into this solution which over time coalesces into drips into the hot area of the corrosion vessel. Rapid evaporation and possibly impact with the ceramic heat shield appear to nebulise the material which is deposited on every surface in the hot zone. It is not clear if this effect

occurs during the actual exposure time or during the cooldown period of the furnace. A schematic of this process is shown in Figure 3.10.



**Figure 3.10: Corrosion vessel schematic describing a possible mechanism for the migration of elements from the 316 stainless steel furnace lid throughout the chamber.**

The deposition of elements, confirmed using EDX to be mostly Fe, introduced an undesirable extra parameter to the corrosion test. To remove or reduce this factor, several possible solutions were considered.

- Increase the temperature of the water that cools the furnace lid (to protect the sealing O-ring). This may stop the condensation of vapours onto the

underside of the lid. However, the condensation effect may still occur as the furnace cools from its test temperature.

- Change the material of the lid to a more resistant material. This option would be expensive and take time to produce.
- Application of a corrosion resistant coating to the areas of the lid that vapours condense onto.

A two layer coating system applied to the 316 stainless steel lid was the method chosen to mitigate the migration of elements from the lid. The surface of the original lid was prepared via sand blasting the underside to create a fresh surface. This was then cleaned using initially acetone followed by isopropanol. Approximately 50  $\mu\text{m}$  of Ni was deposited onto the prepared surface using a brush electroplating technique. An outer layer of polytetrafluoroethylene (PTFE) was applied to the Ni coating using an aerosol. A schematic of this system is shown in Figure 3.11.

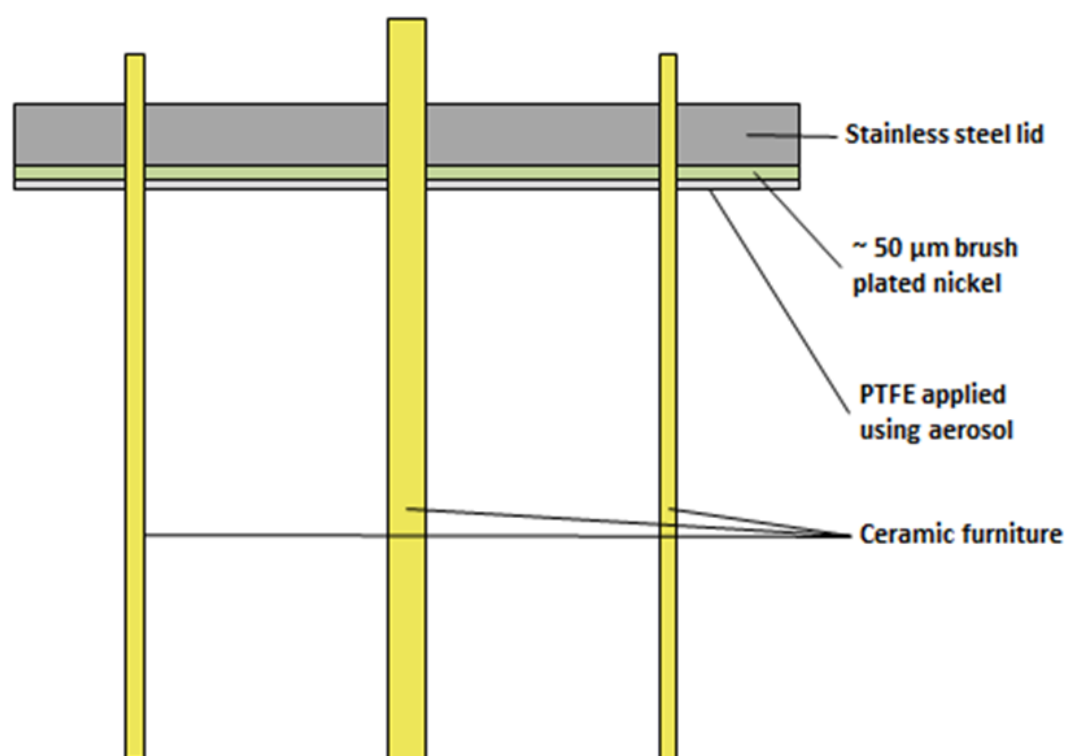


Figure 3.11: Schematic of the corrosion vessel lid modified with corrosion resistant coatings.

## **4. Hot corrosion in simulated gas turbine conditions**

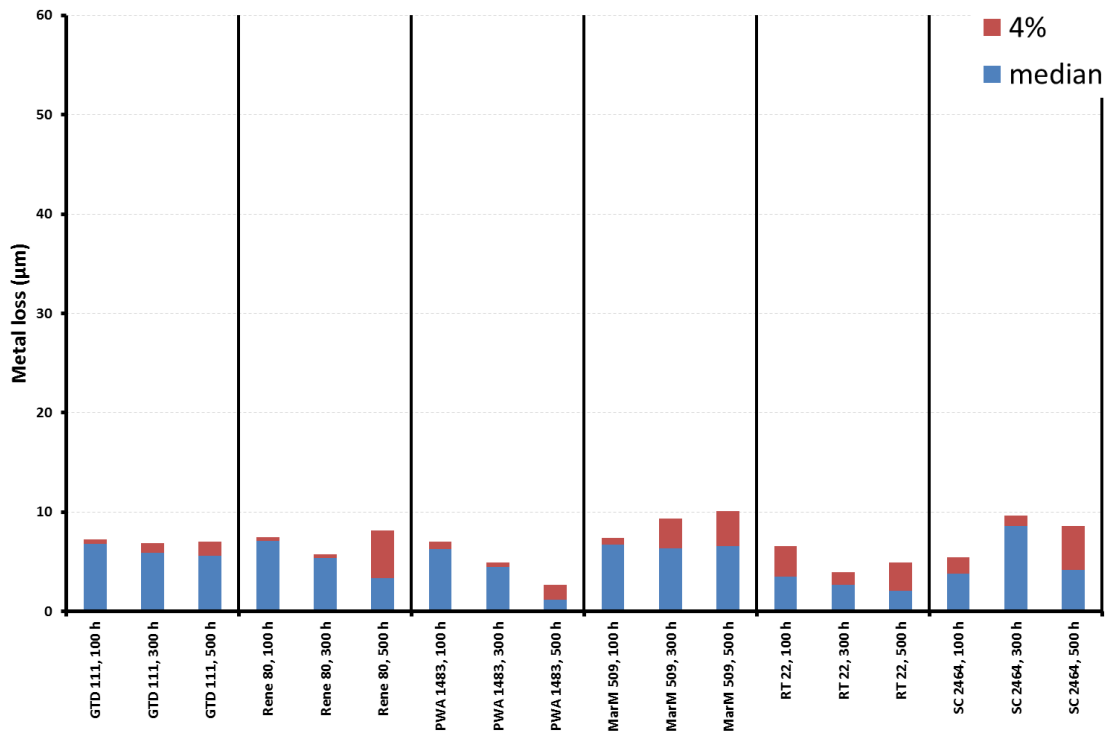
In this chapter metal loss data and changes in surface morphologies are presented and discussed for tests A to C. Weight change data for these tests are found in Appendix A, complete dimensional good metal loss distributions are found in Appendix B, and test parameters are given in Section 3.6.

### **4.1 Test A: simulating desulphurization failure**

This test simulates accelerated corrosion resulting from having to by-pass the final syngas desulphurization stage in a H<sub>2</sub>-rich syngas fired IGCC power plant as well as the water-gas shift reactor and CO<sub>2</sub> separation system. This is considered one of the most likely system failures and would allow higher concentrations of H<sub>2</sub>S to be present within the syngas. The exposure temperature was chosen to maximise type II corrosion which is thought to peak at approximately 700 °C. In practice, the turbine comprises of many different components and stages with variable temperature profile and substantial temperature gradients.

Figure 4.1 presents the good metal loss median and 4% probability of good metal loss exceedance values for all exposures with no deposit applied in atmosphere A at 700 °C. These data show metal loss values that could be considered negligible. That is to say values that could be wholly attributed to measurement error so that good metal loss may not have occurred at all. For the uncoated alloys, the median good metal loss values range from 1.1 to 7.1 µm. Such data suggests that for these uncoated samples either a hot corrosion mechanism did not occur, or that mechanism remained in incubation and did not transition to propagation. This is in agreement with the majority of the literature which states the requirement of a salt deposit [66], [72], [64]. One study suggests that sulphidation features similar to those typically observed in type I hot corrosion may occur in the absence of a deposit if the exposure atmosphere has a sufficiently high S activity [66].

The good metal loss value for the SC2464 coated appears to be at its highest (up to 9.6  $\mu\text{m}$ ) under these conditions after 300 hours of exposure. Two factors that may increase the error associated with these samples are that SC 2464 coatings have a much greater surface roughness than their uncoated counterparts, and that the coatings are easily damaged during the post exposure preparation process.



**Figure 4.1: Median and 4% exceedance values for all material systems exposed with no deposit applied in test A.**

Figure 4.2 presents probability of good metal loss exceedance data for exposures in atmosphere A with  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$  of an 80%  $\text{Na}_2\text{SO}_4$  20%  $\text{K}_2\text{SO}_4$  deposit applied cyclically every 100 hours. The good metal loss trends for the uncoated alloys generally show little metal loss up to 300 hours of exposure but much greater good metal loss by 500 hours. This indicates that between 300 hours and 500 hours the corrosion mechanism over at least part of the sample has transitioned

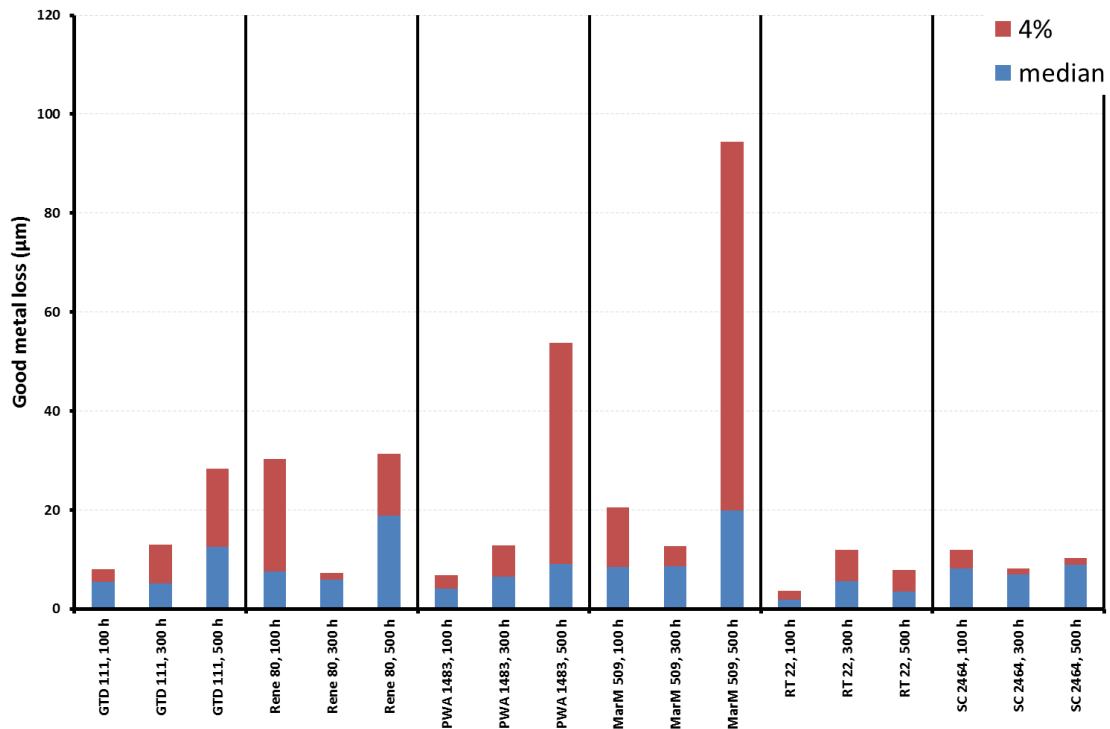
from incubation to propagation. The median good metal loss value can indicate if it is the majority or minority of the surface that is in propagation.

Good metal loss data sets for MarM 509 and Rene 80 after 100 hours of exposure show relatively high 4% probability of good metal loss exceedance values (20.5 and 30.3  $\mu\text{m}$  respectively) compared to the other material systems. Relatively high good metal loss exceedance values with only low probabilities indicate the presence of corrosion pits; however this feature is not shown in the dimensional metrology data for 300 hour exposures. Since these are probability of good metal loss exceedance values, it doesn't necessarily mean pit features don't exist on those particular samples only that they are there with a low probability.

Electron microscopy reveals that precipitate phases within the alloy matrix may act as nucleation points for the formation of pits. This is discussed in Section 7.3 and may explain such high values with a low level of probability of occurrence.

When considering the longest exposure time of 500 hours, the alloy with the greatest degree of good metal loss is MarM 509 with median and 4% exceedance values of 19.9 and 94.4  $\mu\text{m}$  respectively. Although PWA 1483 has the second greatest 4% exceedance value (53.8  $\mu\text{m}$ ), its median value is low (9.1  $\mu\text{m}$ ) compared to the other uncoated alloys. This shows that while the PWA 1483 sample has developed deep pits, the majority of the sample's surface has relatively little good metal loss, so it mostly either remains in incubation or has only recently transitioned into propagation. GTD 111 and Rene 80 both have similar median good metal loss (12.6 and 18.9  $\mu\text{m}$  respectively) and 4% exceedance probability values (28.3 and 31.3  $\mu\text{m}$  respectively) data.

The metallic coatings RT22 and SC2464 both show negligible good metal loss over the all exposure times. These data trends are similar to the exposures with no deposit applied (Figure 4.1) and indicate that the hot corrosion damage has not progressed beyond incubation.



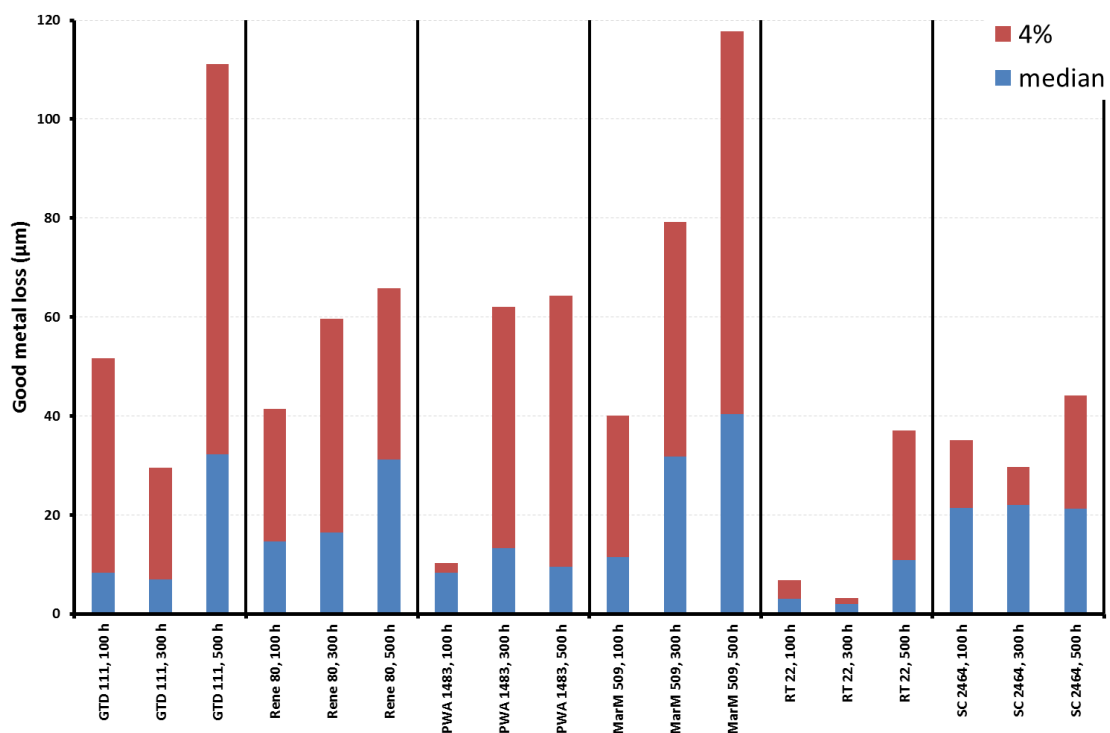
**Figure 4.2: Median and 4% exceedance values for all material systems exposed in test A with a deposit flux of 1.5 µg/cm<sup>2</sup>/h.**

Figure 4.3 shows the median good metal loss and 4% exceedance values for all material systems exposed in atmosphere A at 700 °C with 5 µg/cm<sup>2</sup>/hour of an 80% Na<sub>2</sub>SO<sub>4</sub> / 20% K<sub>2</sub>SO<sub>4</sub> deposit applied cyclically every 100 hours. With the exception of PWA 1483, all the uncoated alloys have suffered significant good metal loss (above 40 µm) over at least part of the sample cross-section after the shortest tested exposure time of 100 hours. This shows that parts of each samples' surface has entered propagation. Comparing this data set with the exposures using a deposit flux of 1.5 µg/cm<sup>2</sup>/hour (Figure 4.2), it appears that increasing the quantity of the deposit flux has shortened the incubation period of the hot corrosion mechanism.

The 4% exceedance value for GTD 111 after 100 hours (51.7 µm) is greater than after 300 hours (29.5 µm). Despite these counterintuitive values, the median good metal loss values are similar (8.3 and 6.9 µm respectively) indicating the majority of both sample surfaces have experienced relatively little good metal loss. Additionally, as with Rene 80 exposed for 300 hours in Figure 4.2, the 4%

probability of good metal loss exceedance value is not necessarily the value of the greatest good metal loss present on the cross section.

After 500 hours MarM 509 again exhibits the greatest degree of good metal loss of the materials exposed at both median (40.4  $\mu\text{m}$ ) and 4% (117.8  $\mu\text{m}$ ) exceedance values. Although the 4% exceedance value of PWA 1483 is relatively high (64.3  $\mu\text{m}$ ) the median value remains low (9.5  $\mu\text{m}$ ). This may indicate a better corrosion performance over the majority of the sample compared to the other uncoated alloys.



**Figure 4.3: Median and 4% exceedance values for all material systems exposed in test A with a deposit flux of 5  $\mu\text{g}/\text{cm}^2/\text{h}$ .**

Of the metallic coatings, SC2464 has suffered similar good metal loss values at all exposure times. The degree of error associated with metallic coatings may be greater than the uncoated alloys: due to their brittle nature and are susceptible to damage during post-test preparation techniques. RT22 exhibits negligible metal loss up for up to 300 hours of exposure indicating the corrosion mechanism has remained in incubation during this period. Between the 300 hour and 500 hour

points, the hot corrosion mechanism has progressed into the propagation stage resulting in higher metal loss values (of up to 37  $\mu\text{m}$ ) after 500 hours.

## **4.2 Test B: simulating firing on natural gas**

This test simulates combusted natural gas as both a reference condition for normal combustion and the result of using a backup fuel should there be a failure of the whole gasification system. Details of the test parameters are given in Section 3.6.

Figures 4.4, 4.5 and 4.6 present median good metal loss and 4% exceedance values for all samples in test B. It is immediately apparent that with the exception of the SC2464 coating and certain MarM 509 specimens, the exposed samples do not exhibit significant good metal loss (below 10  $\mu\text{m}$ ). Such data suggests that the hot corrosion damage mechanism has been unable to progress into the propagation stage and has remained in the incubation stage. In terms of hot corrosion, the most significant difference between atmosphere A (10.5 vol%  $\text{CO}_2$ , 8.5 vol%  $\text{O}_2$ , 90 ppm  $\text{SO}_2$ , 5 vol%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ) and atmosphere B (6.5 vol%  $\text{CO}_2$ , 9 vol%  $\text{O}_2$ , 4 ppm  $\text{SO}_2$ , 10 vol%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ) is expected to be the  $\text{SO}_2$  content. Comparing the data sets from tests A and B therefore shows that lowering the  $\text{SO}_2$  content has lengthened the incubation period of the corrosion damage mechanism and subsequently reduced the corrosion rate which is reflected in lower good metal loss values. One explanation for this that is supported by the literature is that  $\text{SO}_3$  in the gas phase is required to stabilize the deposit melt and keeps the degradation reaction going in a regime of gas phase induced acidic fluxing [66]. The difference in water content (from 5 to 10 vol%) may also have some effect but this is expected to be less than the effect of  $\text{SO}_2$  concentration.

MarM 509 shows slightly greater good metal loss values after its 300 hour exposures with both deposit fluxes. These losses are not seen after 500 hours and could possibly be a consequence of errors, scatter in the incubation to propagation transition time, scatter due to microstructural effects, or a combination of these factors.

Across all three exposure times and deposit fluxes, the median good metal loss values of SC2464 range between 4.2 and 30.8  $\mu\text{m}$ . There does not appear to be any correlation between any of the variables and the good metal loss values. This erratic scattering of data may be the result of damage incurred during post-test sample preparation, or errors associated with the surface roughness of SC2464.

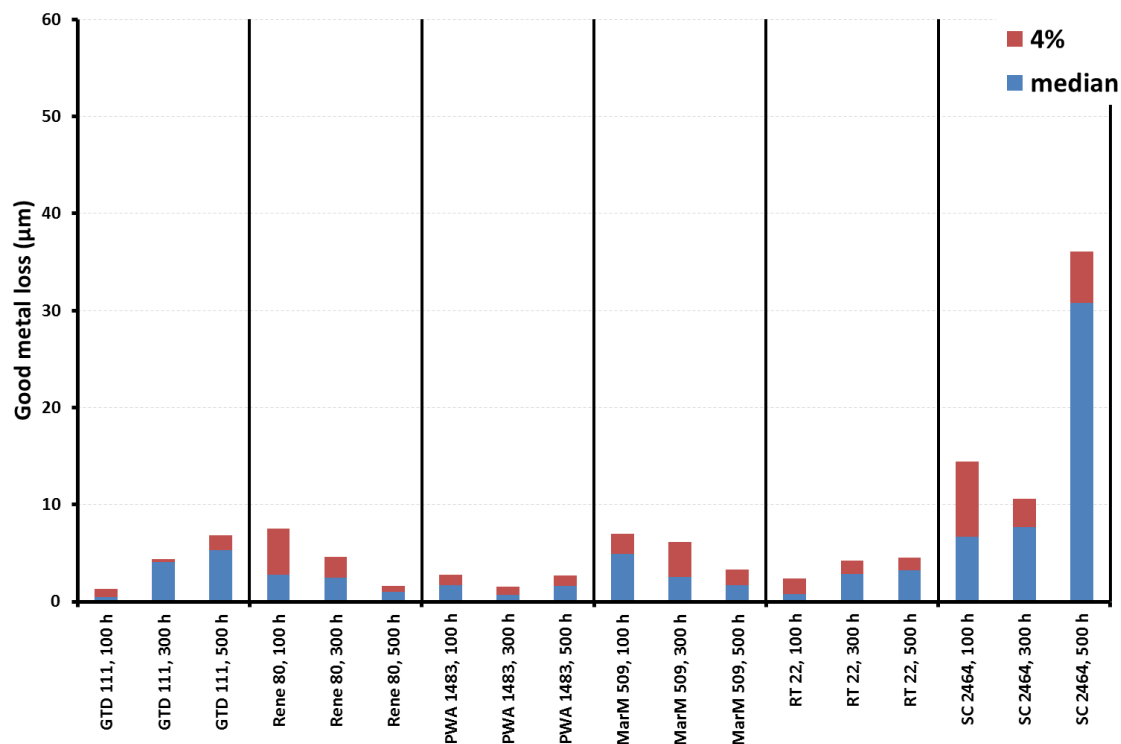


Figure 4.4: Median and 4% exceedance values for all material systems exposed with no deposit in test B.

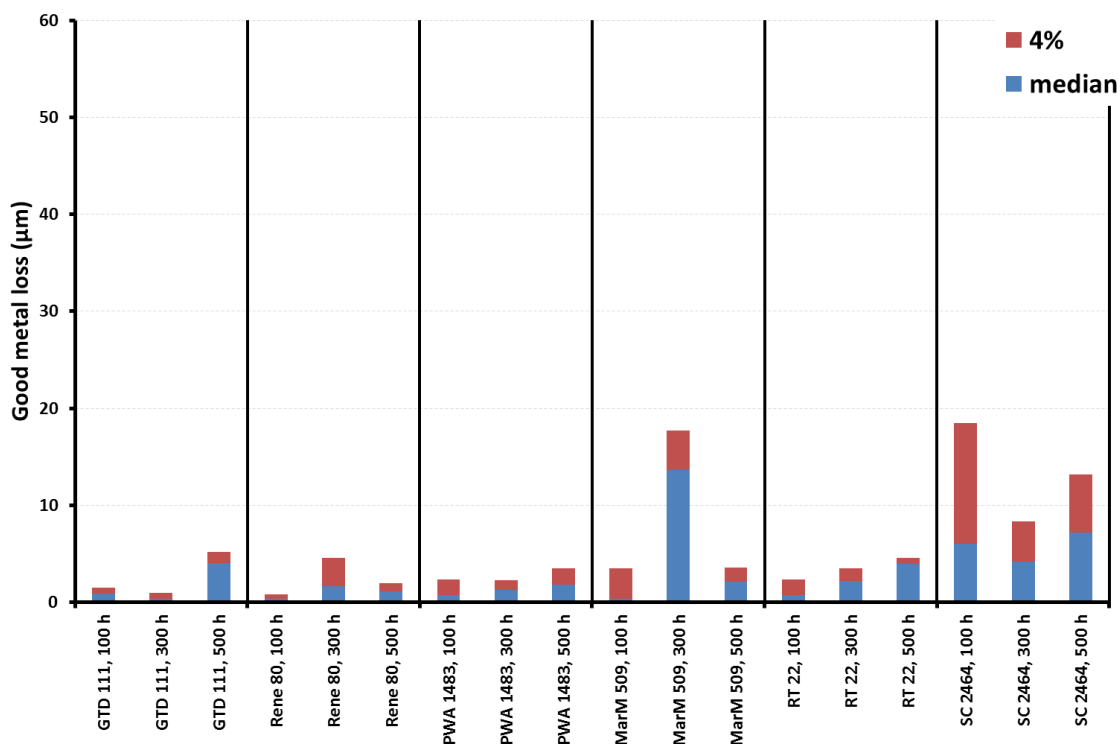


Figure 4.5: Median and 4% exceedance values for all material systems exposed in test B with a deposit flux of 1.5 µg/cm²/h.

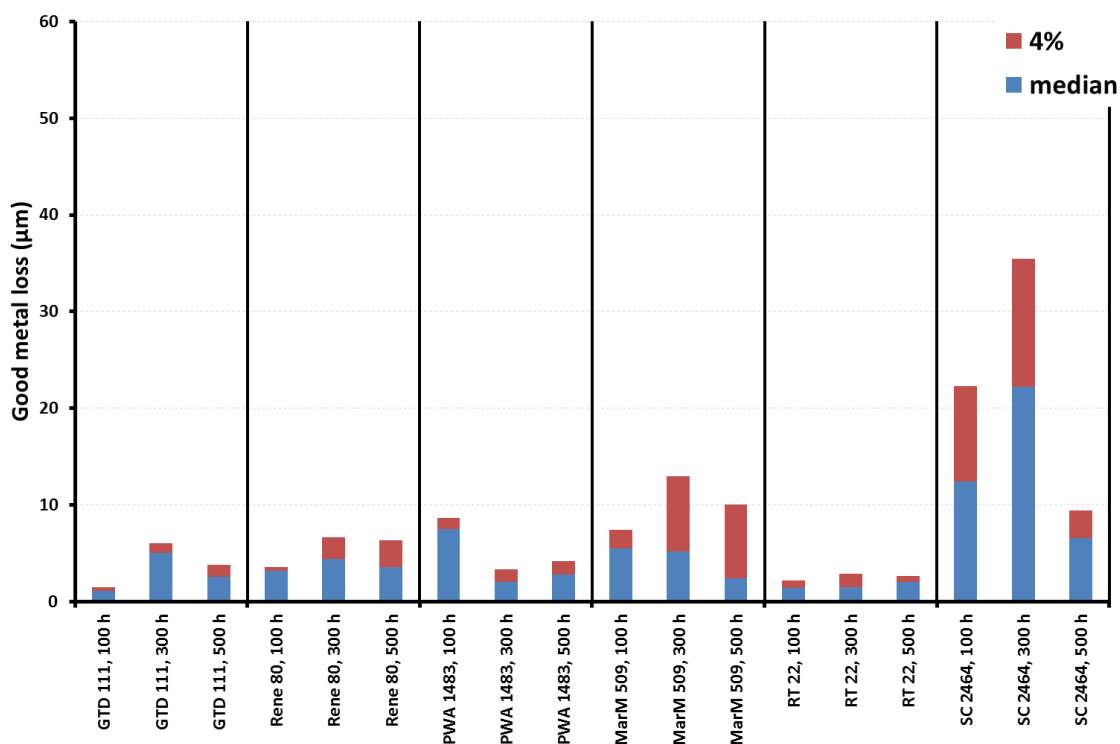


Figure 4.6: Median and 4% exceedance values for all material systems exposed in test B with a deposit flux of 5 µg/cm²/h.

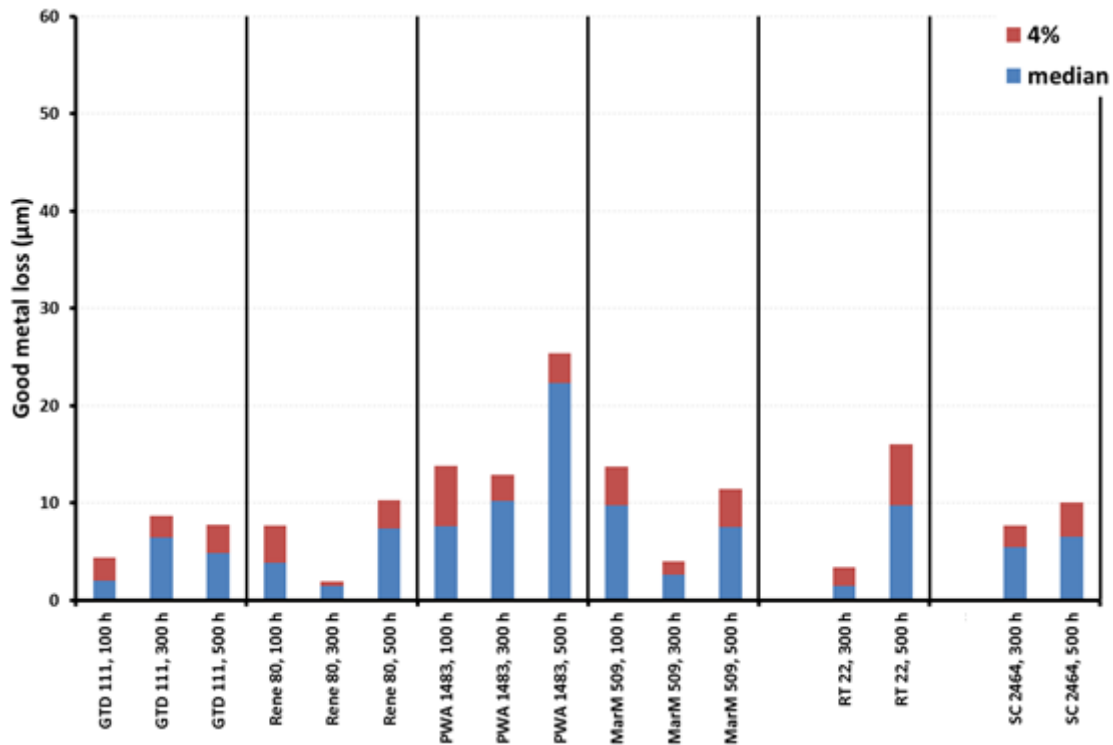
### 4.3 Test C: simulating firing on H<sub>2</sub>-rich syngas

Test C simulates the normal day-to-day running of the gas turbine on H<sub>2</sub> rich syngas (to produce low CO<sub>2</sub> emissions from the gas turbine exhaust). This high H<sub>2</sub> content in the fuel will generate higher levels of H<sub>2</sub>O post combustion than the other considered atmospheres. Full test parameters are found in Section 3.6.

When compared to test B, the difference in SO<sub>2</sub> content, which according to the literature is an important factor in the hot corrosion mechanism [68], [66], is negligible. The O<sub>2</sub> content in these exposures is also similar to test B and, while CO<sub>2</sub> content is lower, this is not thought to be an important factor. The most notable difference between tests B and C is the water contents which are 10 and 20 vol% respectively.

Figure 4.7 depicts good metal loss values for exposures in test C with no deposit applied. In concurrence with the exposures in tests A and B without a deposit (Figures 4.1 and 4.4 respectively), negligible degrees of good metal loss are seen for most samples. PWA 1483 exposed for 500 hours shows a relatively high median good metal loss value of 22.3  $\mu\text{m}$  but a 4% value that is only 3.1  $\mu\text{m}$  higher than the median. This low standard deviation implies a highly even distribution of damage that is not consistent with type II hot corrosion. It is therefore likely that this good metal loss data is caused by a non-systematic error.

Figure 4.7, collectively with Figures 4.1 and 4.4, show that, under these exposure conditions, a deposit is required for the rapid degradation of the materials. This is in agreement with the hot corrosion literature discussed in Section 2.6.

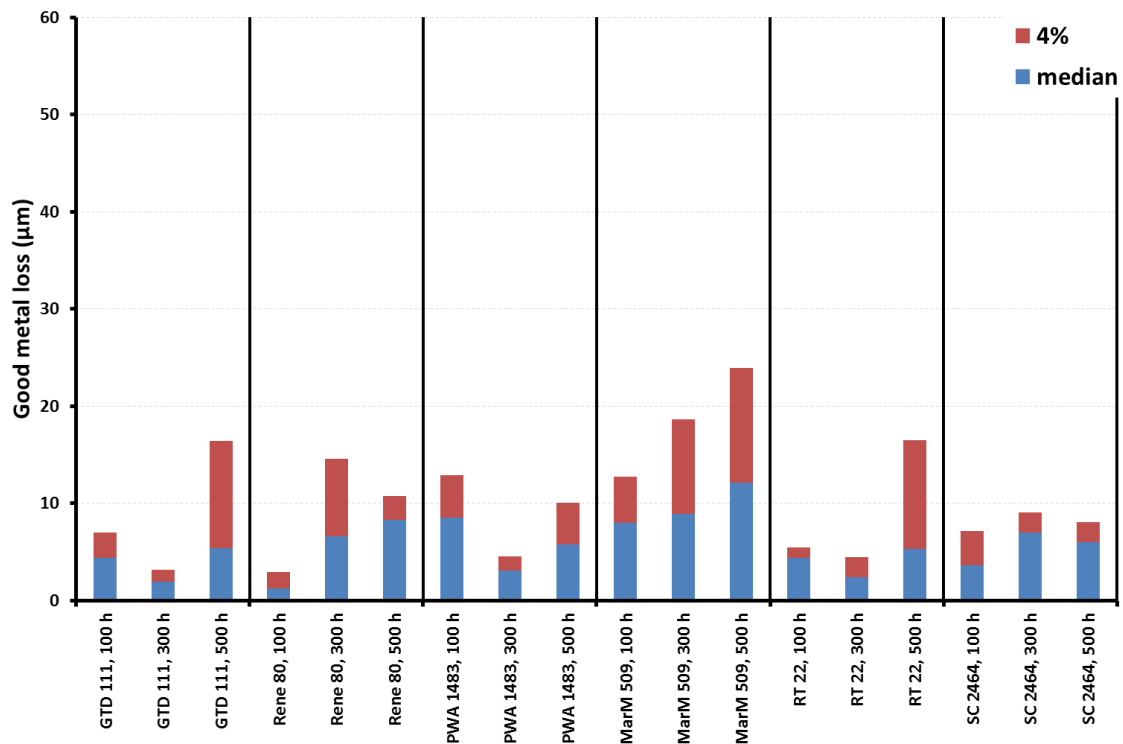


**Figure 4.7: Median and 4 % exceedance values for all material systems exposed with no deposit in test C.**

The median good metal loss and 4% exceedance data for exposures with a deposit flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$  are plotted in Figure 4.8. At 500 hours of exposure, the uncoated Ni-based alloys, GTD 111, Rene 80 and PWA 1483, exhibit negligible (less than  $10 \mu\text{m}$ ) median good metal loss values indicating that the majority of the samples' surfaces have remained in incubation. The comparatively greater 4% probability of good metal loss exceedance values of certain samples (for example, GTD 111 after 500 hours is  $16.4 \mu\text{m}$ ) indicates that at least parts of the samples' surfaces have experienced some form of good metal loss with the damage mode having transitioned from incubation to propagation.

Co-based MarM 509 has suffered the greatest good metal loss values at 300 and 500 hour exposure times. At 500 hours of exposure the median and 4% values are  $12.2$  and  $23.9 \mu\text{m}$  respectively. These data suggest that after 500 hours, the majority of the MarM 509 sample surface is in propagation (having greater than  $10 \mu\text{m}$  of measured metal loss).

The metallic coatings appear to have suffered negligible good metal loss with the exception of RT22 after 500 hours of exposure which has lost at least 16.5  $\mu\text{m}$  over 4% of the sample surface.

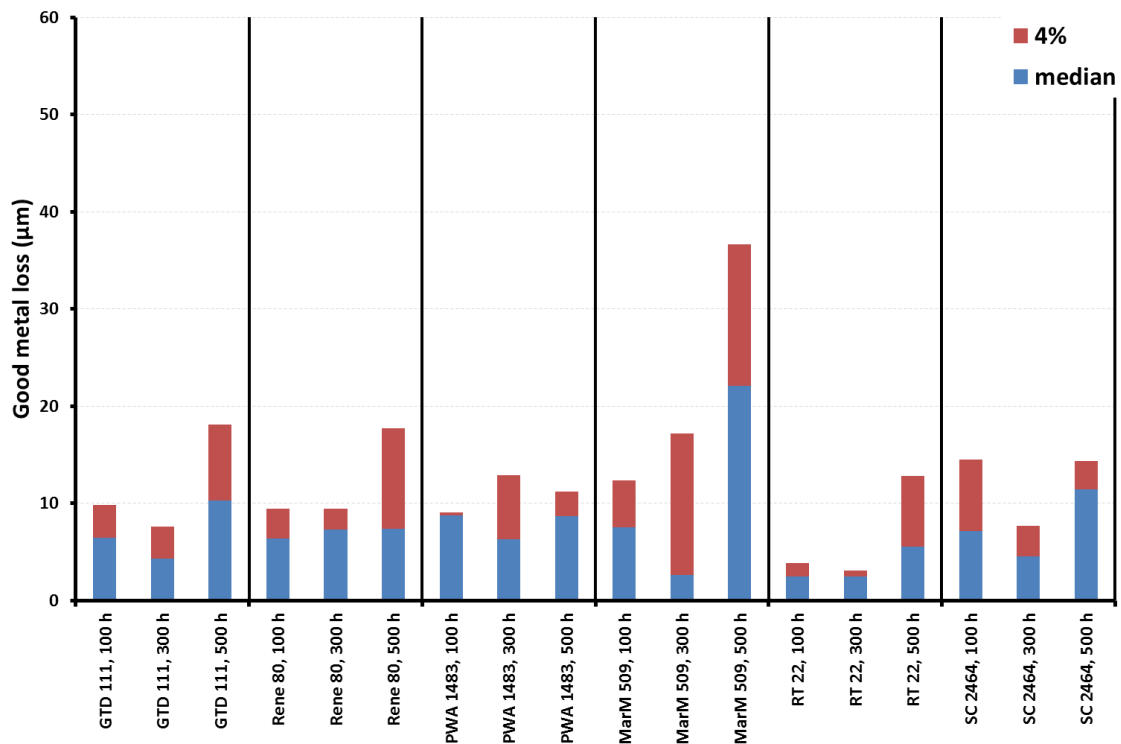


**Figure 4.8: Median and 4 % probability of metal loss exceedance values for all material systems exposed in test C with a deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$ .**

Good metal loss data for exposures in atmosphere C with a deposit flux of 5  $\mu\text{g}/\text{cm}^2/\text{h}$  are presented in Figure 4.9. Of the uncoated samples after 500 hours of exposure MarM 509 again exhibits the greatest degree of good metal loss. The relatively high median value of 22.1  $\mu\text{m}$  indicates that the majority of this sample's surface has entered into the propagation stage of the hot corrosion mechanism. The Ni-based alloys have median values ranging from 7.4 (Rene 80) to 10.3  $\mu\text{m}$  (GTD 111) after 500 hours of exposure; this could be considered marginal as to whether it indicates the occurrence of propagation. The 4% exceedance values

of GTD 111 (18.1  $\mu\text{m}$ ) and Rene 80 (17.7  $\mu\text{m}$ ) are relatively high and therefore show at least part of these samples' surfaces have entered propagation.

The metallic coatings have both suffered comparatively low levels of good metal loss over the exposure period. After 500 hours, the 4% probability of good metal loss exceedance values for RT22 and SC2464 are 12.8 and 14.4  $\mu\text{m}$  respectively. This suggests that, although these coatings are more resistant to this environment than their uncoated counterparts, they are not completely immune to degradation over longer exposures.



**Figure 4.9: Median and 4% probability of metal loss exceedance values for all material systems exposed in atmosphere C at 700 °C with a deposit flux of 5  $\mu\text{g}/\text{cm}^2/\text{h}$ .**

## 4.4 Sample morphology

Figures 4.10, to 4.13 are BSE micrographs of the uncoated alloys GTD 111, Rene 80, PWA 1483 and MarM 509 after 500 hours of exposure in atmosphere A with deposit fluxes of 0, 1.5 and 5  $\mu\text{g}/\text{cm}^2/\text{h}$ . Images on the left are representative of the majority of the sample surface, images on the right are surface corrosion features.

All four of the uncoated alloys feature the remains of interdendritic precipitation which are known to be refractory metal carbides [113], [116]–[118]. These heavy elements show up as particularly bright areas on the backscattered electron images; where these precipitates have degraded this brightness is decreased. For exposures where no deposit was applied (top row), degradation appears confined to alloy precipitates located at the sample surface.

Examples of both internal damage (shown to be the formation of species rich in Cr and S) more usually associated with type I hot corrosion, and pitting features more commonly associated with type II hot corrosion can be observed for all four bare alloys after exposures involving a deposit. The corrosion pits have frequently formed around alloy precipitates although there are also examples of pit formation in areas devoid of precipitates. MarM 509 appears to be an exception to this with degradation occurring exclusively around alloy precipitates which are much more numerous compared to the other alloys.

Of the Ni-based alloys, GTD 111 and PWA 1483 appear to have a greater amount of internal sulphide formation compared to Rene 80. These sulphides appear to be more numerous and penetrate to a greater depth adjacent to corrosion pit features.

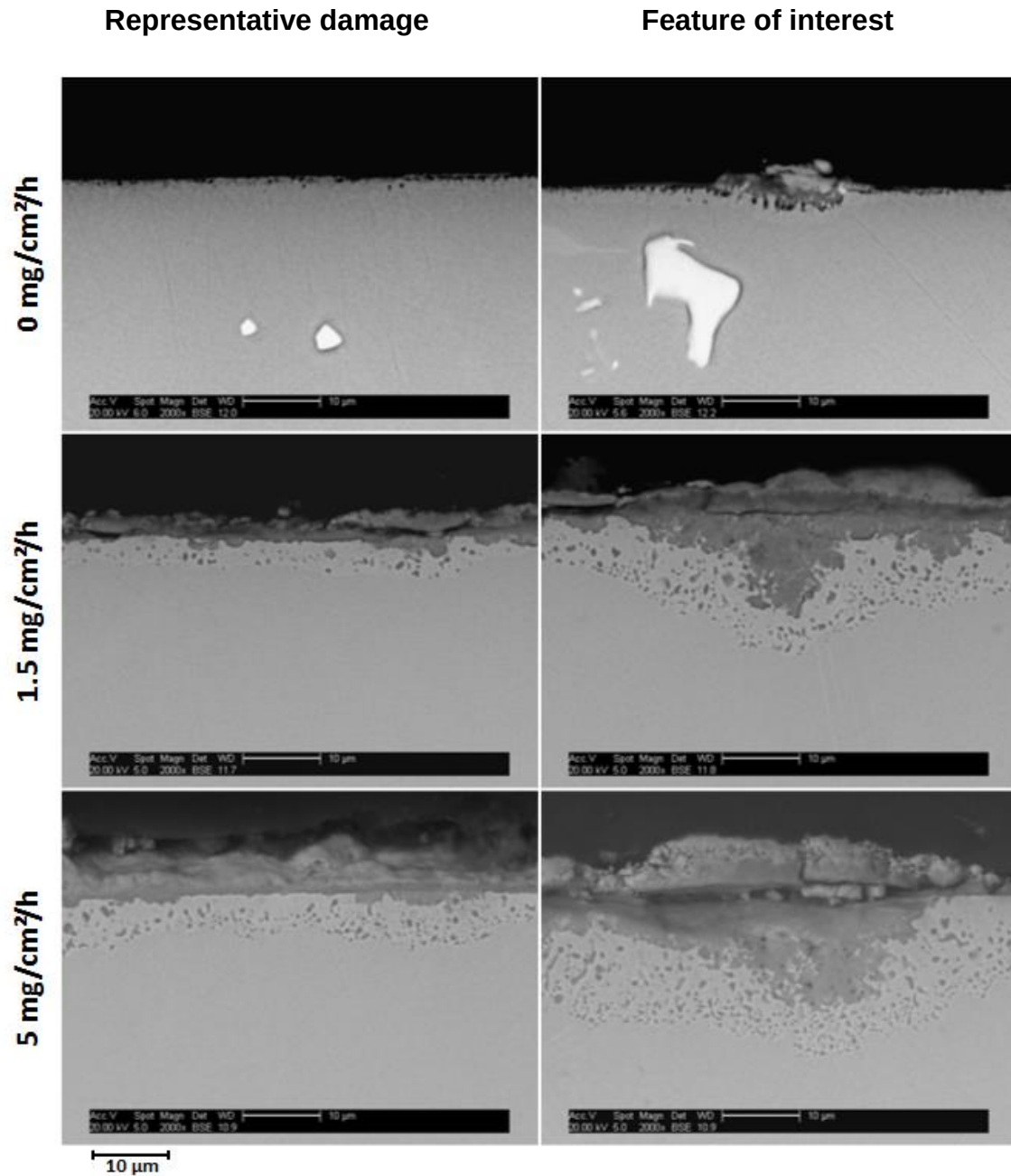


Figure 4.10: BSE micrographs of GTD 111 exposed for 500 hours in atmosphere A with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

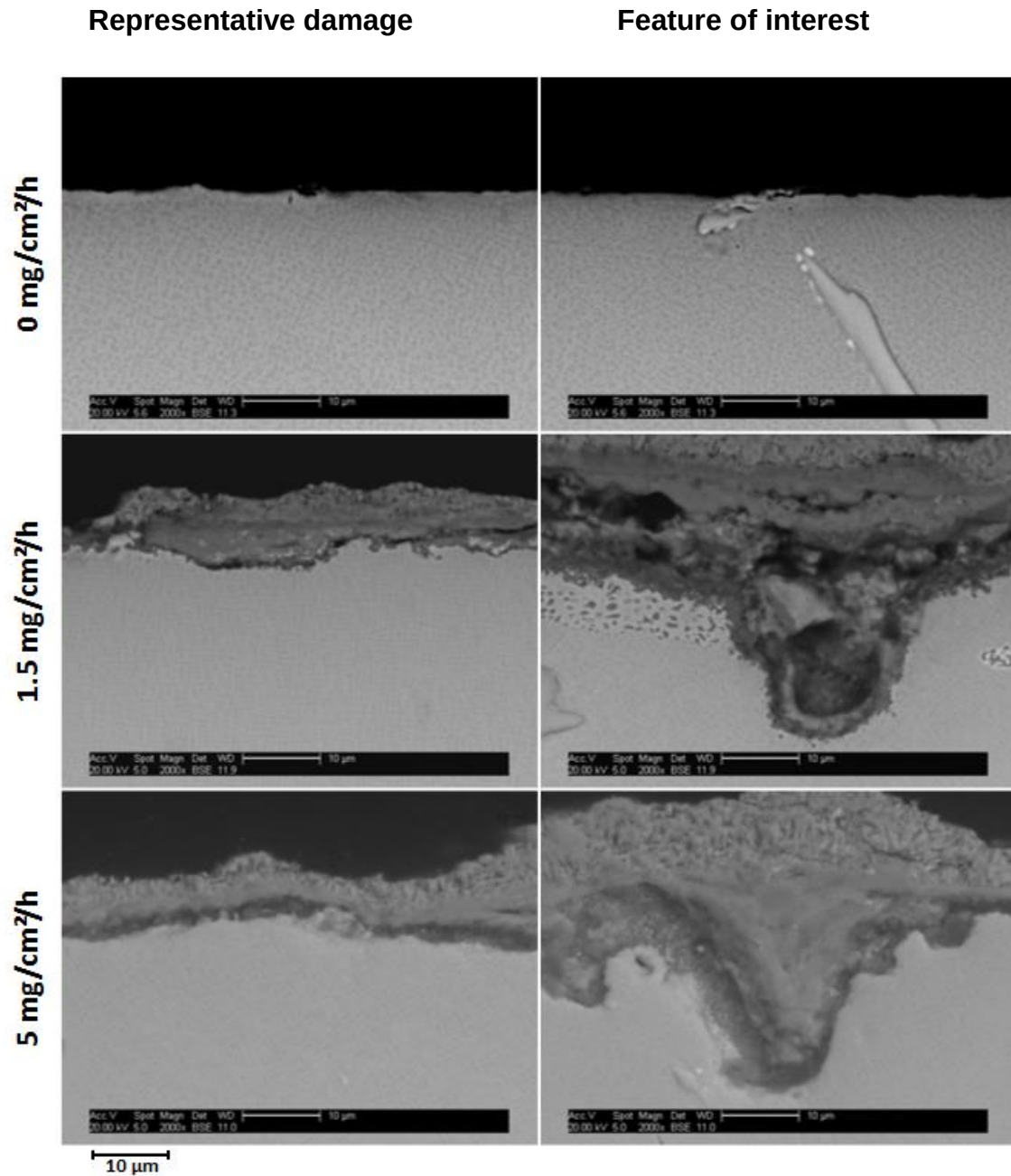


Figure 4.11: BSE micrographs of Rene 80 exposed for 500 hours in atmosphere A with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

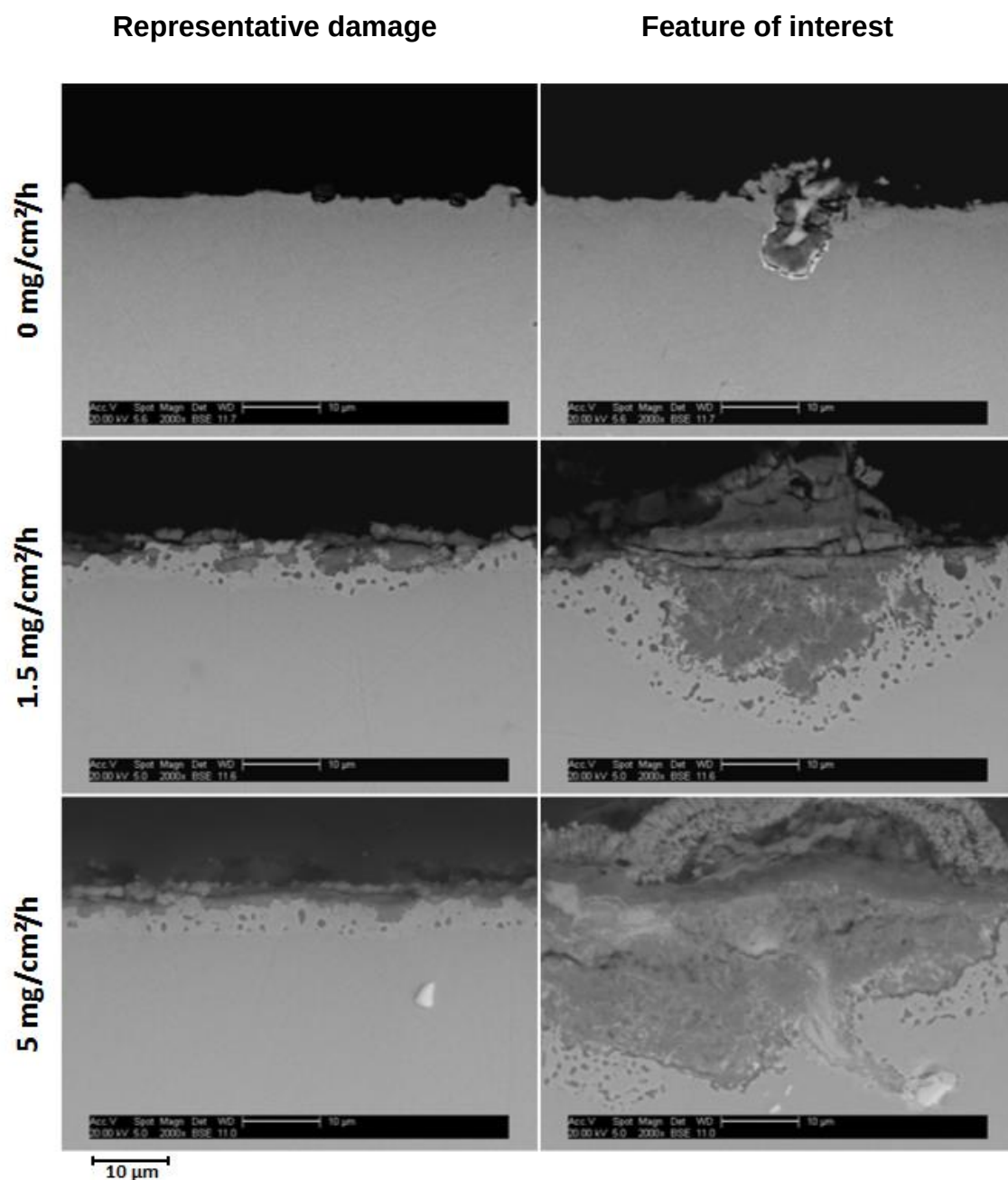


Figure 4.12: BSE micrographs of PWA 1483 exposed for 500 hours in atmosphere A with deposit fluxes of 0, 1.5 and 5  $\mu\text{g}/\text{cm}^2/\text{h}$ . Left side images are representative of the majority of the surface, right side are corrosion features.

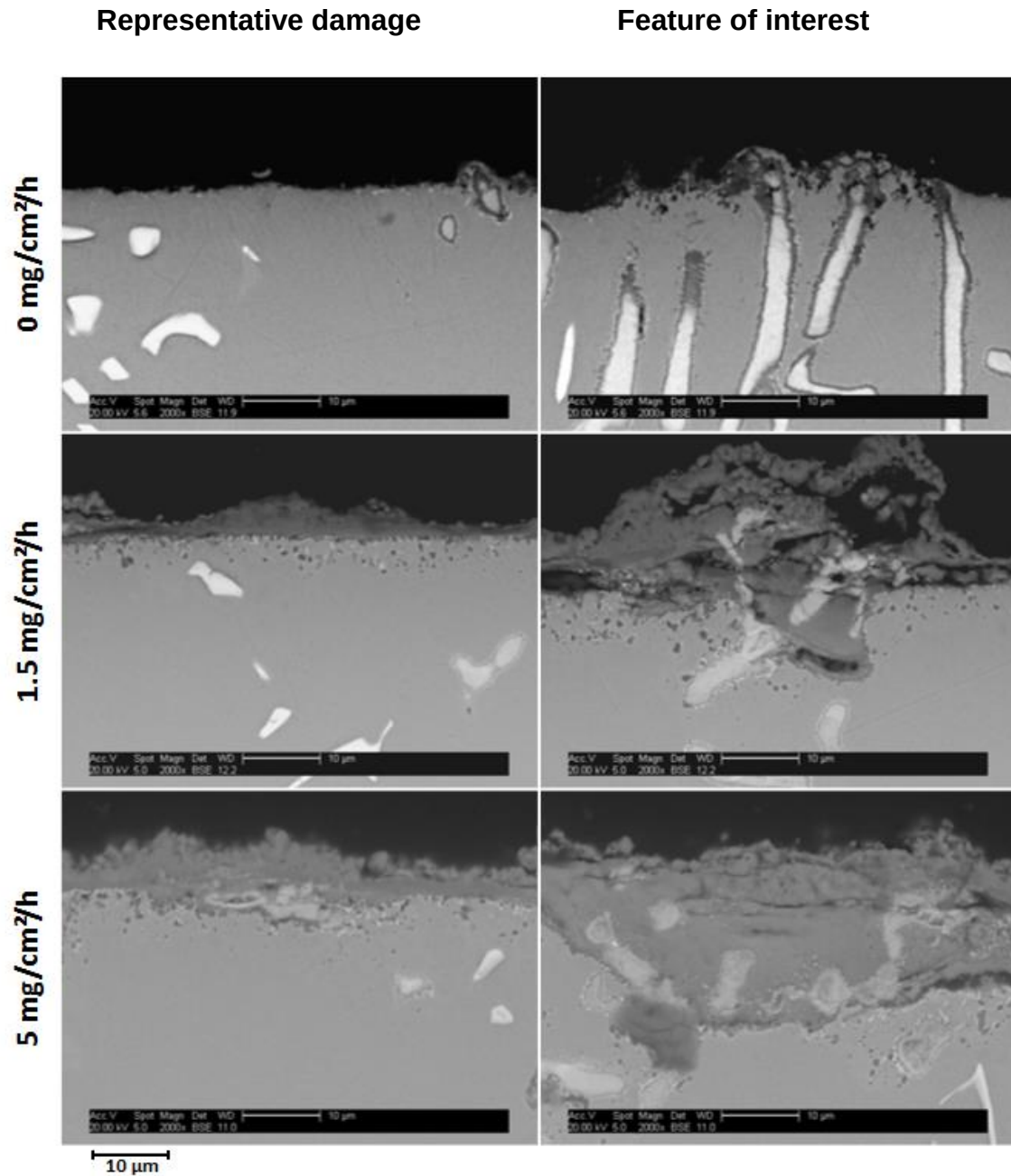


Figure 4.13: BSE micrographs of MarM 509 exposed for 500 hours in atmosphere A with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

BSE micrographs of GTD 111, Rene 80, PWA 1483 and MarM 509 after 500 hours of exposure in atmosphere B with deposit fluxes of 0, 1.5 and 5  $\mu\text{g}/\text{cm}^2/\text{h}$  are shown in Figures 4.14 to 4.17. Compared to test A, surface degradation in test B appears confined to alloy precipitates in contact with or in close proximity to the surface (that may contact the surface outside of the imaging plane), or areas of the alloy adjacent to these precipitates.

The degree of internal sulphidation is greatly reduced compared to exposures in atmosphere A as expected with  $\text{SO}_2$  levels going from 90 ppm (A) to 4 ppm (B). All four alloys exhibit some evidence of internal sulphide species after 500 hours of exposure when a deposit was applied, these appear more numerous when the flux is greater (5 compared to 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$ ).

Figures 4.18 to 4.21 show BSE micrographs of GTD 111, Rene 80, PWA 1483 and MarM 509 after 500 hours of exposure in atmosphere C with deposit fluxes of 0, 1.5 and 5  $\mu\text{g}/\text{cm}^2/\text{h}$ . Similarly to exposures in atmosphere A, when a salt deposit is applied, all four alloys exhibit evidence of internal sulphidation and the formation of pit features. Internal sulphide species appear to have been able to form deeper into the alloy when adjacent to alloy precipitates that contact the surface of the sample. The effect of alloy precipitates on hot corrosion mechanisms is discussed further in Section 7.3.

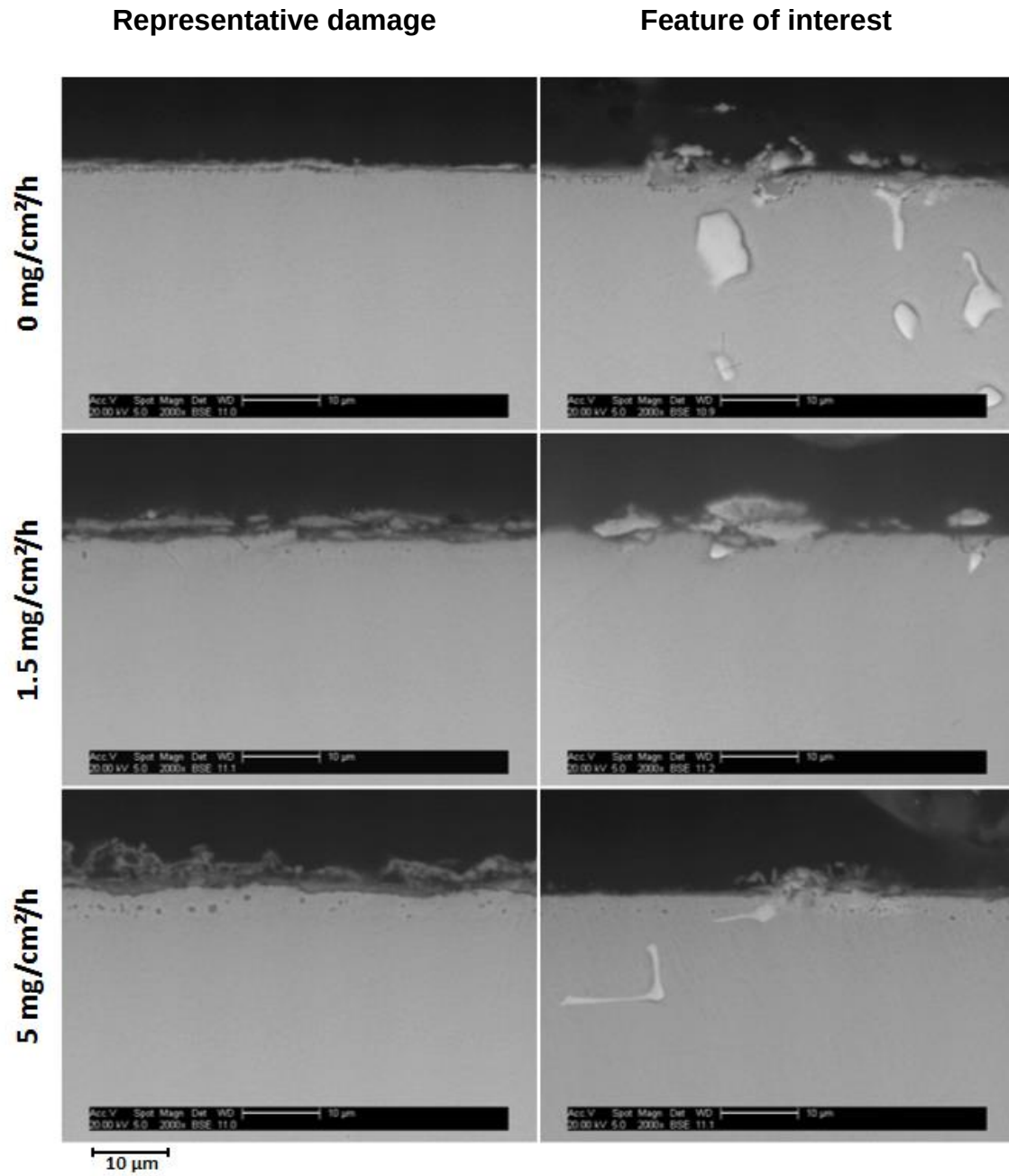


Figure 4.14: BSE micrographs of GTD 111 exposed for 500 hours in atmosphere B with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

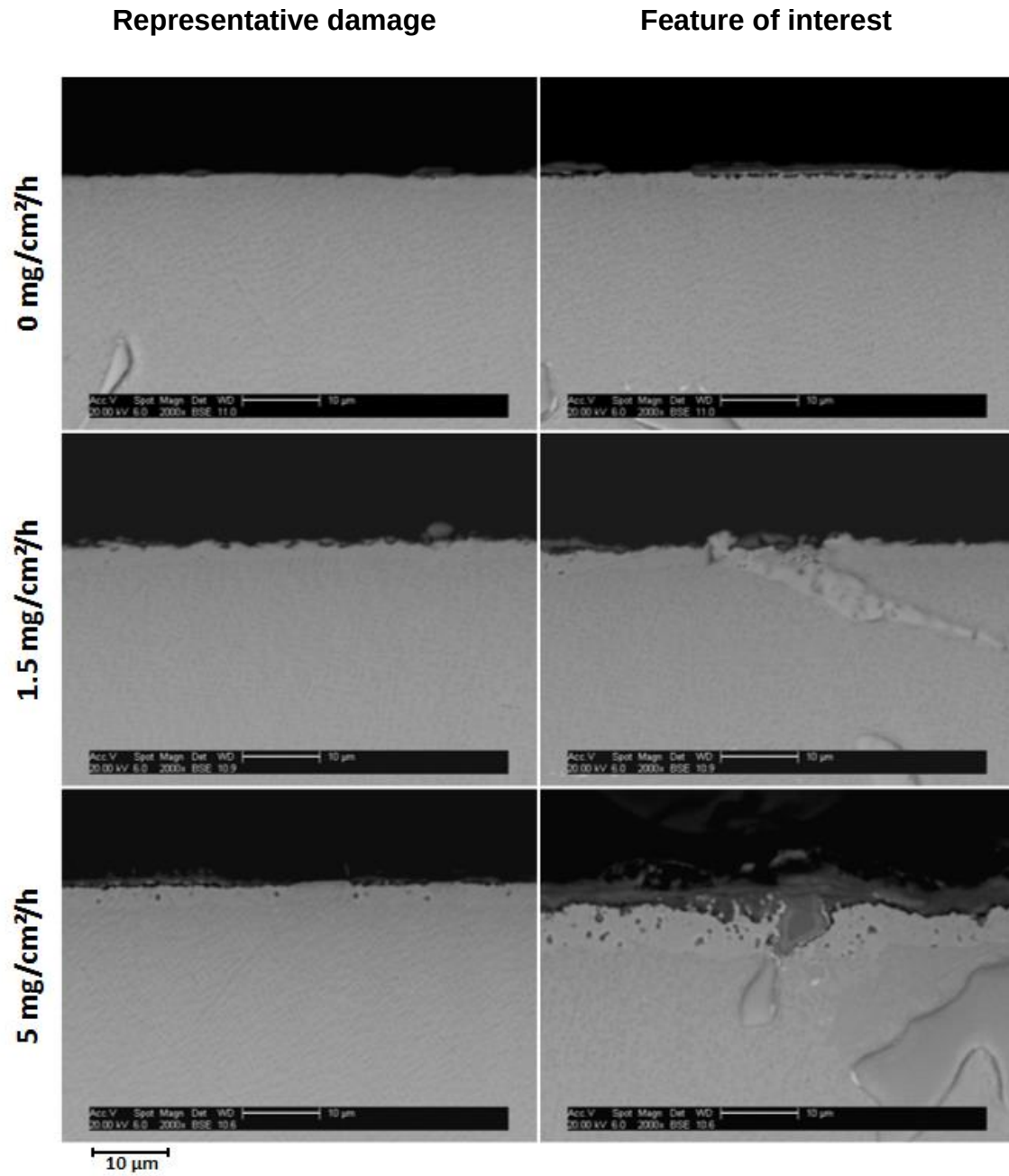


Figure 4.15: BSE micrographs of Rene 80 exposed for 500 hours in atmosphere B with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

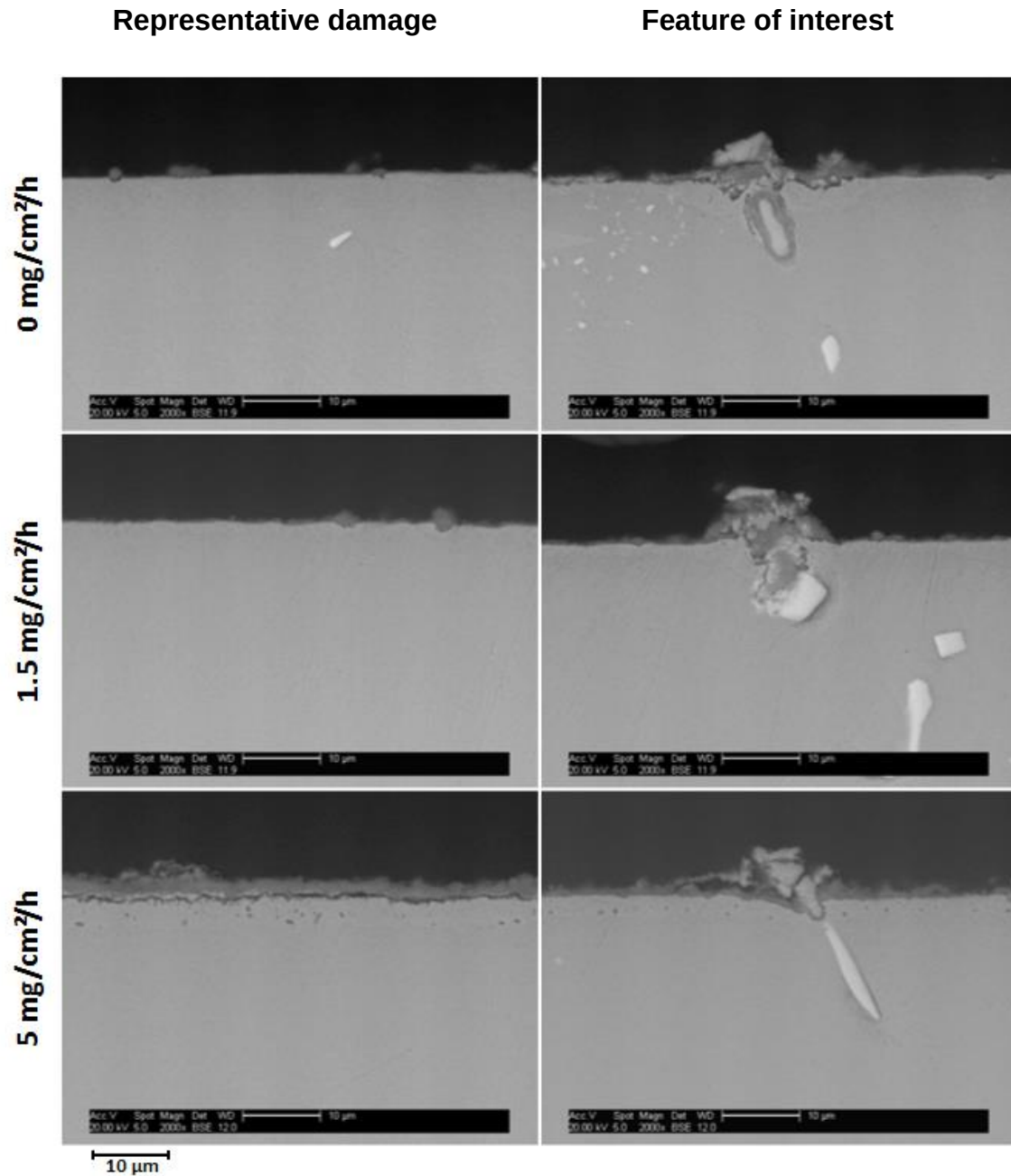


Figure 4.16: BSE micrographs of PWA 1483 exposed for 500 hours in atmosphere B with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

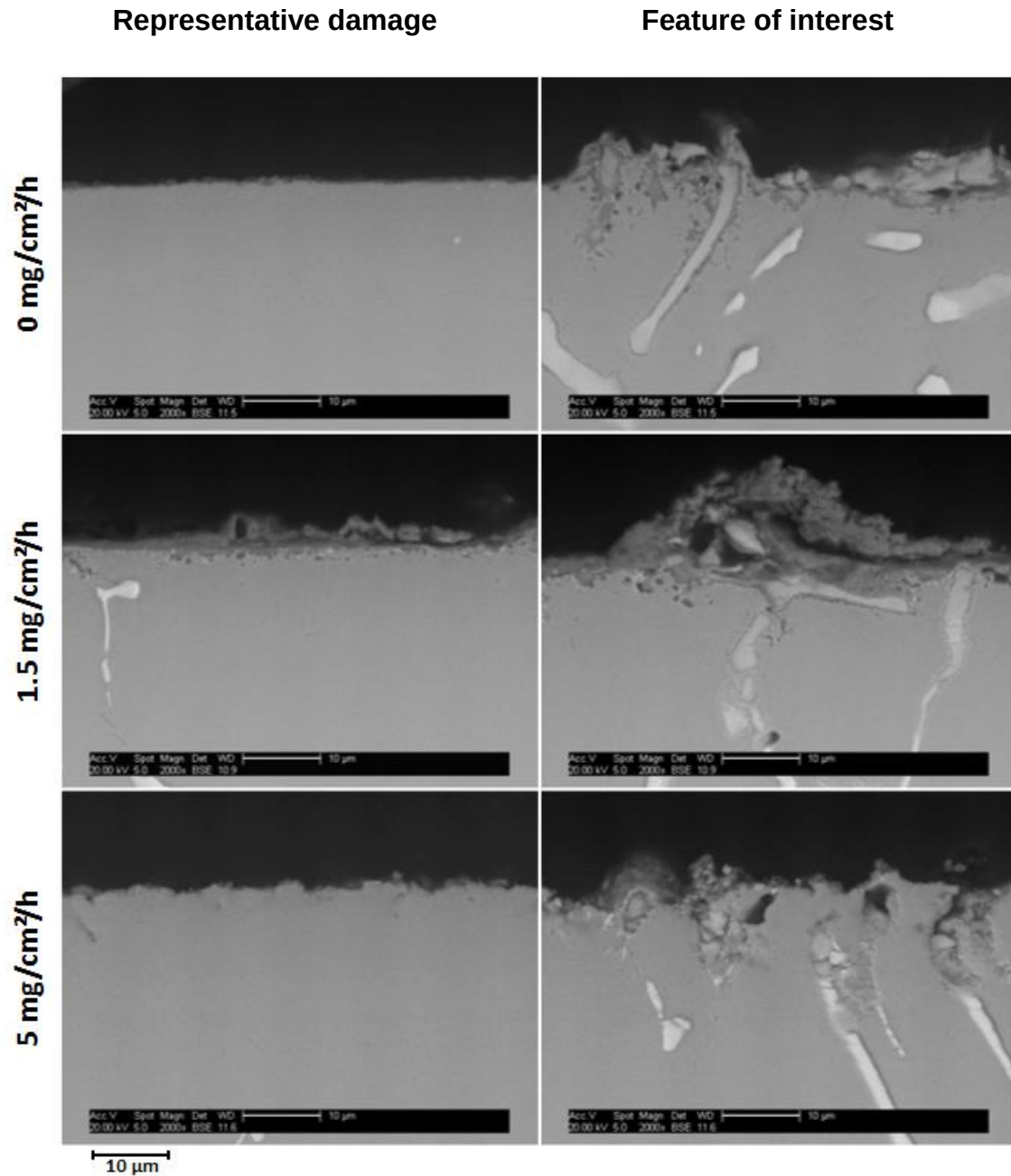


Figure 4.17: BSE micrographs of MarM 509 exposed for 500 hours in atmosphere B with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

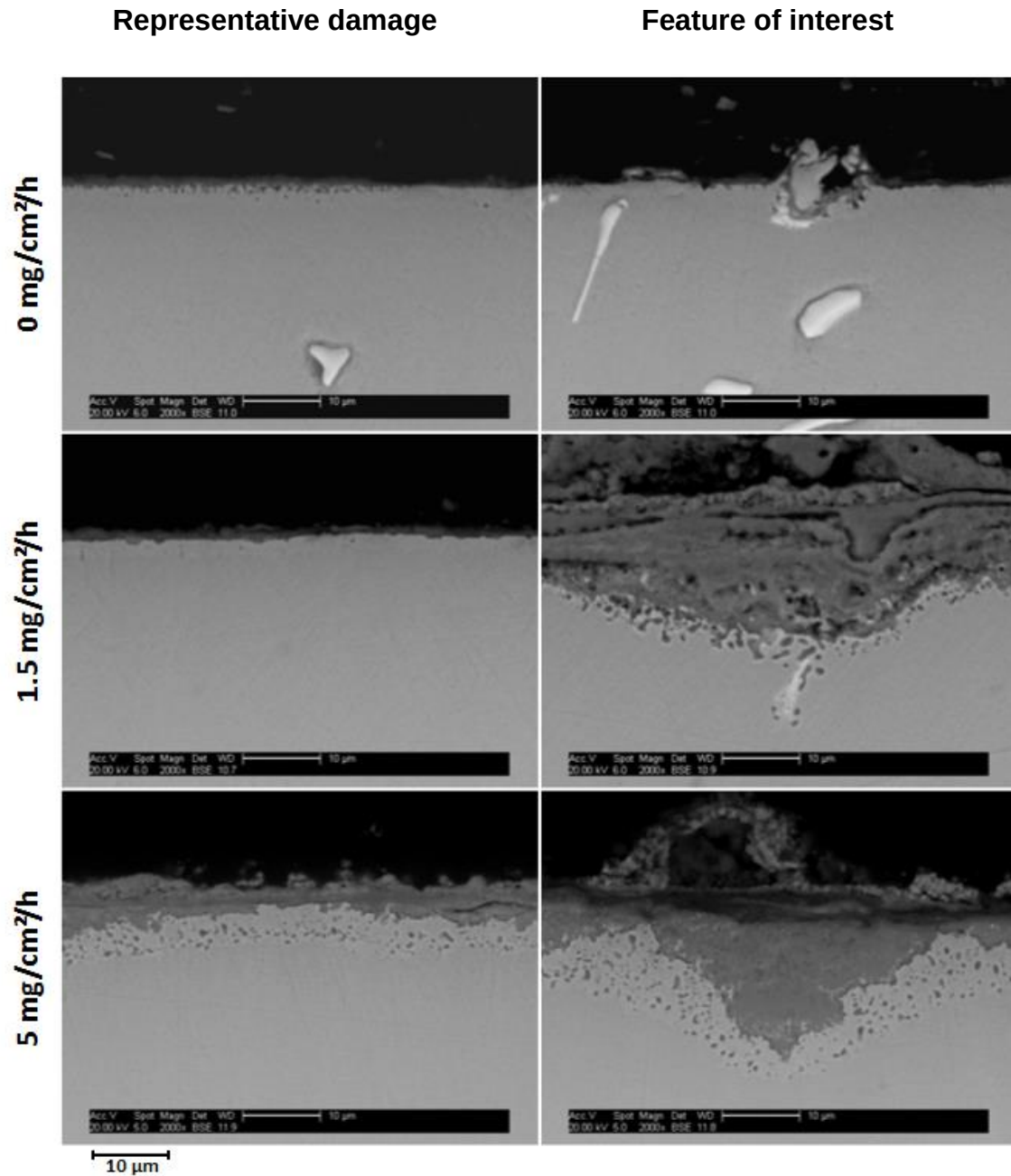


Figure 4.18: BSE micrographs of GTD 111 exposed for 500 hours in atmosphere C with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

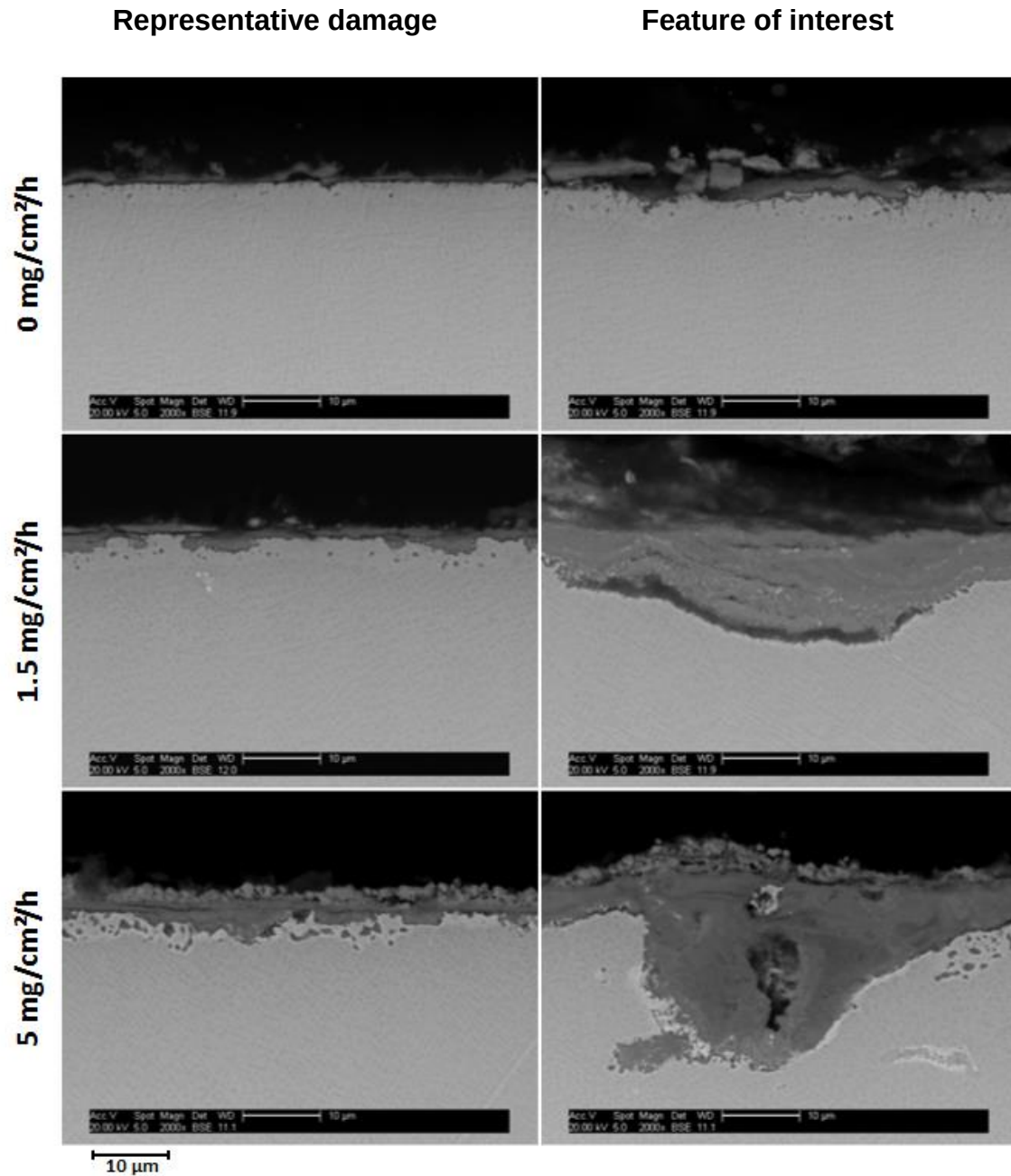


Figure 4.19: BSE micrographs of Rene 80 exposed for 500 hours in atmosphere C with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

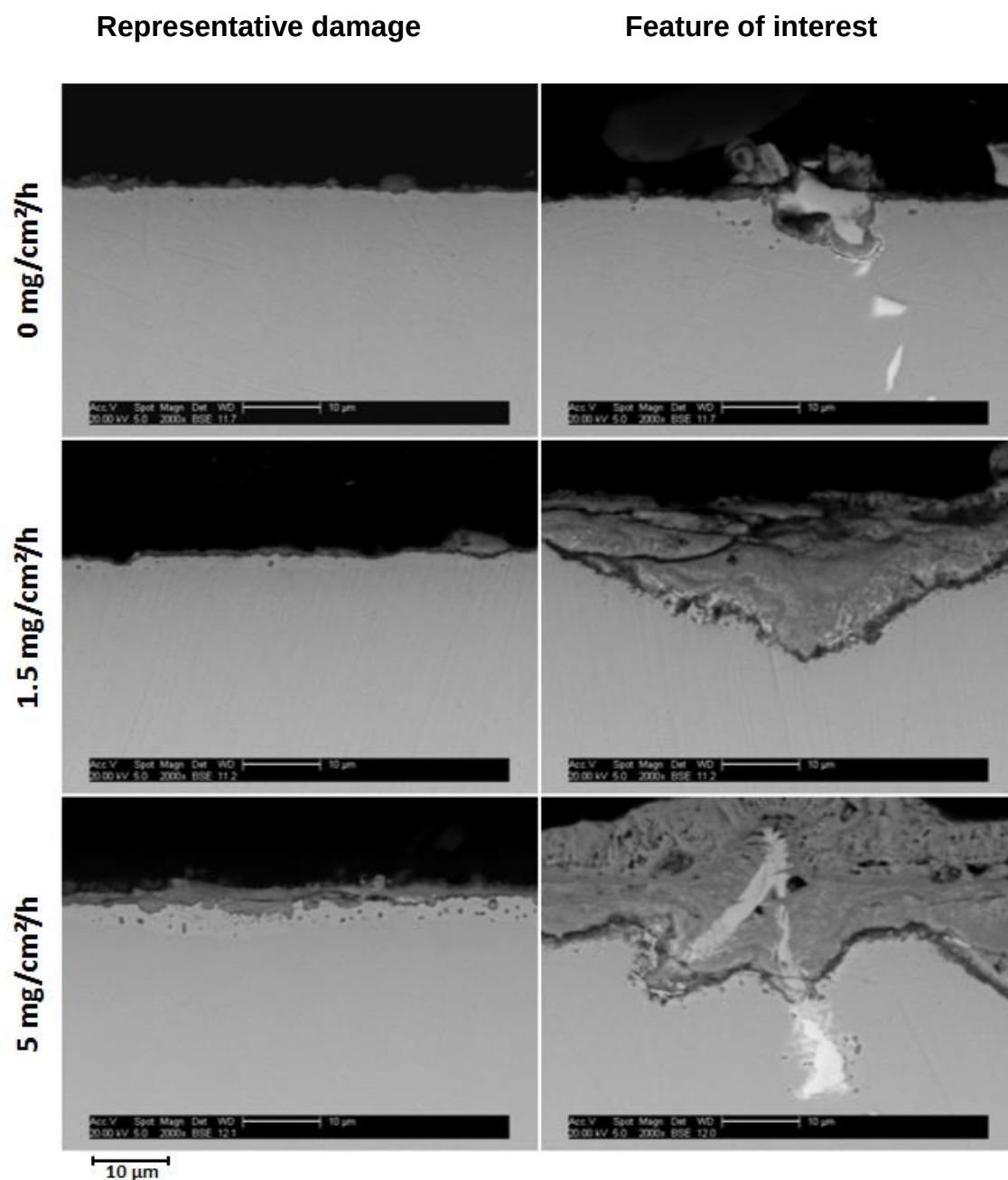


Figure 4.20: BSE micrographs of PWA 1483 exposed for 500 hours in atmosphere C with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

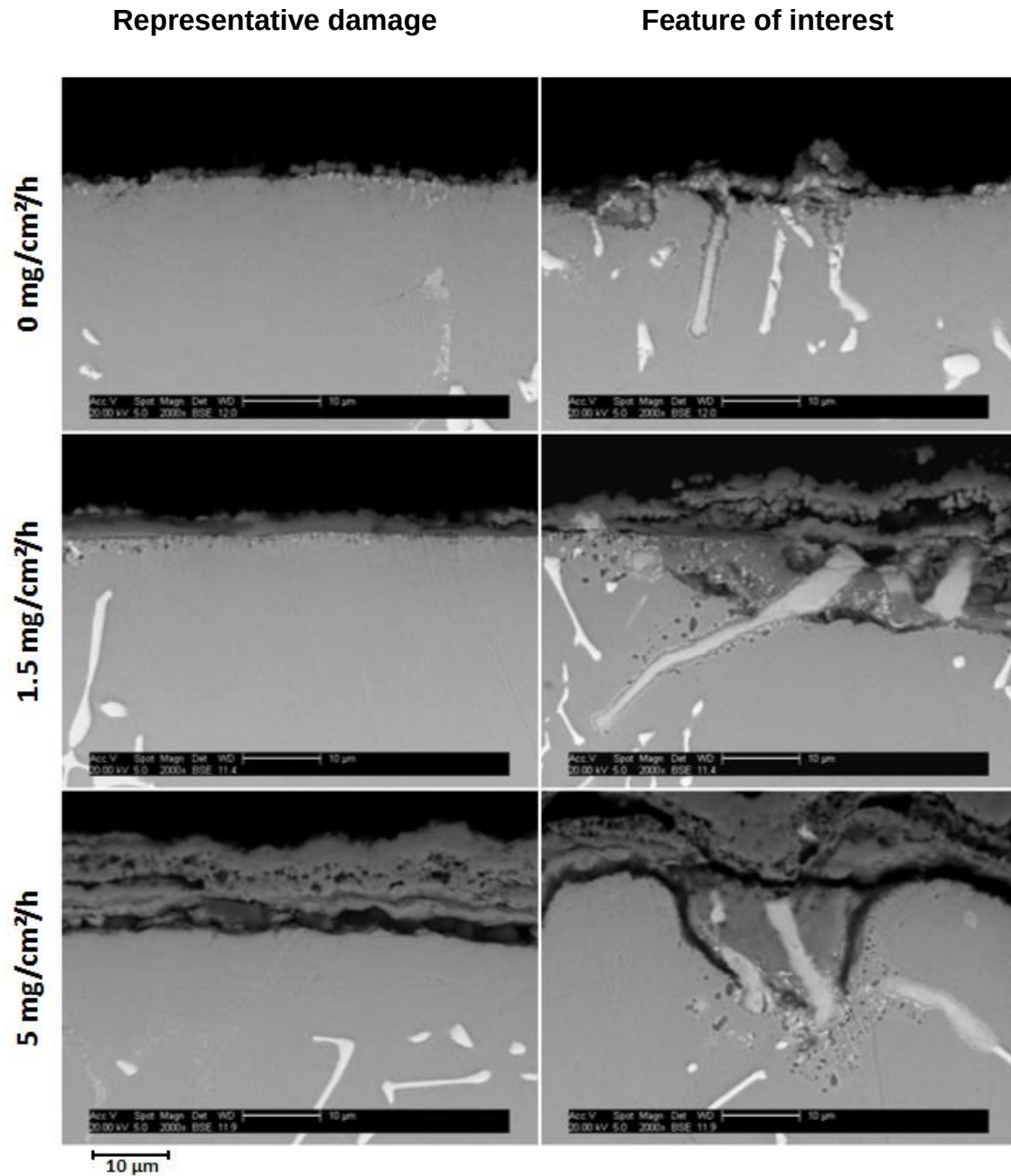


Figure 4.21: BSE micrographs of MarM 509 exposed for 500 hours in atmosphere C with deposit fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h. Left side images are representative of the majority of the surface, right side are corrosion features.

## 4.5 Material comparison

Resistance to environmental degradation is one important consideration in the materials selection for a gas turbine based power plant [21]. The alloys tested in this chapter were all candidate materials for use in the new H<sub>2</sub>IGCC power generation turbines. Figures 4.1 to 4.9 can be used to compare the median good metal and 4% exceedance values under all the exposure conditions. All materials exposed either without a deposit or in atmosphere B did not suffer significant metal loss and can therefore be discounted for the purposes of comparison. Due to the non-uniform degradation that is associated with type II hot corrosion [14], a certain amount of variability is to be expected in these findings. Despite this variability, MarM 509 consistently suffers the greatest degree of good metal loss at 4% probability of exceedance and the greatest median value in all but one exposure.

The higher concentration of SO<sub>2</sub> in atmosphere A (90 ppm) compared to atmospheres B and C (4-5 ppm) makes it more conducive to hot corrosion according to the literature [66]. Figures 4.22 and 4.23 show cumulative probability of good metal loss exceedance data in this more aggressive environment after 500 hours of exposure with an 80% Na<sub>2</sub>SO<sub>4</sub> 20% K<sub>2</sub>SO<sub>4</sub> deposit flux of 1.5 and 5 µg/cm<sup>2</sup>/hr. Of the data generated by the H<sub>2</sub>-IGCC series, these data can be considered the most suitable for comparing the hot corrosion performance of the materials. Figures 4.22 and 4.23 both show that the Co-based alloy MarM 509 has suffered the greatest degree of good metal loss of the materials tested. The Ni-based uncoated alloys GTD 111, Rene 80 and PWA 1483 are more difficult to rank in terms of corrosion performance. GTD 111 suffered a greater degree of good metal loss than either Rene 80 or PWA 1483 when the deposit flux was 5 µg/cm<sup>2</sup>/h. In contrast, when the deposit flux was 1.5 µg/cm<sup>2</sup>/h, Rene 80 had the greater degree of metal loss over the majority of the sample surface but PWA 1483 exhibited the deeper pits. The variability can be attributed to the aforementioned non-uniform nature of type II hot corrosion damage.

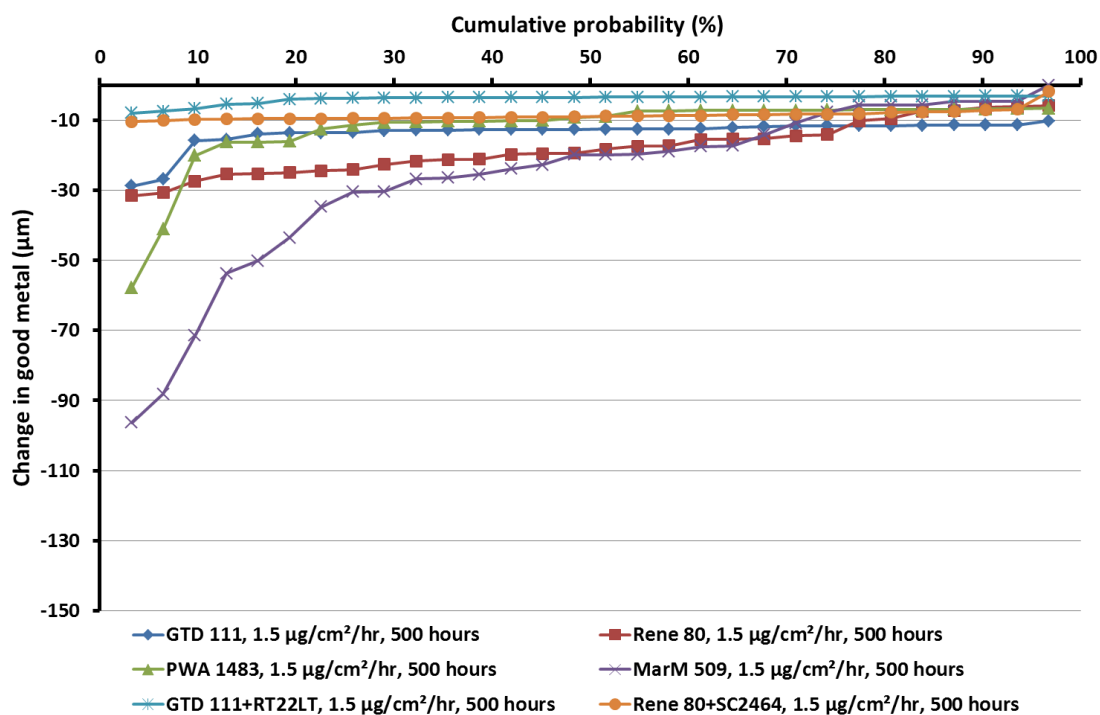


Figure 4.22: Dimensional metal loss as a function of probability for exposures of 500 hours in atmosphere A with a 1.5 µg/cm²/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit flux.

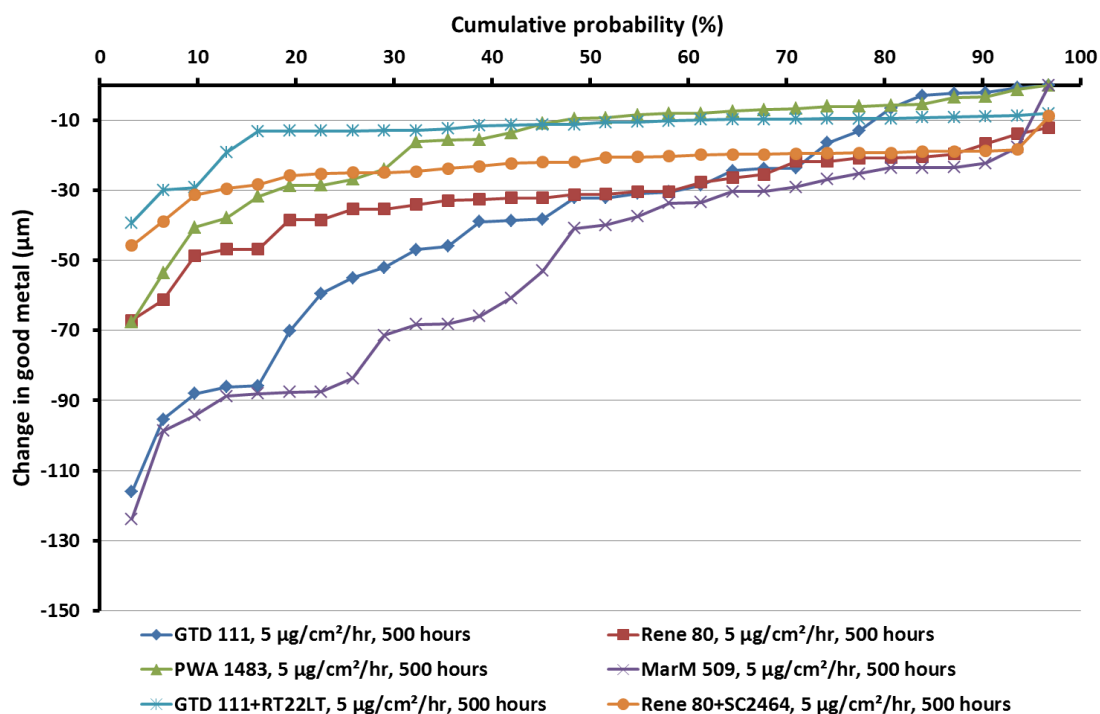


Figure 4.23: Dimensional metal loss as a function of probability for exposures of 500 hours in atmosphere A with a 5 µg/cm²/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit flux.

Cr has been identified in the literature as a key element in the corrosion resistance of alloys at 700 °C [66], [32]. This resistance is achieved through the formation of a protective  $\text{Cr}_2\text{O}_3$  scale. The elemental compositions of the test alloys are given in Table 3.1. The nominal Cr content is ranked in the following % weight order: MarM 509, 23.5%; Rene 80, 14%; GTD 111, 13.5%; PWA 1483, 12.2%.

The Cr content of MarM 509 is significantly greater than that of GTD 111, Rene 80 and PWA 1483, therefore MarM 509's relatively poor corrosion performance may seem surprising. The following factors may provide possible explanations for this phenomenon.

Small quantities of Al are understood to aid the formation of the protective oxide scale by allowing the selective oxidation of Cr at the gas phase or metal oxide interface interface [14]. This is sometimes described as the third element effect. MarM 509 does not use include Al as a constituent element and cannot take advantage of this selective oxidation mechanism.

BSE micrographs (Figures 4.10-4.21) show that corrosion features often form around refractory metal carbides located at the sample surface. MarM 509 has a greater proportion of these carbide phases compared to GTD 111, Rene 80 and PWA 1483. Three possible mechanisms through which surface carbide phases may affect the hot corrosion rate are as follows:

- Localized disruption of the protective scale caused by the precipitate phase creating an area deficient in Cr, the element that forms the protective scale.
- A transport route for corrosive species either through the precipitate or at the phase boundary between the alloy and the precipitate.
- Promoting the alloy induced acidic fluxing mechanism as described in Section 2.6.3.

Perhaps the most obvious difference between MarM 509 and GTD 111, Rene 80 and PWA 1483 is that it is one Co-based alloy compared to three Ni-based alloys. Literature describes Co-based superalloys as having good corrosion resistance

[14], [112] although it is not clear if this is because of the Co base or the addition of other elements and differences in their quantities.

Of the Ni-based alloys GTD 111, Rene 80 and PWA 1483 their responses in terms of hot corrosion resistance are inconsistent. This suggests that Cr content may not be the only factor governing hot corrosion resistance. These alloys have similar Cr contents so variations in other elements may become significant. As stated earlier, small additions of Al are known to promote chromia scale growth through selective oxidation or third element effect. Recent studies suggest that additions of Ta to the material system may improve corrosion resistance in environments conducive to type I hot corrosion [100], [101]. Since features associated with type I hot corrosion have been identified in the corrosion morphology observed in this chapter, it is possible that the Ta content may improve corrosion performance in the H<sub>2</sub>-IGCC conditions. The rank of nominal Al and Ta content of the Ni-based alloys is PWA 1483: Al 3.6%, Ta 5%; GTD 111: Al 3.3%, Ta 2.7%; Rene 80: Al 3%, Ta 0% in terms of weight %. This rank is the inverse of rank in terms of Cr content described earlier. It is possible that the corrosion resistance benefits gained through higher Cr contents is lost through deficiencies in other elements.

## **4.6 Atmospheric comparison**

The H<sub>2</sub>-IGCC hot corrosion test programme involved environments that simulate gas turbine exposure conditions resulting from different potential operating scenarios. The first atmosphere (A) results from considering one of the most likely system failures (that results in having to by-pass the final syngas desulphurization stage, water-gas shift reactor and CO<sub>2</sub> separation system) which would allow higher concentrations of H<sub>2</sub>S to be present within the syngas. Gas B simulates combusted natural gas as both a reference condition and the result of using a backup fuel should there be a failure of the whole gasification system. Condition C simulates the normal day-to-day running on H<sub>2</sub>-rich syngas. The different atmosphere compositions are as follows:

- Atmosphere A: Balance N<sub>2</sub>, 8.5% O<sub>2</sub>, 10.5% CO<sub>2</sub>, 90 ppm SO<sub>2</sub>, 5% H<sub>2</sub>O
- Atmosphere B: Balance N<sub>2</sub>, 9% O<sub>2</sub>, 6.5% CO<sub>2</sub>, 4 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O
- Atmosphere C: Balance N<sub>2</sub>, 10% O<sub>2</sub>, 1.25% CO<sub>2</sub>, 5 ppm SO<sub>2</sub>, 20% H<sub>2</sub>O

Figure 4.24 shows the cumulative probability of good metal loss exceedance plots for GTD 111, Rene 80, PWA 1483 and MarM 509 when exposed to atmospheres A, B and C for 500 hours with an 80% Na<sub>2</sub>SO<sub>4</sub> 20% K<sub>2</sub>SO<sub>4</sub> deposit applied cyclically every 100 hours with a flux of 1.5 µg/cm<sup>2</sup>/h. The rank of degradation under each atmosphere is consistent for each of the different alloys with atmosphere A being the most aggressive and atmosphere B being the least.

SO<sub>2</sub> is known to exist in equilibrium with SO<sub>3</sub> in combustion product gas with relative levels depending on temperature [73]. SO<sub>3</sub> in the gas phase is thought to sustain the hot corrosion reaction by contributing SO<sub>4</sub><sup>2-</sup> ions to the deposit melt in one of the possible hot corrosion reactions [76]. This may explain why the atmosphere with the highest concentration of SO<sub>2</sub> (atmosphere A) is also the most aggressive.

When comparing atmosphere B with atmosphere C, the difference in O<sub>2</sub>, CO<sub>2</sub> and SO<sub>2</sub> content are relatively minor and therefore unlikely to have a significant effect on hot corrosion mechanisms and hence the rate of attack. The difference in water vapour content may be more significant with atmosphere B containing 10% and C containing 20%. The majority of the literature for chromia forming alloys reports increased oxidation rates in atmospheres containing water vapour at high temperatures (700-1000 °C) [46]. Alloys designed for use in high temperature environments typically rely on the formation of a continuous and protective oxide scale to provide corrosion resistance [29]. The increase in oxidation rate is claimed to be a consequence of the degradation of the alloy's protective oxide scale with some authors attributing this to formation of CrO<sub>2</sub>(OH)<sub>2</sub> [46] and others attributing it to the formation of cracks [47]. The length of time before incubation transitions to propagation is thought to correspond to the degradation rate of the protective chromia scale. This may explain why the data shows greater metal loss under the atmosphere with a higher concentration of H<sub>2</sub>O while the concentration of SO<sub>2</sub> is approximately the same.

The relationship between hot corrosion and atmospheric water vapour content is further explored in Chapter 5.

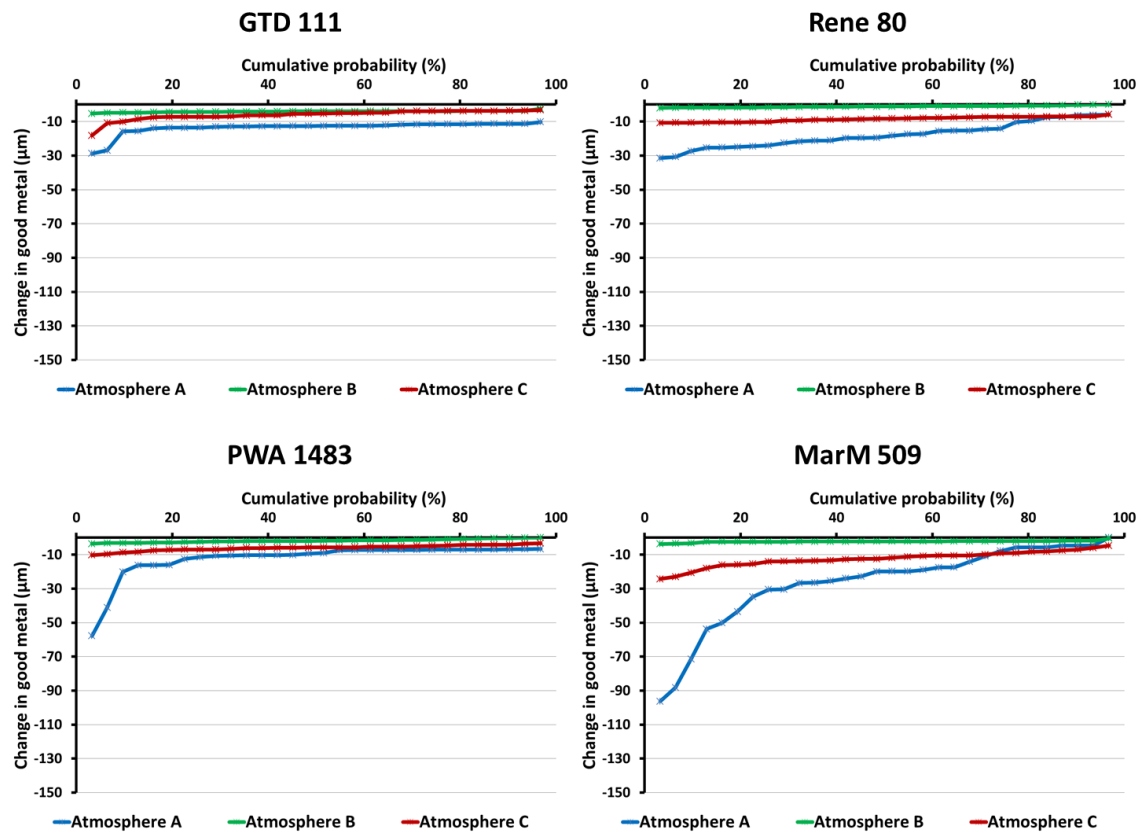
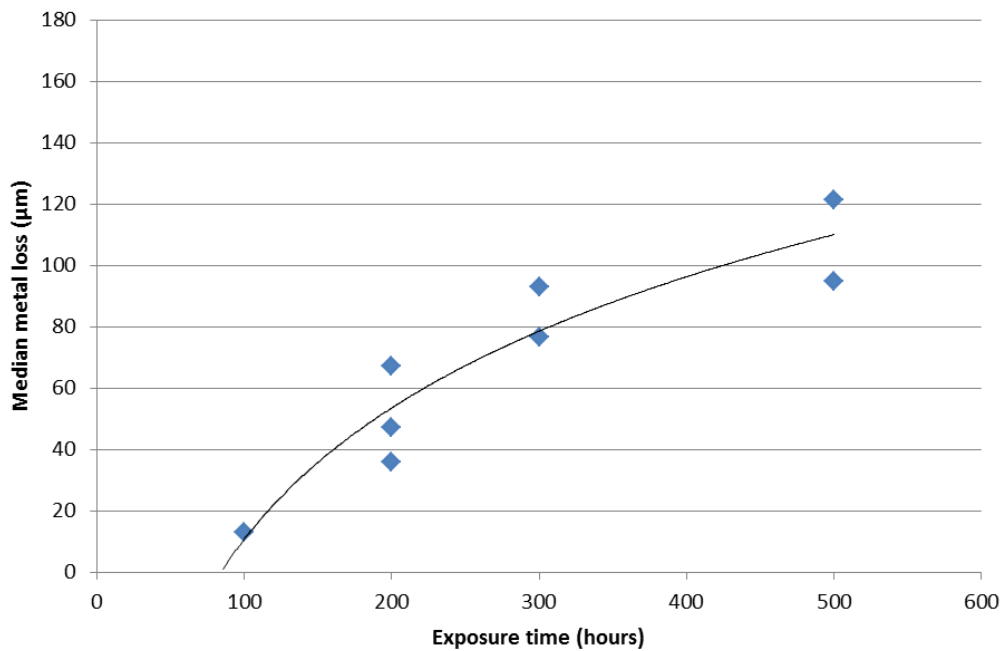


Figure 4.24: Dimensional metal loss as a function of probability for GTD 111 (top left) Rene 80 (top right) PWA 1483 (bottom left) and MarM 509 (bottom right). Materials exposed at 700 °C for 500 hours with a 1.5 μg/cm<sup>2</sup>/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

## 4.7 Reaction kinetics

The hot corrosion mechanism has been described in the literature (Section 2.6.1) as occurring in two stages [74]. These are an incubation period characterised by relatively low metal loss where the protective oxide scale undergoes modification to allow for rapid metal loss in the second stage referred to as propagation. From an engineering perspective the length of the incubation stage is important since the rapid degradation associated with the propagation stage is likely to herald the imminent failure of a component.

Other studies have used empirical data to determine the length of the incubation period under accelerated hot corrosion test conditions [32], [99]. Such empirical models can use data taken at points in time when the sample is in propagation and extrapolate backwards either to the X axis (zero metal loss) or a second line extrapolated using data points in the incubation period. Median metal loss values convey if the majority of the sample surface degradation distribution is in incubation or propagation and are often used in such plots. Figure 4.25 is an example empirical model for the superalloy Udimet 720 exposed in an atmosphere of air with 300 ppm SO<sub>2</sub> at 700°C with a 98 mol% Na<sub>2</sub>SO<sub>4</sub> 2 mol% NaCl deposit applied with a flux of 10 µg/cm<sup>2</sup>/h of. Under these conditions the empirical model predicts an incubation period of approximately 80 hours.



**Figure 4.25: Median metal loss for U720 at 700°C with a deposition flux of 10 µg/cm<sup>2</sup>/h of a 98% Na<sub>2</sub>SO<sub>4</sub> 2% NaCl deposit [32].**

The methodology employed in these tests produced data distributions at 100, 300 and 500 hours of exposure. Although the number of data points available are insufficient to build reliable empirical models, useful information as to the approximate length of the incubation period of each material can be derived.

A certain amount of good metal loss may be attributed to error in the measurement technique (discussed in Section 7.1). In addition, due to the possible self-healing nature of the protective scale on some alloys, there may be a small degree of good metal loss while the corrosion mechanism remains in incubation. Because error values are not a constant, any hypothetical value of good metal loss used to categorise if a sample is in incubation or propagation will not be reliable. In this study, an arbitrary value of 10 µm of metal loss was chosen to distinguish between incubation and propagation.

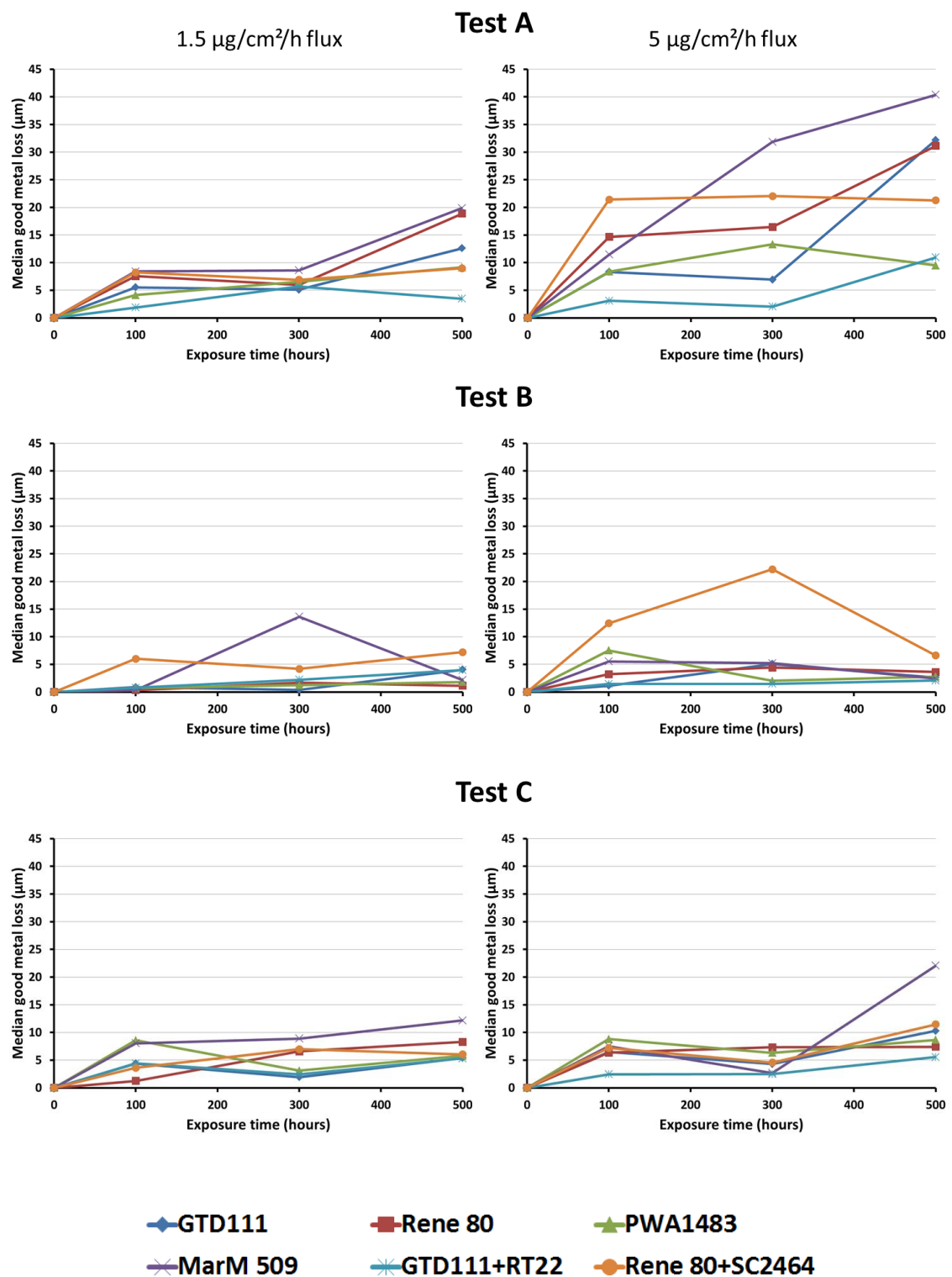


Figure 4.26: Median good metal loss plots over time at 700 °C with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit applied at a flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  (left) and 5  $\mu\text{g}/\text{cm}^2/\text{h}$  (right).

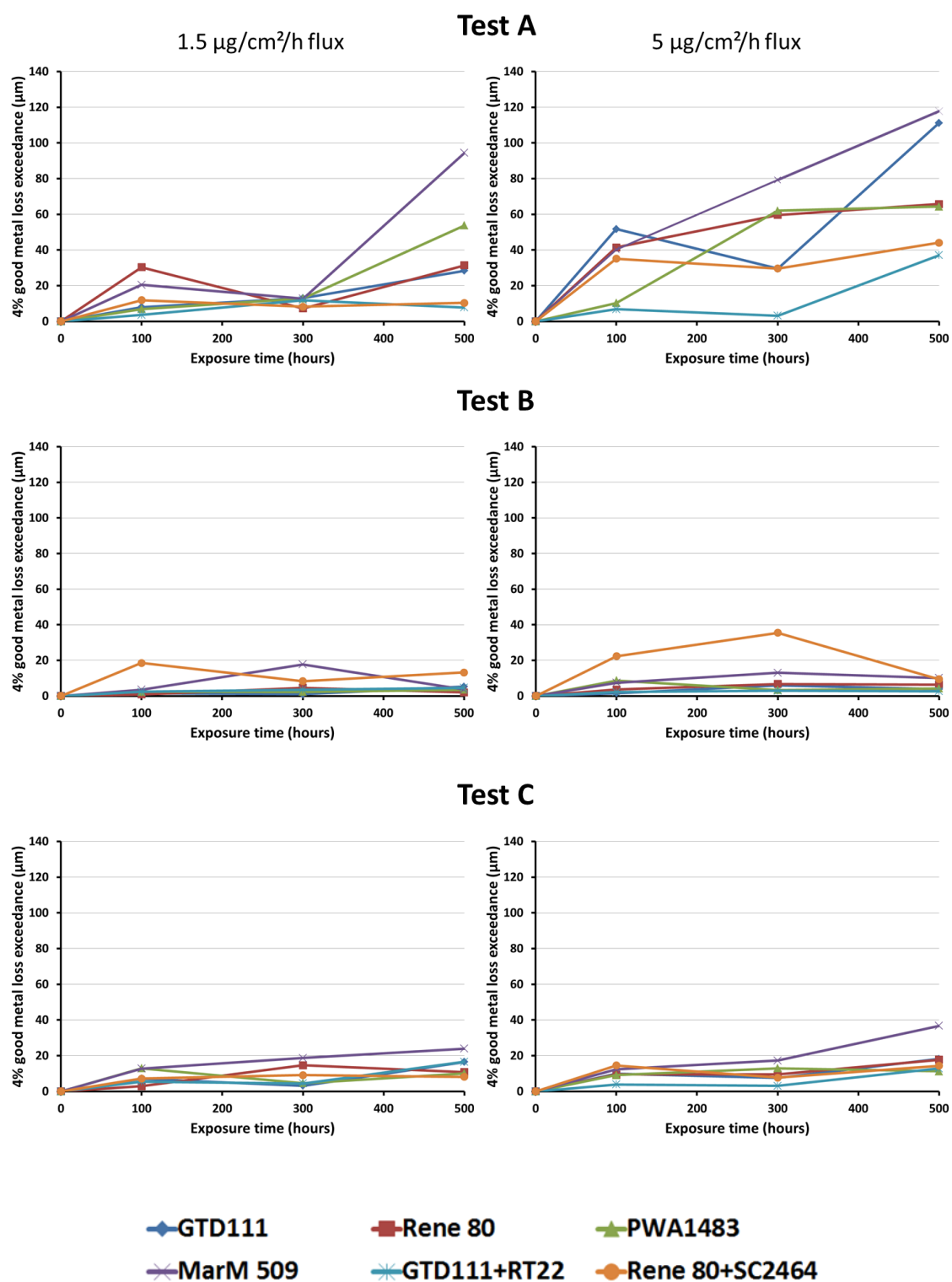


Figure 4.27: 4% exceedance values over time at 700 °C with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit applied at a flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  (left) and 5  $\mu\text{g}/\text{cm}^2/\text{h}$  (right).

Figures 4.26 and 4.27 show the median good metal loss and 4% exceedance trends over time for the samples exposed with a 80% Na<sub>2</sub>SO<sub>4</sub> 20% K<sub>2</sub>SO<sub>4</sub> deposit applied at a flux of 1.5 µg/cm<sup>2</sup>/h and 5 µg/cm<sup>2</sup>/h. The data for exposures with no deposit applied was omitted since negligible metal loss can be observed in Figures 4.1, 4.4 and 4.7 with some exceptions that may be attributed to non-systematic error.

Over time, the good metal loss trend for a material undergoing hot corrosion degradation is expected to initially remain relatively low before increasing rapidly. These features should correspond to the incubation stage and propagation stage of the hot corrosion mechanism respectively. Generally speaking this kind of trend can be seen in the data presented in Figure 4.26. Some data trends appear to peak at either 100 or 300 hours; it is not logically possible for this to happen and such trends must be explained by either systematic or non-systematic errors.

Some data trends do not pass the 10 µm threshold over the 500 hour period. For the median value (Figure 4.26) this indicates the majority of the sample surface likely remaining in incubation. For the 4% exceedance value (Figure 4.27) this indicates at least 96% of the surface remaining in incubation.

In test A with a deposition flux of 1.5 µg/cm<sup>2</sup>/h, PWA 1483 and the metallic coatings RT22 and SC2464 remain in incubation over 500 hours over the majority of their surfaces (median value) while transition into propagation over at least 4% of their surfaces occurs before 300 hours of exposure. In test A with a deposition flux of 5 µg/cm<sup>2</sup>/h, the only material with the majority of its surface remaining in incubation was PWA 1483; this observation is marginal with a median good metal loss value of 9.5 µm at 500 hours, but a median metal loss value of 13.3 µm was measured at 300 hours. The 4% exceedance value shows that at the 5 µg/cm<sup>2</sup>/h flux, at least 4% of the PWA 1483 surface entered into propagation before 300 hours of exposure.

In test B. Figures 4.26 and 4.27 generally show that the majority of the surfaces of all the materials have remained in incubation at both levels of flux. The exceptions to this are for the metallic coating SC2464 and the MarM 509 sample exposed for 300 hours at a flux of 1.5 µg/cm<sup>2</sup>/h. The greater roughness of

SC2464 and brittle nature of metallic coatings that could be damaged during preparation may possibly account for the greater metal loss values of SC2464.

In test C with a flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$  all the materials except MarM 509 remain with the majority of their surface in incubation based on median metal loss (Figure 4.26). When the flux is increased to  $5 \mu\text{g}/\text{cm}^2/\text{h}$  it is only Rene 80, PWA 1483 and RT 22 that have remained in incubation. Relative to the other materials systems, the 4% exceedance values (Figure 2.27) of MarM 509 are greater after 300 and 500 hours of exposure for both fluxes.

In test A with a deposit flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$  the materials that did not remain in incubation over the 500 hour period were GTD 111, Rene 80 and MarM 509. All three of these uncoated alloys entered into propagation over the majority of their surface at a point between 300 and 500 hours. The 4% exceedance values indicate that parts of Rene 80 and MarM 509 could have entered propagation before 100 hours of exposure time. When the flux is increased to  $5 \mu\text{g}/\text{cm}^2/\text{h}$ , the length of the incubation period for the majority of the surface of Rene 80, MarM 509 and the coating SC2464 appears to be shortened to below 100 hours of exposure whereas for GTD 111 and PWA 1483 it is shown to be between 300 and 500 hours.

In test C with a deposit flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$ , the only material to progress into propagation over the majority of its surface was MarM 509. With a flux of  $5 \mu\text{g}/\text{cm}^2/\text{h}$ , GTD 111, Rene 80, PWA 1484, MarM 509 and SC2464 all surpass the  $10 \mu\text{m}$  threshold, indicating that the majority of their surfaces have entered into propagation, at a point between 300 and 500 hours.

Figures 4.26 and 4.27 both show that increasing the deposit flux consequently shortens the length of the incubation stage of the hot corrosion mechanism. This appears to be true for both the bare alloys and the alloy coatings. This effect is not seen in test B, but this is probably due to the exposure times not being long enough to observe the transition into propagation.

## 4.8 Effect of flux

Figure 4.28 shows the median good metal loss (left images) and 4% exceedance values (right graphs) for exposures in tests A, B and C at 700 °C with 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposition fluxes of 0, 1.5 and 5 µg/cm<sup>2</sup>/h after 500 hours of exposure.

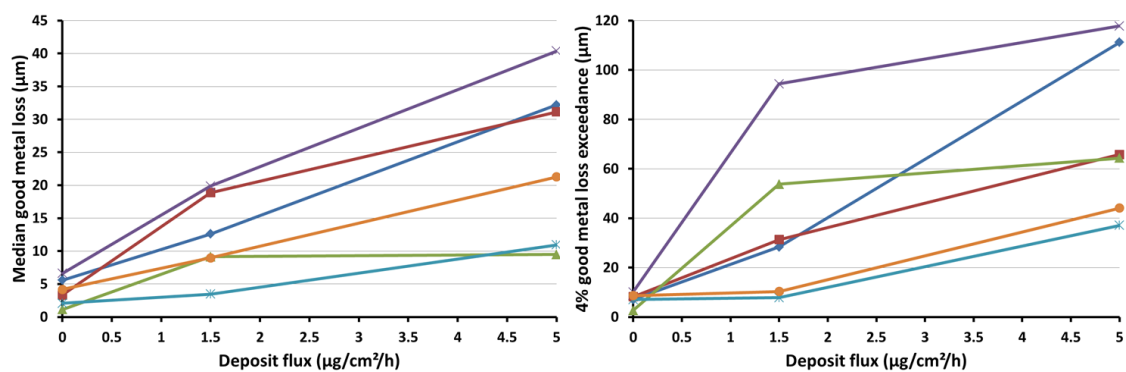
The degradation mechanism occurring in the absence of a deposit is likely dominated by oxidation and not hot corrosion. For this reason, good metal loss data for a deposit flux of 0 µg/cm<sup>2</sup>/h may not be important to the effect of deposit flux on degradation caused by hot corrosion. In addition to this, data sets that do not leave incubation or are in incubation at a deposit flux of 1.5 µg/cm<sup>2</sup>/h but in propagation at 5 µg/cm<sup>2</sup>/h may be unreliable. Finally, the effect of scatter for the 4% exceedance value is greater than for the median value.

Most of the median data for test A is either in propagation or close to propagation with a deposit flux of 1.5 µg/cm<sup>2</sup>/h. The gradient between a flux of 1.5 and 5 µg/cm<sup>2</sup>/h is given below. Of these, PWA 1483 stands out as significantly lower than the others. More data could determine if this is a factor caused by error or scatter, or if it is that the median value is still in incubation with a flux of 1.5 µg/cm<sup>2</sup>/h.

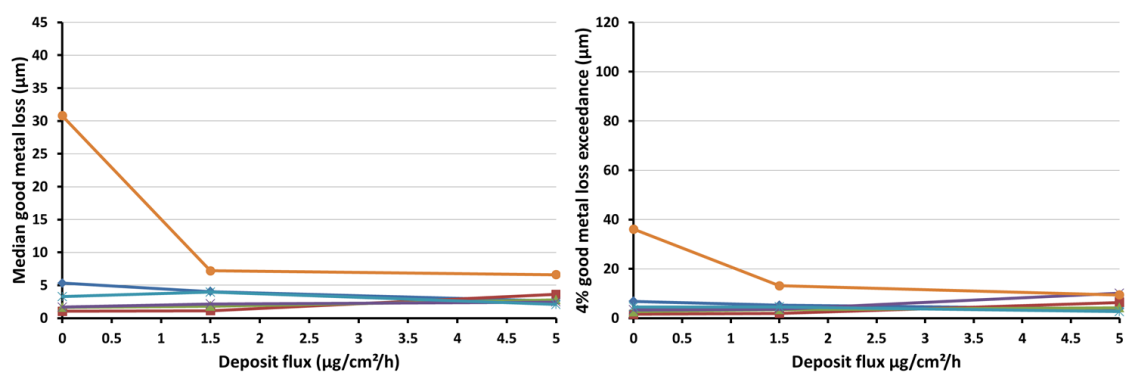
- GTD 111: 5.6 µm/µg/cm<sup>2</sup>/h
- Rene 80: 3.5 µm/µg/cm<sup>2</sup>/h
- PWA 1483: 0.1 µm/µg/cm<sup>2</sup>/h
- MarM 509: 5.8 µm/µg/cm<sup>2</sup>/h
- RT22: 2.1 µm/µg/cm<sup>2</sup>/h
- SC2464: 3.5 µm/µg/cm<sup>2</sup>/h

It is likely that as deposition flux is increased there will be a point of saturation where increasing the flux further no longer shortens the length of incubation. This value may be different for differing gas compositions as the deposit melt is thought to be stabilized by SO<sub>3</sub> in the gas phase. Further research could be carried out to explore this relationship in addition to factors such as different alloys, deposit types and atmospheric water contents.

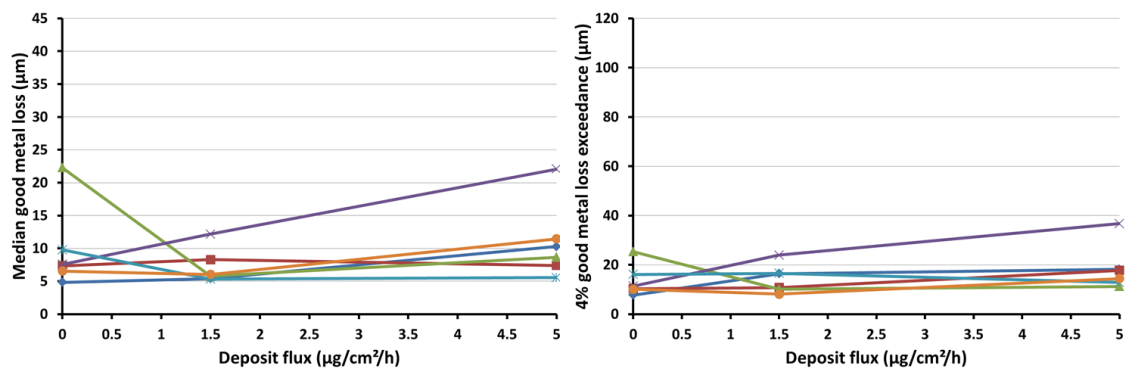
### Test A



### Test B



### Test C



◆ GTD111      ■ Rene 80      ▲ PWA1483  
 ✕ MarM 509      ✱ GTD111+RT22      ◆ Rene 80+SC2464

Figure 4.28: Median good metal loss (left) and 4% exceedance values (right) after 500 hours of exposure in atmosphere A at 700 °C with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit flux of 0, 1.5 and 5  $\mu\text{g}/\text{cm}^2/\text{h}$ .

## 4.9 Corrosion morphology

Figures 4.10 to 4.12 show backscattered electron images of GTD 111, Rene 80, PWA 1483 and MarM 509 after 500 hours of exposures in atmospheres A, B and C. After exposure in atmospheres A and C, samples exhibit features indicative of both type I (internal sulphides) and type II (pits) hot corrosion. This mixed mode of hot corrosion is confirmed using EDX mapping in Figures 4.29 and 4.30 for GTD 111 and MarM 509 after 500 hours of exposure in atmosphere A with a deposition flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$ .

The GTD 111 map (Figure 4.29) shows that corrosion product both inside the pit and along the sample's surface are oxides that have formed in two layers. The inner layer is made up mostly of Cr, Ti and Al oxides and the outer layer of mostly Ni and Co oxides. This corrosion product does not appear to contain any S and there is no evidence of the alkali metals from the deposit. The multiple layers of corrosion products is a classic feature of type II hot corrosion where elements with a greater affinity for  $\text{O}_2$  (such as Cr and Al) precipitate out deeper in the region undergoing corrosion attack, whereas complex ions of less reactive elements (such as Ni and Co) migrate to the gas phase interface where there is a higher partial pressure of  $\text{O}_2$  before precipitating.

The internal damage is made up of S-containing species (most likely to be sulphides) that have diffused inwards; this area also appears to be depleted of Cr. This even distribution of internal sulphides closely matches type I corrosion damage which is usually associated with higher temperature exposures

As with the Ni-based GTD 111 map, the Co-based MarM 509 (Figure 4.30) also exhibits evidence of mixed mode corrosion albeit with a lesser degree of internal damage. Within the MarM 509 corrosion product and extending into the alloy, there are a series of W and Ta carbide precipitates. The effect these precipitates may have on the corrosion process is further discussed in Section 7.3.

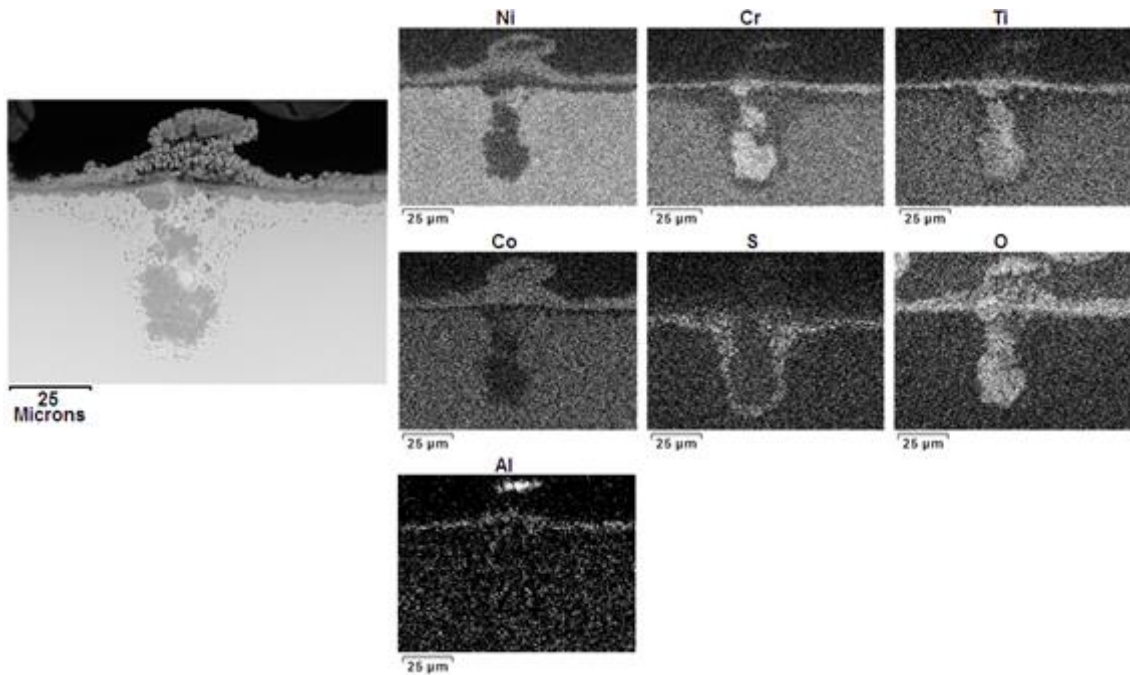


Figure 4.29: BSE image and EDX map of a corrosion feature on GTD 111 after 500 hours of exposure in atmosphere A with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit with a flux of 1.5 μg/cm<sup>2</sup>/h.

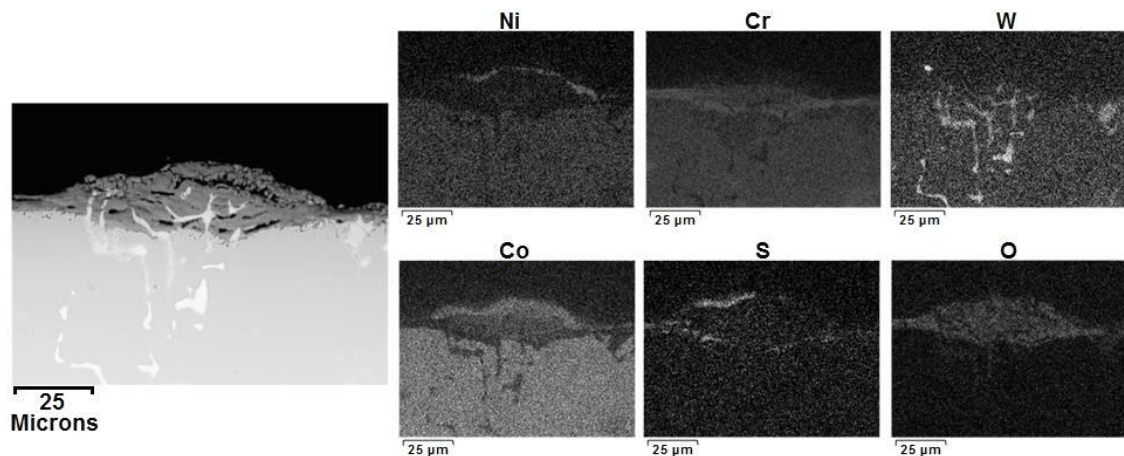


Figure 4.30: BSE image and EDX map of a corrosion feature on MarM 509 after 500 hours of exposure in atmosphere A with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit with a flux of 1.5 μg/cm<sup>2</sup>/h.

## **5. The effect of water vapour on Type II hot corrosion**

### **5.1 The effect of water vapour: Introduction**

In Chapter 4, the hot corrosion performance of several superalloys in different atmospheres was compared. Of these atmospheres, tests B and C varied significantly only in their water vapour concentration (10% and 20% vol.) as the only significant difference. An increase in the rate of good metal loss was observed at the higher level of water vapour and ESEM analysis revealed hot corrosion in the form of a mixed pitting and internal attack.

In this chapter, the relationship between water vapour concentration and type II hot corrosion is investigated in greater detail. In Chapter 4, the observation of water vapour concentration increasing the corrosion rate was made at relatively low levels of SO<sub>2</sub> (4-5 ppm). In this chapter, to ensure a stable hot corrosion regime and to produce data comparable to other studies (for example [104], [32], [99]), a concentration of 300 ppm SO<sub>2</sub> was chosen.

To provide a baseline exposure condition to which atmospheres containing differing levels of water vapour could be compared, one set of exposures was carried out in the absence of water vapour. Two following sets of exposures with atmospheres containing 10% and 20% water vapour made up the scope of this avenue of research.

### **5.2 The effects of water vapour: results**

#### **5.2.1 0% water vapour results**

Figures 5.1 and 5.2 show the good metal loss exceedance plots for PWA 1483 and MarM 509 respectively. PWA 1483 exhibits little good metal loss at exposure times of 50 and 100 hours indicating the hot corrosion mechanism has remained in incubation over these periods. At some point between 100 and 200 hours of exposure, PWA 1483 appears to transition into the propagation stage of the

damage mechanism displaying rapid metal loss over the majority of the alloy surface. This trend has continued to the 500 hour maximum test exposure period.

Similarly to PWA 1483, MarM 509 (Figure 5.2) appears to have remained in incubation for the first 100 hours of exposure with negligible metal loss. At 200 hours parts of the alloy surface appear to have transitioned into propagation, with metal loss greater than 10  $\mu\text{m}$ , while the majority of the sample has remained in incubation. By 500 hours of exposure time, the majority of the alloy surface (approximately 70%) has entered propagation.

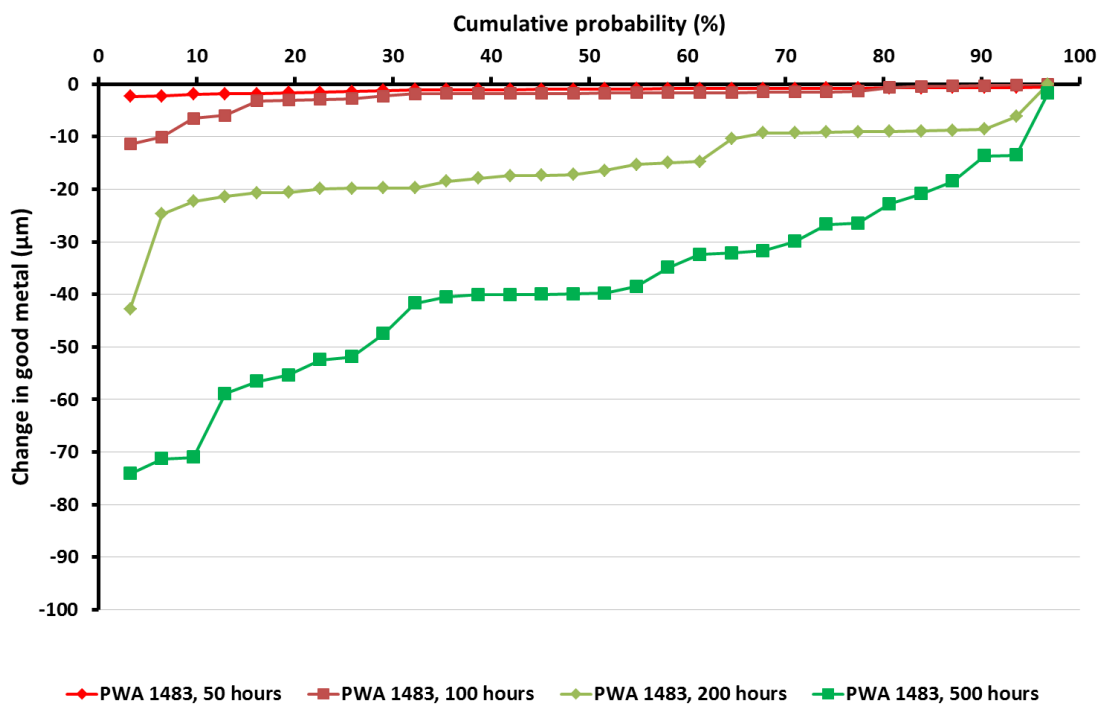


Figure 5.1: : Cumulative probability plot of good metal loss for PWA 1483 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm  $\text{SO}_2$  and 0%  $\text{H}_2\text{O}$ . The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20 (Na/K) $_2\text{SO}_4$ .

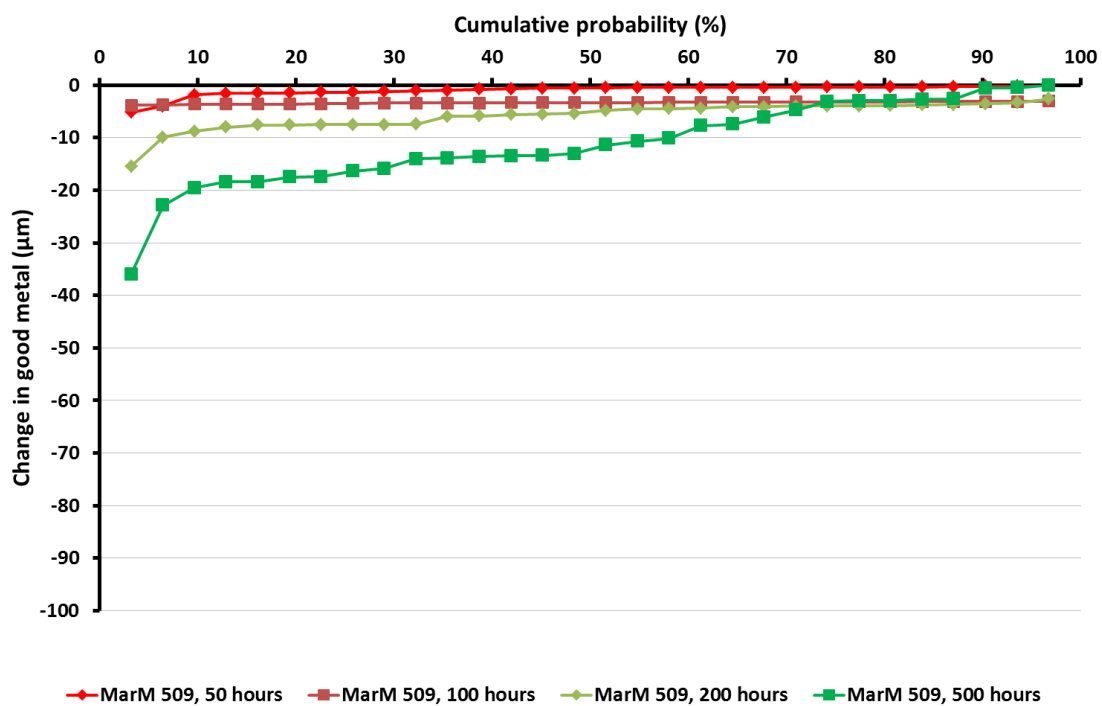
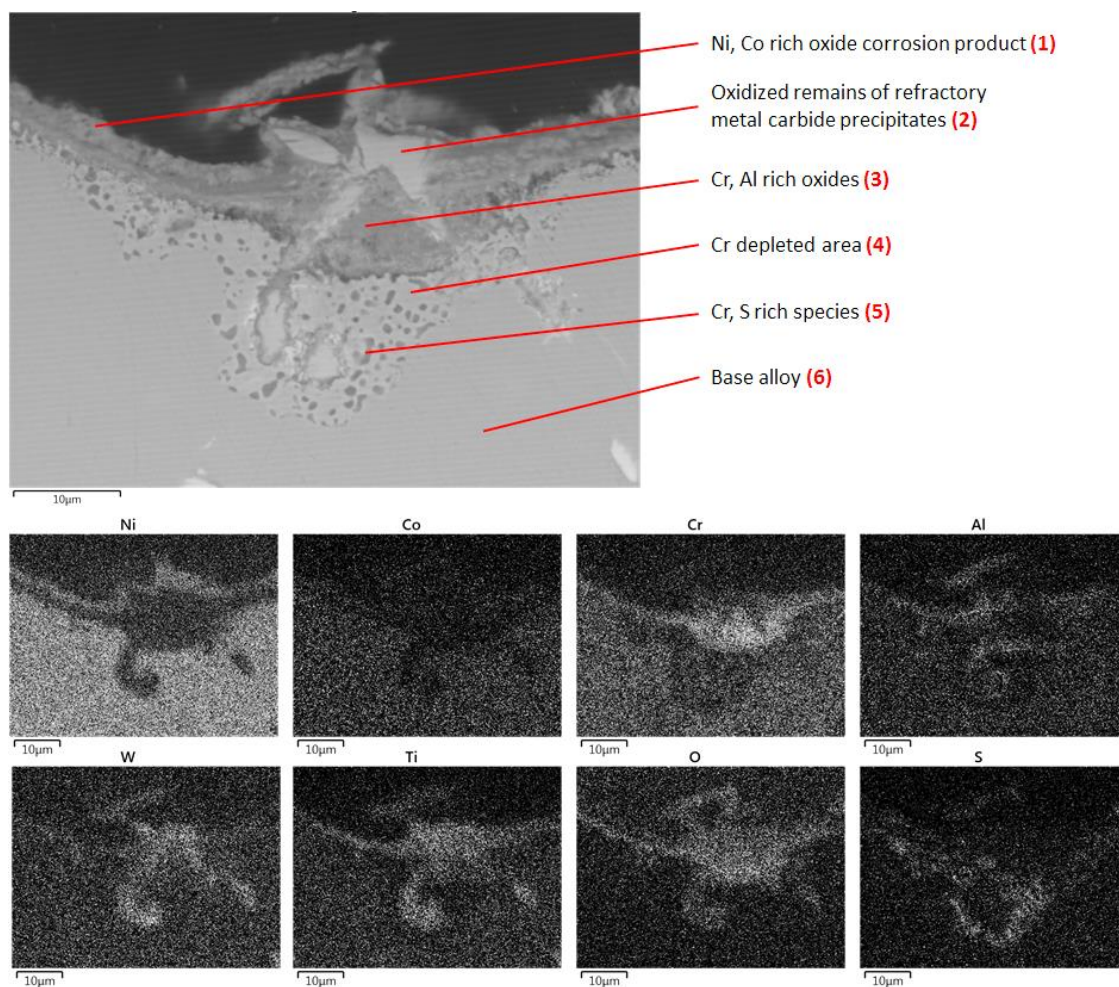


Figure 5.2: Cumulative probability plot of good metal loss for MarM 509 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O. The deposit flux was 1.5 μg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.

### 5.3.2 0% water vapour micrographs

Figure 5.3 shows a backscattered electron image with point quantification and EDX map of a corrosion feature on PWA 1483 after 500 hours exposure. The morphology shown in Figure 5.3 exhibits features associated with both internal sulphidation and pitting. The depth at which S or sulphides were observed is greatest (approximately 12  $\mu\text{m}$ ) at the base of the pit. Point analysis shows these precipitates to be rich in Cr while the surrounding metal in this region depleted in Cr.

The external corrosion product has formed two distinct layers, an inner layer that is made up mostly of Cr, Ti and Al rich oxides and an outer layer of mostly Ni and Co rich oxides. These corrosion products appear to contain some S; this may be unreacted deposit or misidentified Mo. Within the corrosion product and extending into the region of internal sulphidation at the base of the pit, there are the remains of a refractory metal carbide that has been oxidized. The effects of alloy carbide precipitates near the alloy's surface are discussed in Section 7.3.



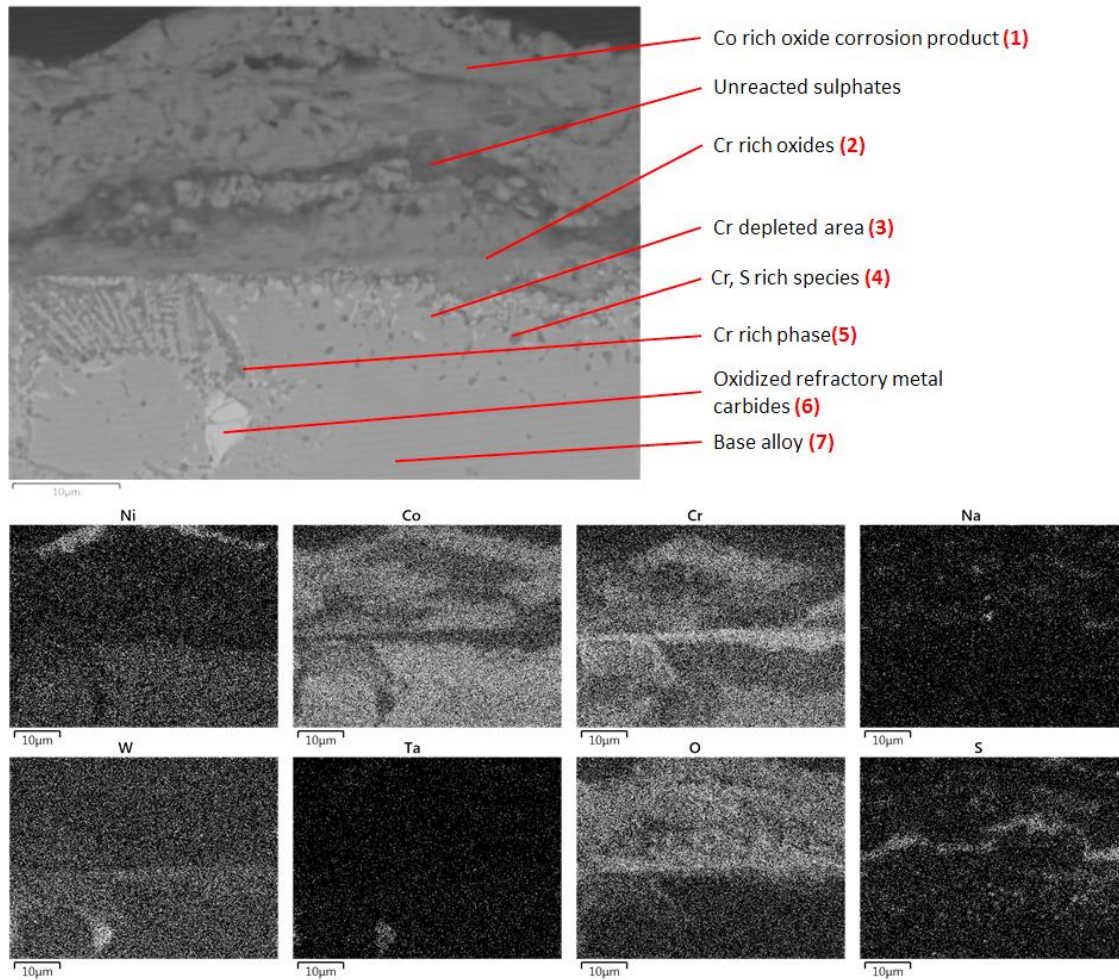
|     | Ni   | Co  | Cr   | Al  | Ti   | W   | Ta   | Mo   | S   | O    | Na  |
|-----|------|-----|------|-----|------|-----|------|------|-----|------|-----|
| (1) | 40.4 | 5.9 | 6.3  | 1.5 | 2.3  | 7.7 | 8.7  | 10.3 | 0.7 | 15.8 |     |
| (2) | 24.6 | 3.6 | 10.1 | 1.7 | 10.1 | 4.2 | 20.8 | 2.5  | 0.1 | 18.2 |     |
| (3) | 22.7 | 4.2 | 22.5 | 1.9 | 6.2  | 6.9 | 11.3 | 1.5  | 0.6 | 20.6 | 1.3 |
| (4) | 60.7 | 8.4 | 6.5  | 2.4 | 2.3  | 2.8 | 2.5  | 1.4  | 1.2 | 6.4  | 1.3 |
| (5) | 45.8 | 8.1 | 11.5 | 1.7 | 4.1  | 3.7 | 3.9  | 2.3  | 8.8 | 6.6  | 1   |
| (6) | 55.5 | 7.4 | 10.4 | 3.5 | 4.7  | 7.5 | 4.1  | 0.9  |     | 6    |     |

Figure 5.3: Backscattered electron image with EDX point analyses (wt%) and elemental maps of corrosion features on PWA 1483 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. Atomic % EDX data given in Figure D.1.

Figure 5.4 shows a backscattered electron image, EDX map and point analyses of MarM 509 after 500 hours exposure. As with PWA 1483 (Figure 5.3), Cr-rich S species have formed within the metal adjacent to the surface and the corrosion product has formed in layers based on the constituent elements' affinity for O<sub>2</sub>. Within the corrosion product, the EDX maps show the presence of Na and S; this is likely unreacted sulphates from the deposit.

Adjacent to the alloy surface, on the left side of Figure 5.4, there are the partially oxidized remains of a binary phase rich in Cr and W. Within this region there do not appear to be any internal sulphide species. The point analysis for this region shows the Cr content to be slightly less than that of the base alloy; this may be misleading since the metal adjacent to this feature may be depleted in Cr from the formation of Cr sulphides.

Immediately below the Cr-rich binary phase, the oxidized remains of a Ta-rich carbide phase can be seen. This phase is situated approximately 15 µm below the current alloy/corrosion product interface; for it to have oxidized it is likely that inward migration of O<sup>2-</sup> occurred through the adjacent Cr-rich binary phase. Otherwise, it is possible that this Ta-rich carbide phase may be connected to the surface outside of the imaging plane. Within the alloy surrounding this Ta-rich phase Cr and S-rich phases have formed (assumed to be Cr sulphides). Section 7.3 discusses how the carbide precipitate phases may provide transport routes for O and S beneath the alloy surface.



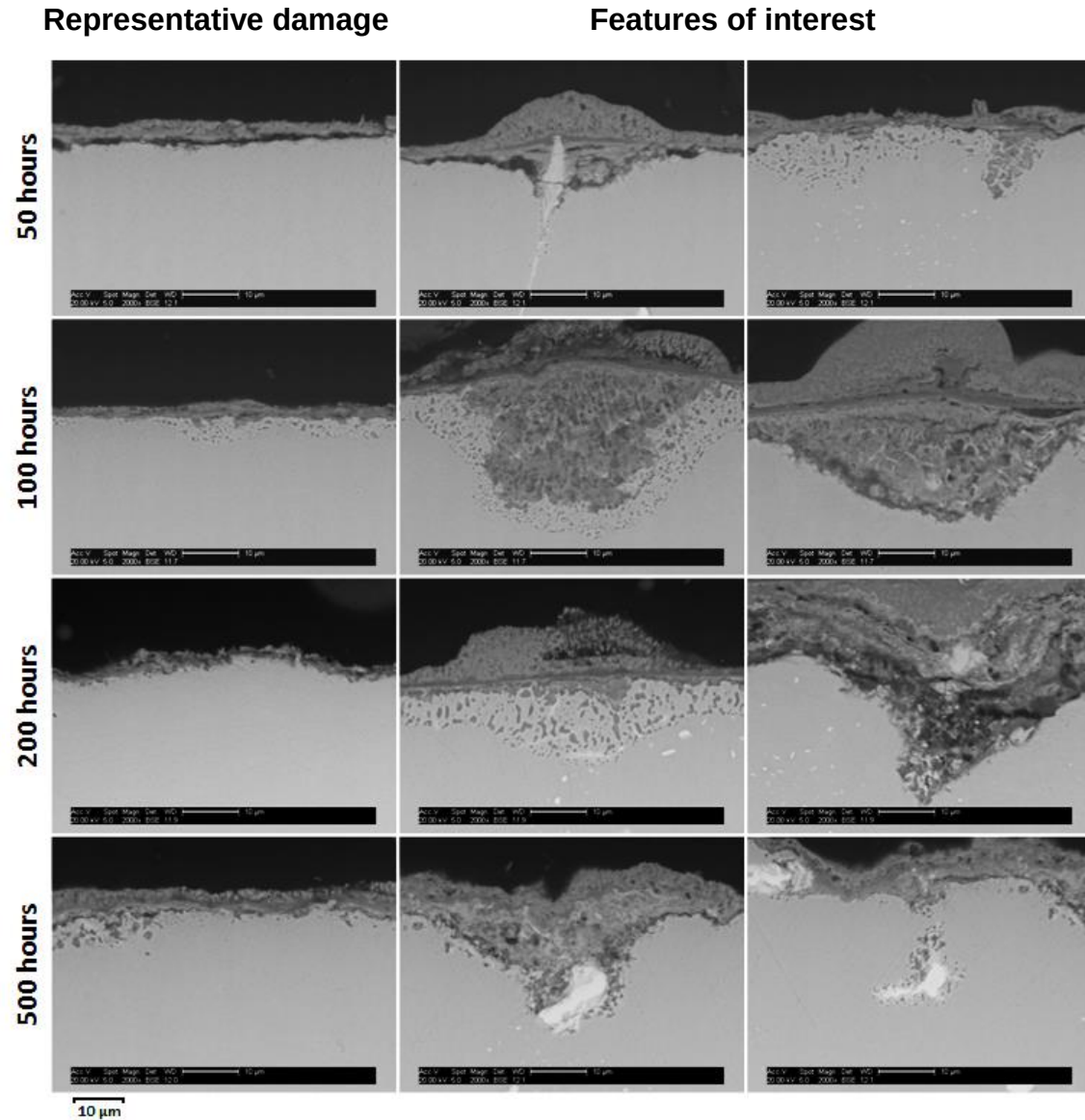
|     | Ni   | Co   | Cr   | W    | Ta   | S   | O    | Na  |
|-----|------|------|------|------|------|-----|------|-----|
| (1) | 4.4  | 43.7 | 8.8  | 6.8  | 12.4 |     | 21.3 | 2.0 |
| (2) | 2.8  | 18.8 | 34.5 | 6.9  | 8.8  | 4.4 | 21.4 | 1.7 |
| (3) | 9.4  | 47.7 | 12.9 | 10.7 | 11.7 | 0.6 | 6.9  |     |
| (4) | 6.9  | 41.6 | 17.5 | 10.5 | 8.9  | 6.0 | 6.3  | 1.5 |
| (5) | 6.3  | 34.5 | 20.7 | 13.0 | 9.3  | 2.0 | 11.9 |     |
| (6) | 3.8  | 21.7 | 12.2 | 8.9  | 35.8 | 1.2 | 14.4 |     |
| (7) | 10.7 | 51.6 | 23.2 | 11.6 | 2.2  | 0.7 |      |     |

Figure 5.4: Backscattered image with EDX point analyses (wt%) and elemental maps of corrosion features on MarM 509 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. Atomic % EDX data given in Figure D.2.

Figure 5.5 shows backscattered electron images for PWA 1483 for each exposure time. The left hand images are representative of the majority of the sample while the centre and right hand images are notable features. It can be seen that both pit features and internal damage (shown in Figure 5.3 to be Cr and S rich species) are present at all exposure times. The distribution of internal sulphide species is shown to be non-uniform; this is in contrast to typical type I corrosion that is described in the literature [14] to be of uniform distribution.

The pit features in Figure 5.5 are often formed around precipitates of refractory metal carbides located adjacent to the alloy surface. These can be seen either remaining at the surface or within the corrosion product. Not all the pit features appear to have formed around alloy precipitates. After 100 hours exposure the central and right images both show pit features at different positions on the sample surface. Internal damage is visible in the alloy adjacent to the alloy/corrosion product interface of the central image. In contrast to this, the pit feature shown in the right hand image does not exhibit sulphide species adjacent to the metal interface around the pit. A possible explanation for these two different morphologies is that two different corrosion fronts occur sequentially. An initial corrosion front, potentially driven by basic fluxing, forms Cr-sulphide species adjacent to the alloy-gas phase interface. A following second front of acidic fluxing, possibly facilitated by the depletion of Cr in this region (caused by the formation of Cr sulphide), is able to dissolve the remaining metal which is subsequently re-precipitated as oxides in layers based on the elements affinity for  $O_2$ . It is possible that all evidence of internal sulphidation could be removed by the second, acidic fluxing front leaving a pit feature typical of type II hot corrosion. This mixed mode of hot corrosion fluxing is discussed further in Section 7.4.

These images also show that at least part of the alloy surface has progressed into propagation albeit at a proportion of the sample surface lower than 3.6 % according to the probability of metal loss exceedance plot in Figure 5.1.



**Figure 5.5:** Backscattered electron images of PWA 1483 after exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O with a deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. Left images are representative of the majority of the sample, centre and right images are selected corrosion features.

Backscattered electron images representing of the majority of the surface (left images) and notable corrosion features (centre and right images) for MarM 509 over all tested exposure times are presented in Figure 5.6. Evidence of sulphidation can be seen after 50 hours exposure in the area adjacent to the surface surrounding a partially oxidized refractory metal carbide precipitate that intersects the surface. At the 50 hour exposure period, this form of internal damage appears restricted to areas where alloy precipitates have disrupted the

alloy surface. At exposure times of 100 hours and above, evidence of internal damage can be seen over the majority of the surface and is not restricted only to the areas surrounding surface precipitates.

After longer exposure times (200 and 500 hours) the carbide precipitates have oxidized to a greater depth below the remaining alloy surface than after shorter exposure times. The corrosion damage for MarM 509 appears to be distributed around the carbide precipitates with no pit features forming in areas devoid of these carbide precipitates, although internal sulphidation can be seen to occur in such areas. This is in contrast to PWA 1483 that did feature pitting in areas without carbide precipitates. The percentage area of the alloy that is made up of carbide precipitates is much greater in MarM 509 than PWA 1483 (shown in Table 3.3 to be 6.2% compared to 0.9% respectively); so for MarM 509 there is less surface area devoid of precipitates and a shorter distance between the precipitates. Secondly, the greater concentration of Cr in MarM 509 (23.5% compared to 12.2%) may allow better healing of the  $\text{Cr}_2\text{O}_3$  scale that retards the onset of hot corrosion. Where alloy precipitates break the surface, either the formation of  $\text{Cr}_2\text{O}_3$  is disrupted or alloy induced acidic fluxing (as described in the literature Section 2.6) may occur allowing hot corrosion damage.

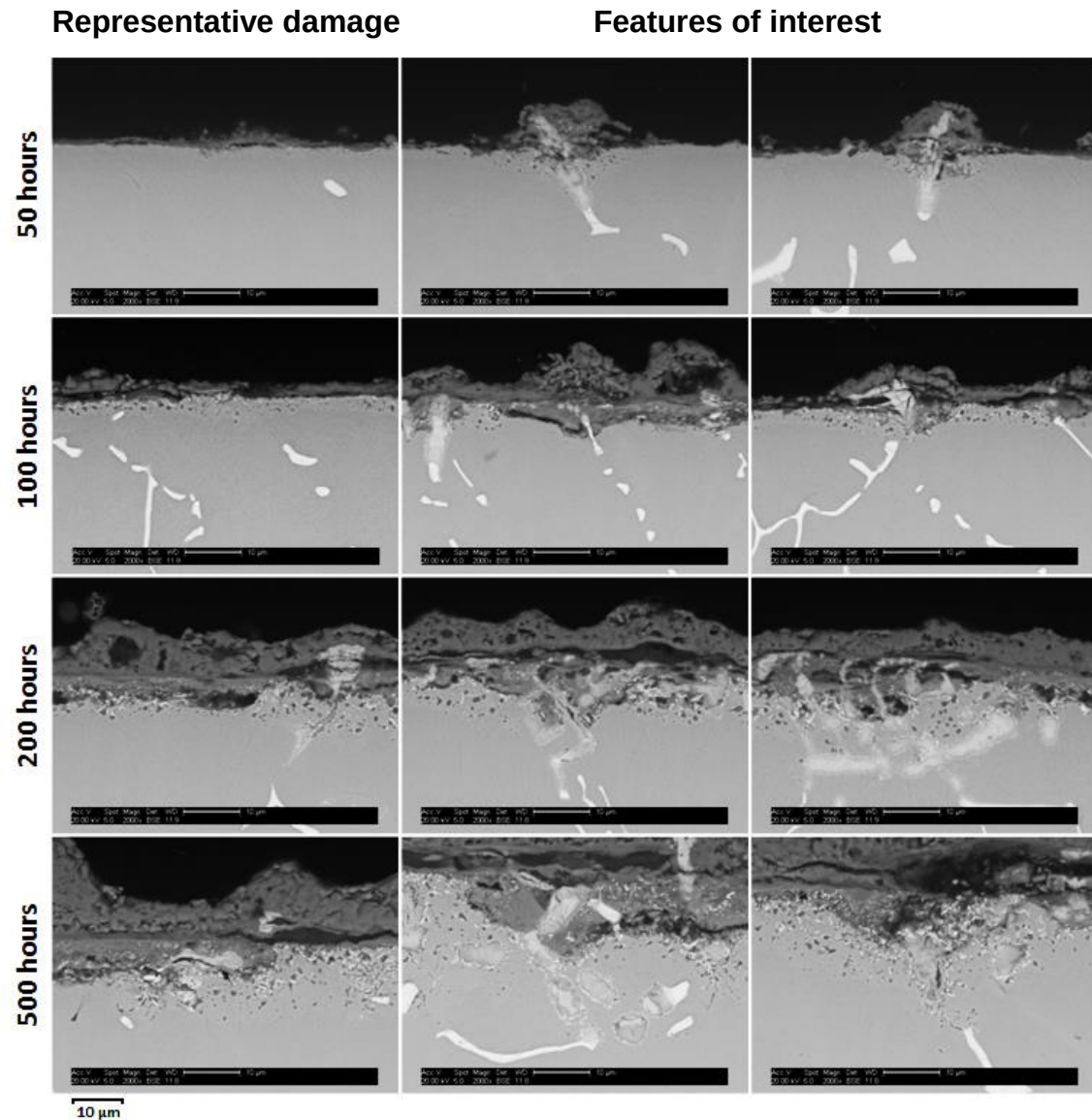


Figure 5.6: Backscattered electron images of MarM 509 after exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O with a deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. Left images are representative of the majority of the sample, centre and right images are selected corrosion features.

### 5.3.3 10% water vapour results

Figures 5.7 and 5.8 show the good metal loss data for exposures with 10% water vapour added to the test atmosphere. Over the 50 and 100 hour exposure times, PWA 1483 exhibits negligible good metal loss over the majority of the sample's surface, although at a low level of probability there is an increase in good metal loss indicating the presence of pits. At 200 hours of exposure, the majority of the sample still has negligible good metal loss although more of the surface (approximately 20%) appears to have transitioned into propagation with deeper pits. As the exposure period is extended to 500 hours, more of the sample surface has transitioned from incubation to propagation (approximately 70% of the sample surface with pit depths measured up to approximately 55  $\mu\text{m}$ ). It should be noted that parts of the sample still remain in incubation at 500 hours.

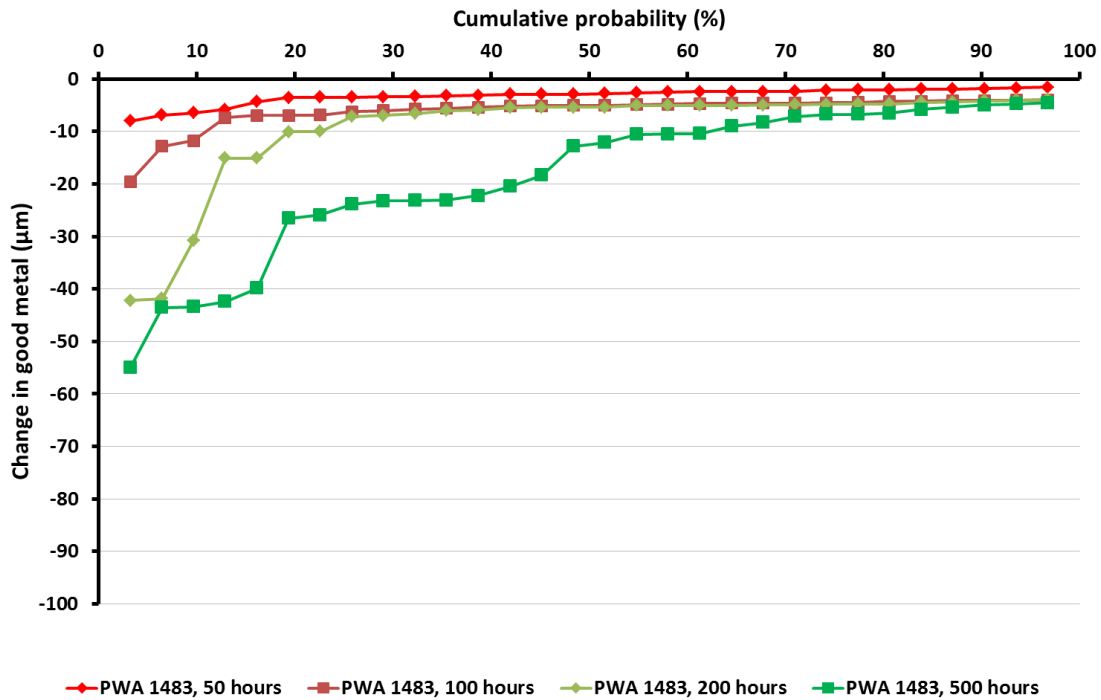


Figure 5.7: Cumulative probability plot of good metal loss for PWA 1483 exposed for up to 500 hours at 700  $^{\circ}\text{C}$  in an air atmosphere with 300 ppm  $\text{SO}_2$  and 10%  $\text{H}_2\text{O}$ . The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20  $(\text{Na/K})_2\text{SO}_4$ .

MarM 509, (Figure 5.8) appears to have remained in incubation for the first 200 hours of exposure. At 500 hours of exposure approximately 70% of the surface has over 10  $\mu\text{m}$  of metal loss with much higher metal loss (up to approximately 60  $\mu\text{m}$ ) recorded for less than 10% cumulative probability indicating a few, relatively deep pit, features.

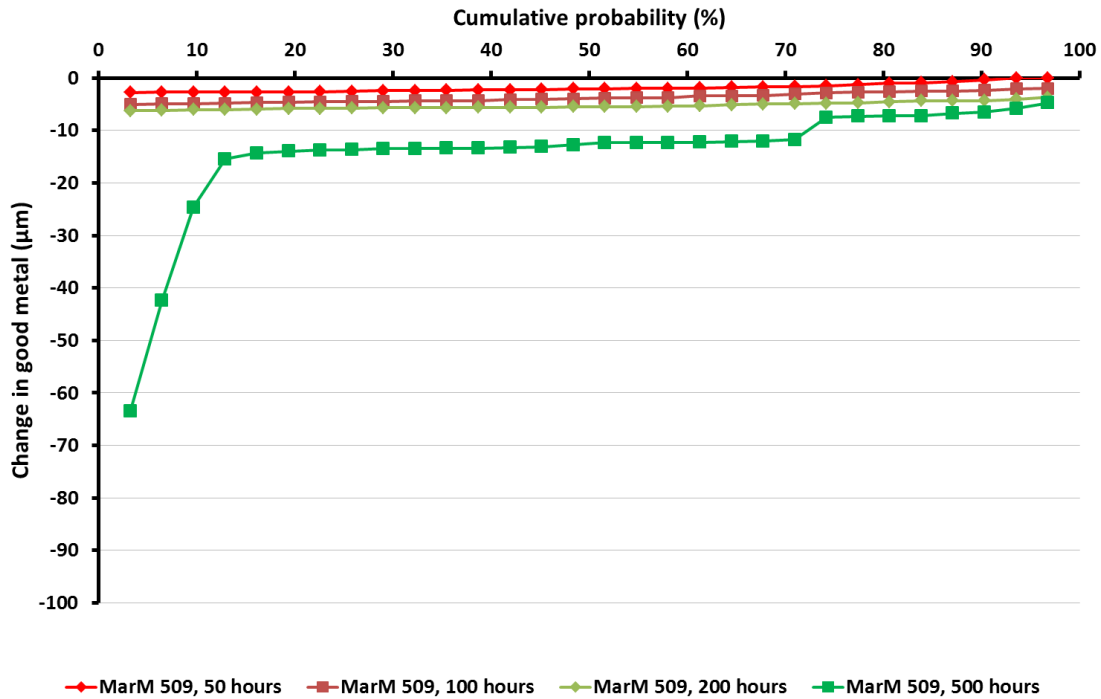
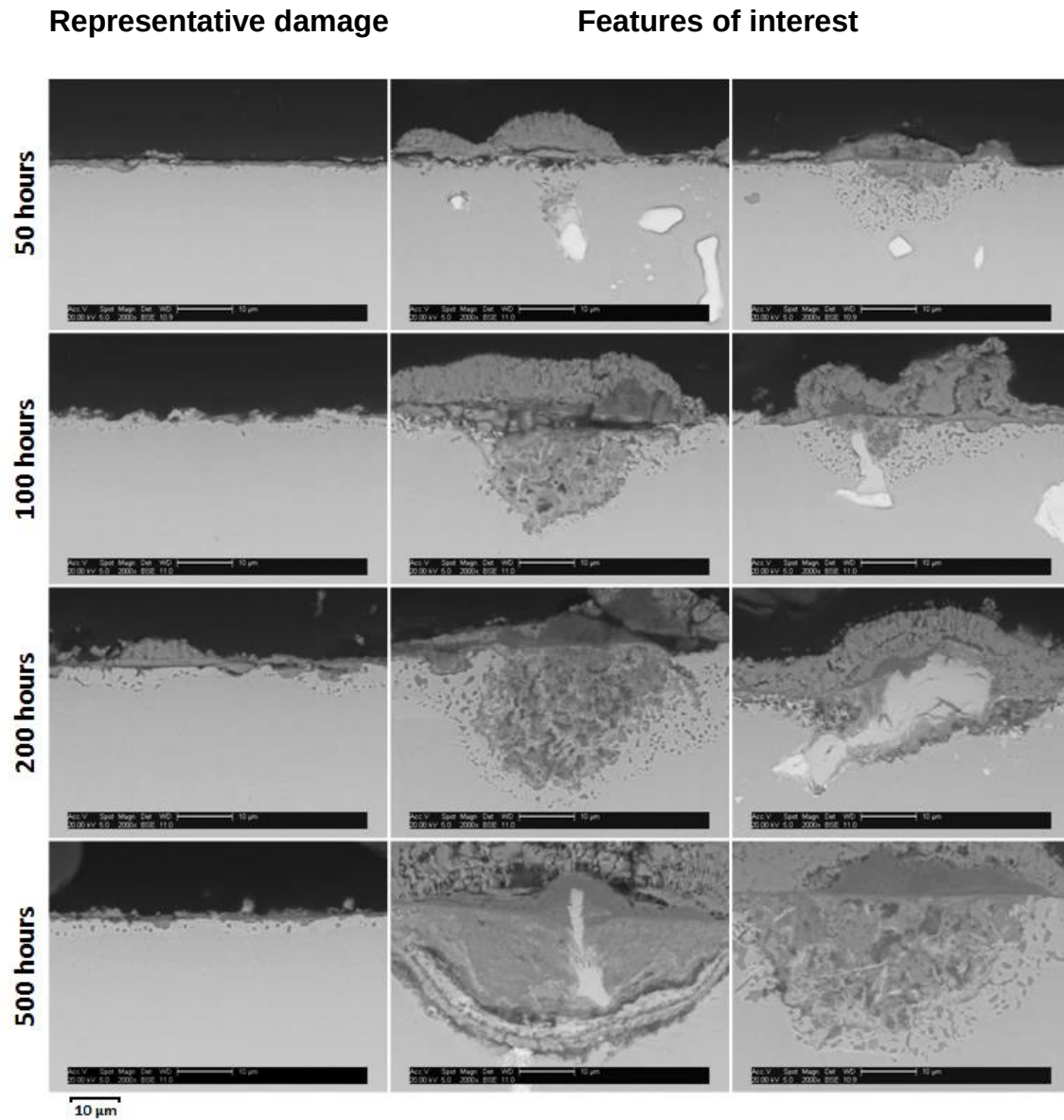


Figure 5.8: Cumulative probability plot of good metal loss for MarM 509 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 10% H<sub>2</sub>O. The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.

### 5.3.4 10% water vapour micrographs

Figure 5.9 shows backscattered electron images of PWA 1483 after exposure at 700 °C in an atmosphere of 300 ppm SO<sub>2</sub> in air and 10% water vapour with 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit. The types of hot corrosion features shown in the centre and right side images are similar to those shown in Figure 5.6 for exposures in atmospheres with no water vapour. These features are internal S-rich precipitates, which are unevenly distributed, pit features and a corrosion product layered based on the elements affinity for O<sub>2</sub>. Such features are often

located close to alloy carbide precipitates however there are examples that have developed in the absence of these precipitates.



**Figure 5.9: Backscattered electron images of PWA 1483 after exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 10% H<sub>2</sub>O with a deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. Left images are representative of the majority of the sample, centre and right images are selected corrosion features.**

Figure 5.10 is a collection of backscattered electron images of MarM 509 after exposure at 700 °C in an atmosphere of 300 ppm SO<sub>2</sub> in air and 10% water vapour with 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. The corrosion features have developed around alloy precipitates adjacent to the surface that have either

oxidised or been partially oxidised. S-rich precipitates have formed within the alloy close to the carbide precipitates that are in contact with the surface in some images but not in others. The imaged areas that are representative of the majority of the sample surfaces (left side) show several microns of corrosion product on the metal surface. There are also some internal S-rich precipitates with a low frequency and at shallow depth (approximately 1  $\mu\text{m}$ ).

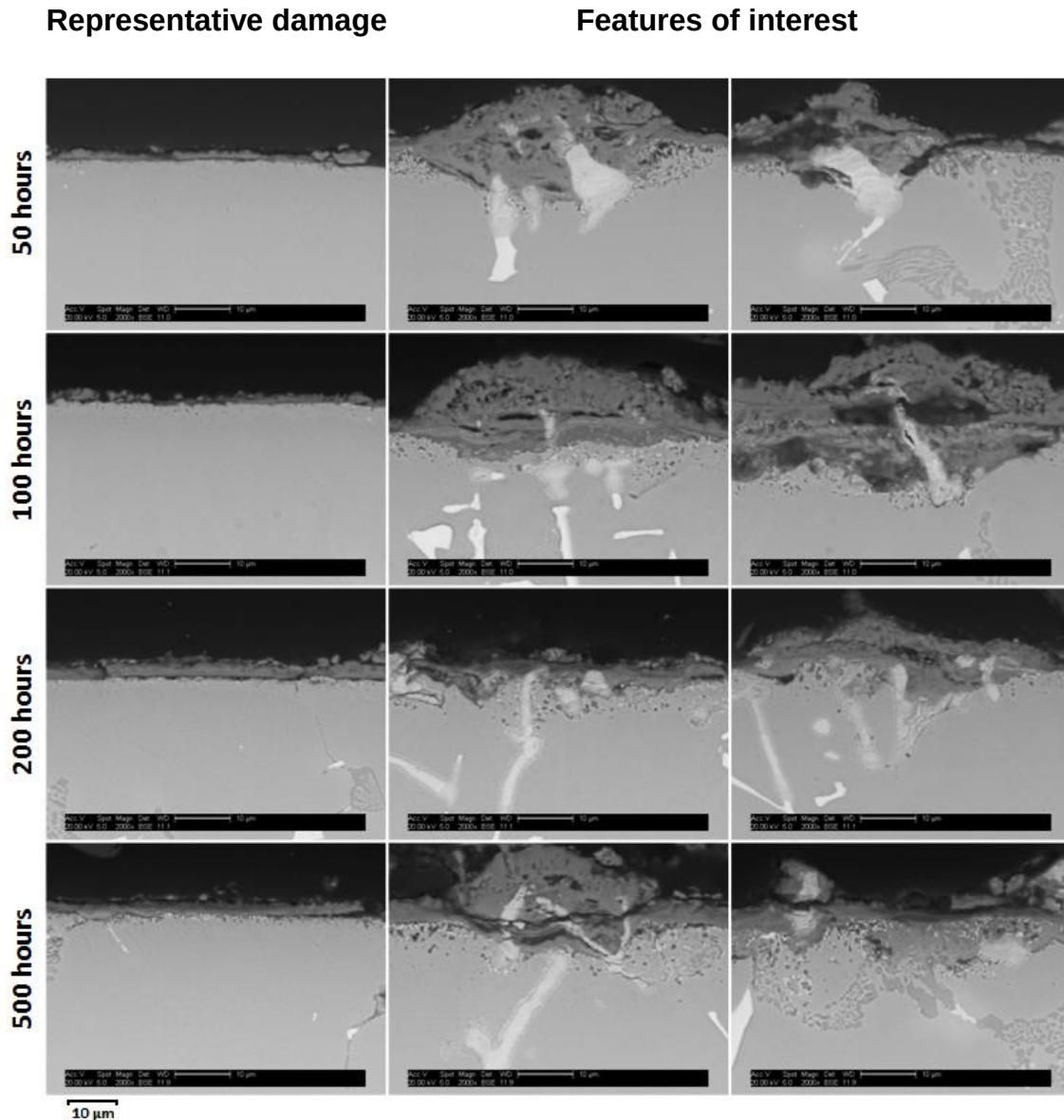


Figure 5.10: Back scattered electron images of MarM 509 after exposure at 700 °C in an air atmosphere with 300 ppm  $\text{SO}_2$  and 10%  $\text{H}_2\text{O}$  with a deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  80/20  $(\text{Na/K})_2\text{SO}_4$ . Left images are representative of the majority of the sample, centre and right images are selected corrosion features.

### 5.3.5 20% water vapour results

Change in good metal data for exposures with test atmospheres containing 20% water vapour are presented in Figures 5.11 and 5.12 for PWA 1483 and MarM 509 respectively. For exposures of 50, 100 and 200 hours, nearly all of the surface of PWA 1483 has low levels of good metal loss with a small increase of good metal loss (approximately 10  $\mu\text{m}$ ) at the lowest cumulative probability level. At 500 hours of exposure, the alloy has suffered metal loss greater than 10  $\mu\text{m}$  over 80% of the sample surface. Approximately 15% of the surface has metal loss greater than 30  $\mu\text{m}$ ; this can be attributed to pit features.

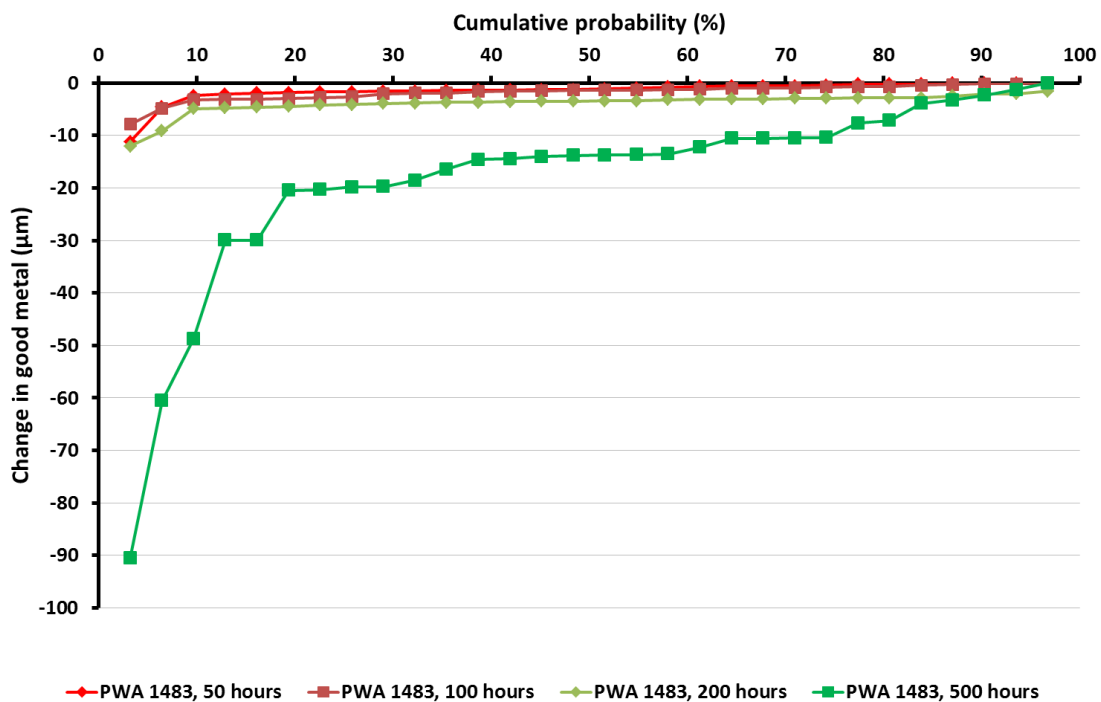


Figure 5.11: Cumulative probability plot of good metal loss for PWA 1483 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm  $\text{SO}_2$  and 20%  $\text{H}_2\text{O}$ . The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20  $(\text{Na/K})_2\text{SO}_4$ .

The data trends for MarM 509 shown in Figure 5.12 describe negligible good metal loss over the whole 500 hour period although a small increase in good metal loss can be observed with increasing exposure time. At the lowest level of cumulative probability there is a relatively small, but still notable, greater good

metal loss of between 3 and 5  $\mu\text{m}$  compared to the median. These could be interpreted as the beginnings of pit features.

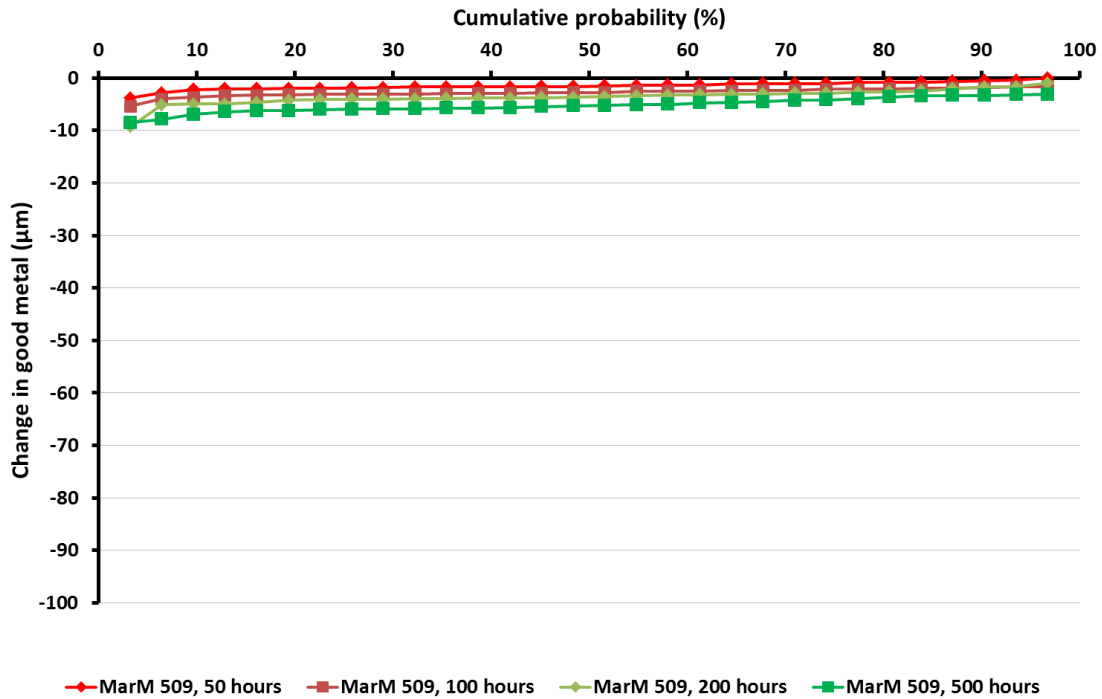
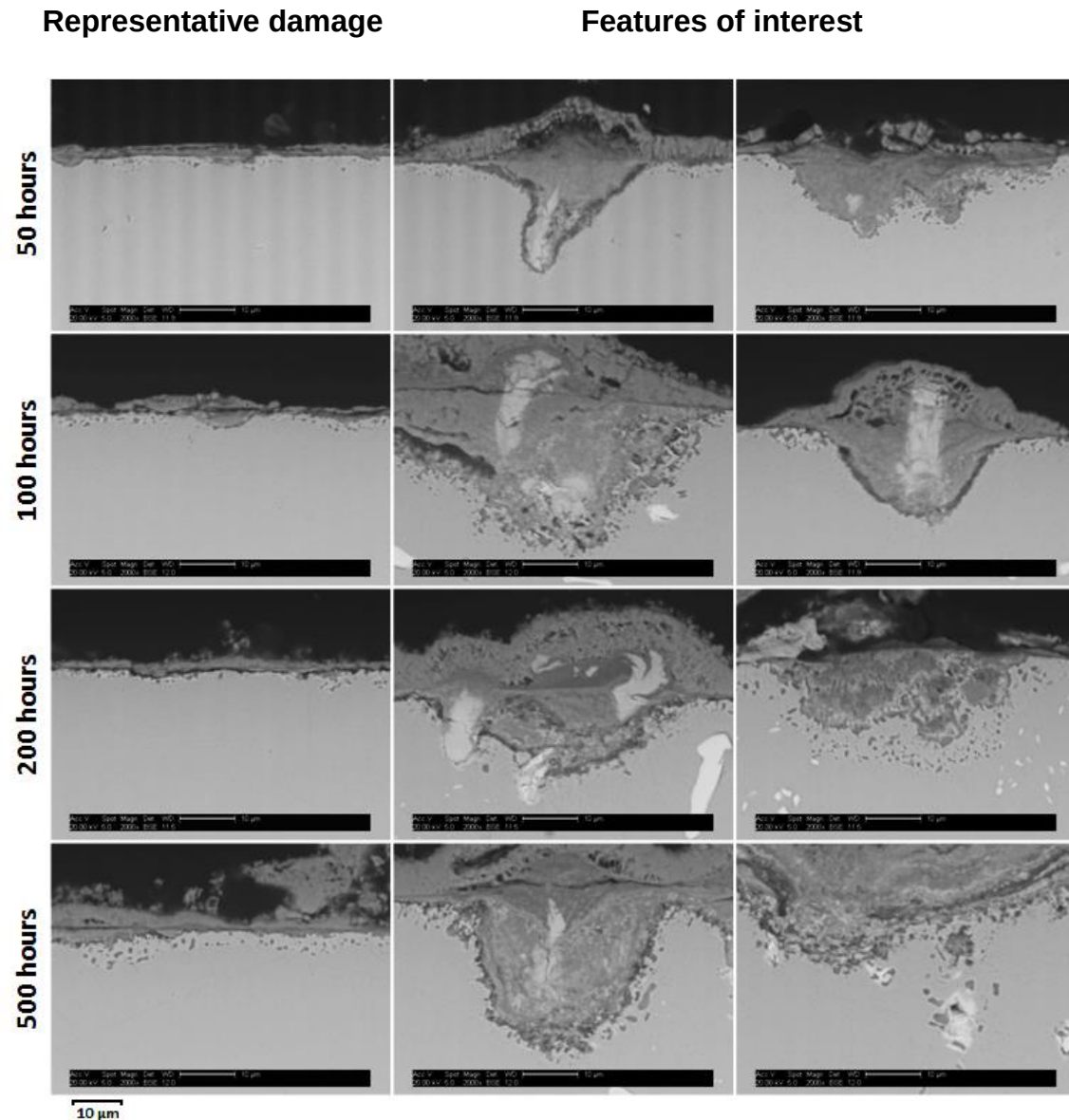


Figure 5.12: Cumulative probability plot of good metal loss for MarM 509 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm  $\text{SO}_2$  and 20%  $\text{H}_2\text{O}$ . The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 4/1 (Na/K) $_2\text{SO}_4$ .

### 5.3.6 20% water vapour micrographs

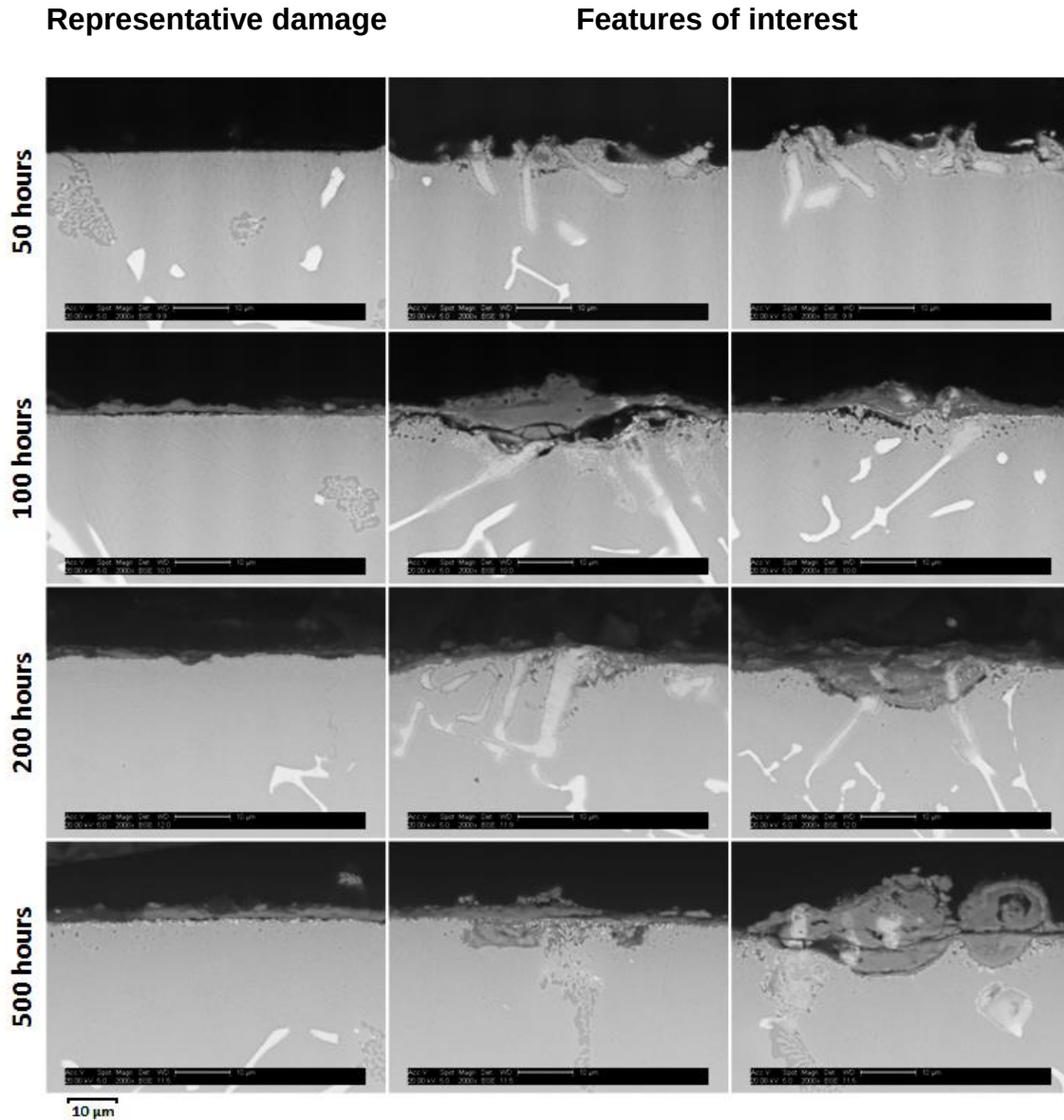
Backscattered electron images for PWA 1483 exposed in the test environment with a water vapour content of 20% are shown in Figure 5.13. As seen in exposures with 0 and 10% water vapour (Figures 5.5 and 5.9 respectively), corrosion features (centre and right images) indicate a mixed mode of internal damage and pitting forms hot corrosion. The greatest levels of damage were most often observed around alloy precipitates but some appear to have formed in the absence of precipitates. Where it is present, the internal damage observed adjacent to the pit features is of varying depth. This suggests that these features may be at different stages of their development.



**Figure 5.13:** Backscattered electron images of PWA 1483 after exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 20% H<sub>2</sub>O with a deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20 (Na/K)<sub>2</sub> SO<sub>4</sub>. Left images are representative of the majority of the sample, centre and right images are selected corrosion features.

Figure 5.14 shows backscattered electron images for MarM 509 for all exposure times in the test atmosphere (300 ppm SO<sub>2</sub> in air) with 20% water vapour. The images representative of the majority of the samples' surfaces (left side) appear to have developed a thin layer of corrosion product after 100 hours of exposure. By 500 hours, some internal sulphide precipitates can be observed although there are generally less of these than can be observed after 500 hour exposures in

atmospheres with 0 and 10% water vapour (Figures 5.6 and 5.10). Corrosion features (centre and right images) are clustered around alloy precipitates. These can be seen (by their darker shade) to have already oxidised after 50 hours of exposure. The formation of sulphide precipitates near to these carbide precipitates is inconsistent, perhaps due to the internal sulphidation being at different stages of development.



**Figure 5.14:** Backscattered electron images of MarM 509 after exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 20% H<sub>2</sub>O with a deposit flux of 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub> SO<sub>4</sub>. Left images are representative of the majority of the sample, centre and right images are selected corrosion features.

## 5.4 The effects of water vapour: discussion

Figures 5.15 and 5.16 show the median good metal loss data trends over time with the differing concentrations of water vapour for the alloys PWA 1483 and MarM 509 respectively. Generally speaking, median good metal loss values are lower when the concentration of water vapour in the test atmosphere is higher (at 500 hours exposure and 0, 10 and 20% water vapour, PWA 1483 has 39.9, 12.5 and 13.8  $\mu\text{m}$ , and MarM 509 has 12.2, 12.6 and 5.3  $\mu\text{m}$ ). This general trend differs between the alloys: PWA 1483 has a greater median good metal loss with 0%  $\text{H}_2\text{O}$  but similar trends for 10 and 20%  $\text{H}_2\text{O}$  whereas MarM 509 exhibits similar trends for 0 and 10% good metal loss but lower for 20%  $\text{H}_2\text{O}$ .

The data range bars in Figures 5.15 and 5.16 indicate the maximum and minimum measured good metal loss of the 30 selected locations on each sample's surface. There does not appear to be a correlation between the maximum measured metal loss and  $\text{H}_2\text{O}$  content of the atmosphere. This indicates that the development of the deepest pits is caused by a different factor such as refractory metal precipitates or a localised area of particularly strong acidic or basic fluxing. It can be noted that the data range limit bars show that over all tested exposure times and atmosphere  $\text{H}_2\text{O}$  contents, at least part of the samples' surfaces has remained in incubation and that the damage is unevenly distributed.

### 5.4.1 The effects of water vapour: reaction kinetics

In terms of the type II hot corrosion mechanistic progression from incubation to propagation, for the majority of the sample's surface, PWA 1483 in a 0%  $\text{H}_2\text{O}$  atmosphere appears to transition at approximately 100 hours. With two data points (200 and 500 hours) in propagation, the gradient between them gives a rate of propagation metal loss; this equals 0.077  $\mu\text{m}/\text{h}$ . For the 10 and 20%  $\text{H}_2\text{O}$  atmospheres, the data suggests that the transition occurs at times between 200 and 500 hours.

For MarM 509, the incubation to propagation transition in 0 and 10% H<sub>2</sub>O atmospheres appears to occur at some point between 200 and 500 hours. In the 20% H<sub>2</sub>O atmosphere, the sample has remained in incubation over the whole 500 hour exposure period with the data range limit bar indicating a maximum good metal loss below 10 µm.

For a more accurate determination of the reaction kinetics, a greater number of time intervals would be required. Ideally these exposure times would be closer to the point of transition from incubation to propagation with at least two data points in the propagation stage to allow for backwards extrapolation.

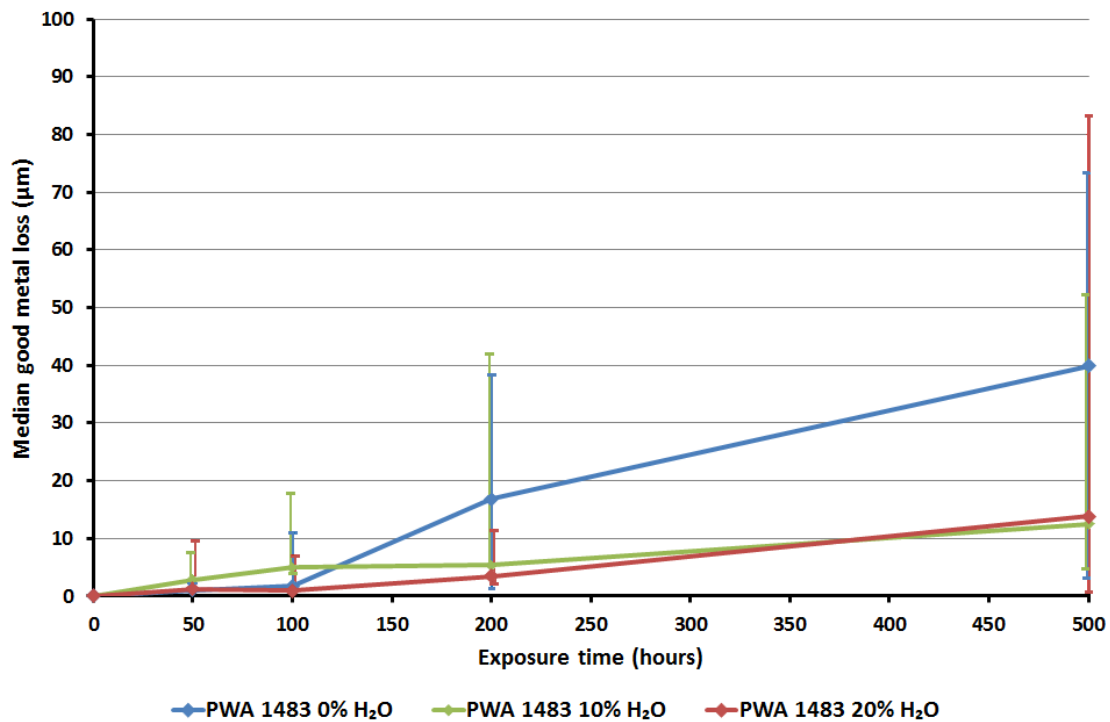


Figure 5.15: Median good metal loss data trends with time for PWA 1483 exposed in an air atmosphere with 300 ppm SO<sub>2</sub> and 0, 10 and 20% H<sub>2</sub>O. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.

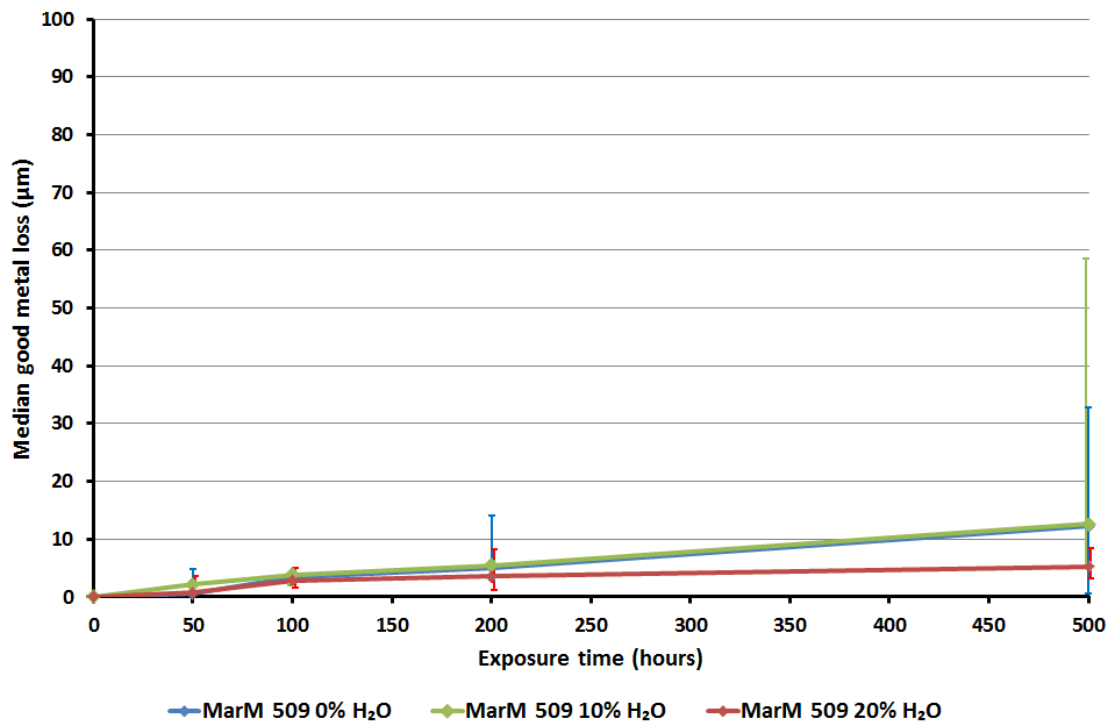


Figure 5.16: Median good metal loss data trends over time for MarM 509 exposed in an air atmosphere with 300 ppm SO<sub>2</sub> and 0, 10 and 20% H<sub>2</sub>O. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.

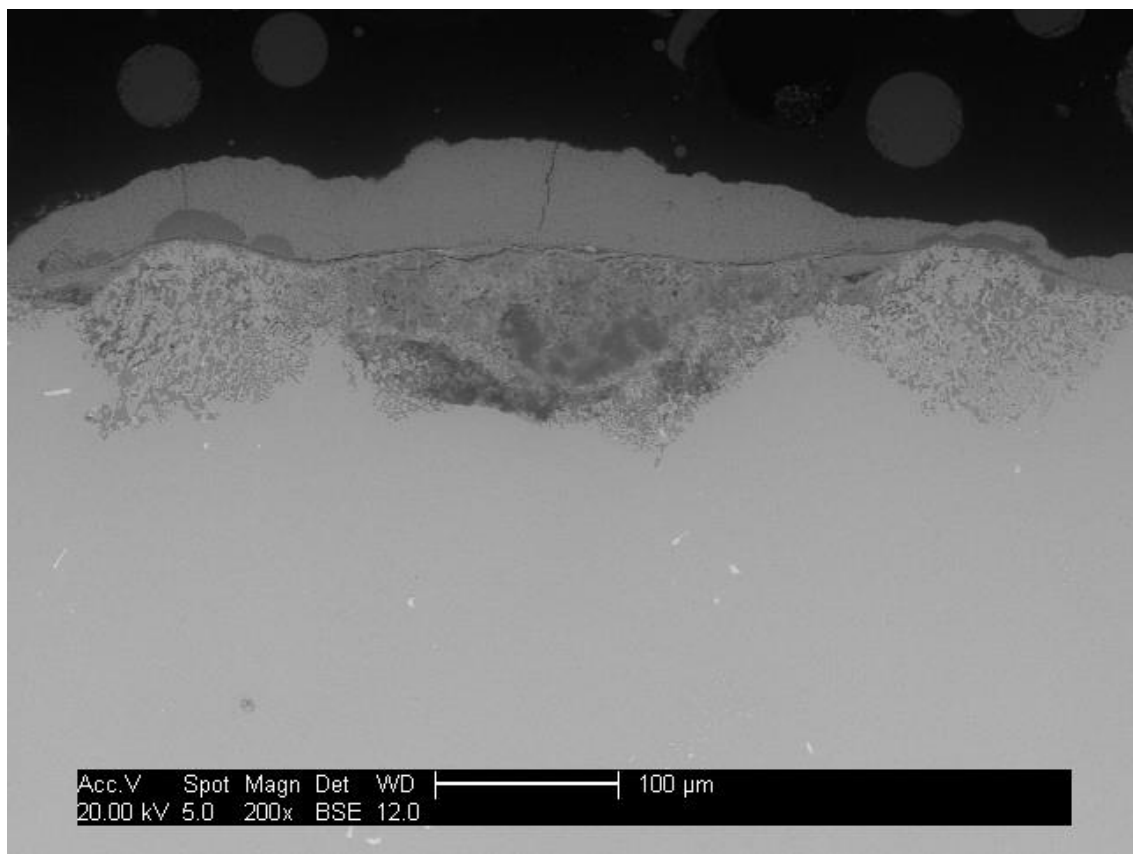
These data trends appear contrary to the findings of Section 4.6 that observed greater good metal loss with an increase in concentration of water vapor from 10 to 20%. The key difference between the two sets of exposures is the test atmosphere. These were test B gases (6% CO<sub>2</sub>, 8% O<sub>2</sub>, 3.6 ppm SO<sub>2</sub>, 10% H<sub>2</sub>O, balance N<sub>2</sub>) and C (1% CO<sub>2</sub>, 8% O<sub>2</sub>, 3.6 ppm SO<sub>2</sub>, 20% H<sub>2</sub>O, balance N<sub>2</sub>) for the initial exposures and 300 ppm of SO<sub>2</sub> in air for exposures in this Chapter. Between these exposure atmospheres, the difference in the concentration of SO<sub>2</sub> is likely to be the most significant parameter. SO<sub>x</sub> from the gas phase is believed to increase the acidity of the molten deposit [66]. It is likely that at lower levels of SO<sub>2</sub>, alloy induced fluxing mechanisms of refractory metal carbides (of which MarM 509 has more than PWA 1483) become more important than gas phase fluxing mechanisms. Alternatively, it may be possible that the presence of water vapour could be exacerbating the basic fluxing mechanism or retarding acidic fluxing.

### 5.4.1 The effects of water vapour: morphology

Backscattered electron images for PWA 1483 (Figures 5.5, 5.9 and 5.13 for atmospheres with 0, 10 and 20 % H<sub>2</sub>O respectively) show similar corrosion features irrespective of the H<sub>2</sub>O content of the atmosphere. The damage is unevenly distributed around the metal surface in the form of pitting. These pits have often formed around carbide precipitates but not exclusively so. Sometimes the pits also have internal sulphide precipitates close to the metal/external corrosion product interface but the occurrence of this is inconsistent. It is possible that pit development could occur in two stages. Initially a localised area of strong basicity in the deposit allows for the formation of internal sulphide species (shown in Figure 5.3 to be rich in Cr). As the chemistry of the melt alters to become more acidic, a second corrosion front can attack the localised area that is now deficient in Cr, this consequently can remove the evidence of the initial sulphidation reaction. This mechanism is further discussed in Section 7.4.

Figure 5.17 is a backscattered electron image of a corrosion pit and internal sulphides on PWA 1483 after 500 hours of exposure in the atmosphere containing 0% H<sub>2</sub>O. The pit appears part way through its development with large areas at either side of the pit containing internal sulphides to a depth of approximately 90 µm and some sulphides existing below the base of the pit. It can be hypothesized that, had the exposure continued, all the areas containing internal sulphide species would be enveloped by the pit to leave damage more typical of that associated with type II hot corrosion in the literature (no internal damage) [14].

If this hypothesis is correct, it should be noted that this may not necessarily be the only method for the formation of pit features. If the basicity of the melt is insufficient for internal sulphidation then it may be possible for a pit to develop through acidic fluxing without internal sulphides forming. Because evidence of the sulphides may be removed during acidic fluxing, this may be indeterminable through observations.



**Figure 5.17: Backscattered electron micrograph showing the formation of a pit feature on PWA 1483 after 500 hours of exposure in the corrosion atmosphere with 0% H<sub>2</sub>O.**

The corrosion features observed to develop on MarM 509 (Figures 5.6, 5.10 and 5.14 for atmospheres with 0, 10 and 20 % H<sub>2</sub>O respectively) are also consistent across all levels of water vapour tested. Unlike PWA 1483, these features have exclusively developed around carbide precipitates adjacent to the alloy surface. The formation of internal sulphide precipitates can be observed below the sample surfaces close to the carbide precipitates at all levels of water vapour tested. The proliferation of these sulphide precipitates and the depth to which they penetrate into the alloy appear to be lower as the level of water vapour in the gaseous environment increases.

## **6. Alloy induced hot corrosion investigation**

In Chapters 4 and 5, microscopy analysis of samples exposed to corrosive environments revealed that damage is frequently distributed around carbide precipitates within an alloy's matrix. The superalloy samples used in this research are known to form protective chromia scales that can delay the onset of hot corrosion mechanisms [15]. Carbide precipitates located at or near the surfaces of the samples may disrupt the continuity of the surface and cause localized areas to be lean in Cr and consequently unable to develop a protective chromia scale. An alternative explanation for the distribution of damage around alloy precipitates is the alloy induced hot corrosion mechanism described in Section 2.6.3 [84].

It is not clear to what degree the alloy induced hot corrosion mechanism affects the localized degradation of the alloy around precipitates, or how much of the damage is caused by the inability to develop a protective chromia scale. Thus this chapter investigates the alloy induced hot corrosion mechanism to confirm the localized damage is not solely the consequence of a disrupted chromia scale.

### **6.1 Deposit modification**

Previous studies [86], [85], [66] have identified Mo-rich particles within an alloy matrix as containing one of the elements that can induce acidic fluxing. Mo was therefore chosen as an addition to the 80% Na<sub>2</sub>SO<sub>4</sub> & 20% K<sub>2</sub>SO<sub>4</sub> (molar %) salt deposit applied to samples before exposure in hot corrosion tests. Using this technique, the added Mo is situated on the samples' surfaces within the deposit melt and not within the alloy matrix. This eliminates the possibility that the degradation arose as a consequence of Cr lean regions on the alloy surface disrupting the scale.

If the addition of Mo particles were to induce or exacerbate alloy induced acidic fluxing then one would expect to see greater metal loss values when compared to an exposure under the same conditions without additions of Mo. On the other hand if alloy induced acidic fluxing were not to occur then no changes in metal

loss values and similar hot corrosion morphology would be expected. Section 5.2 describes and presents metal loss data for corrosion test using the same parameters but without the addition of Mo.

Mo was deposited on test samples immediately after the application of the salt deposit using the pneumatic spray method described in Section 3.2 with the following differences. Isopropanol was used as the medium for the application of Mo; this prevented the redistribution or removal of the soluble salt species previously applied to the sample. Mo particles between 2 and 5  $\mu\text{m}$  were chosen, this allowed for easy application and an even distribution across the samples' surfaces.

One of the possible chemical reactions occurring during alloy induced acidic fluxing described in the literature (Section 2.6.3) has a molar ratio of 1:1  $\text{MoO}_3$  to  $\text{Na}_2\text{SO}_4$ . The relative atomic mass of these compounds is approximately equal (144 and 142 respectively) while the relative atomic mass of Mo is 96. By using the same flux weight of salt deposit and Mo deposit, there should be an excess of Mo available for acidic fluxing reactions.

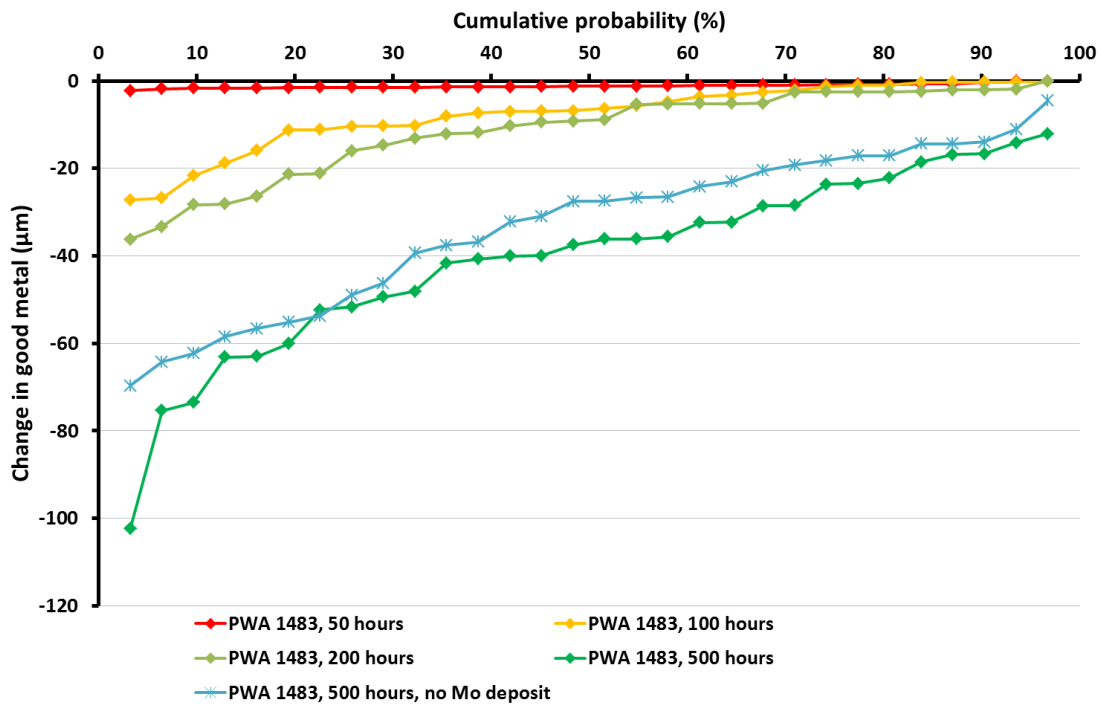
An additional sample was exposed for 500 hours without the Mo portion of the deposit added. This acted as a reference to compare the effect of Mo additions to the deposit. It also duplicated the conditions of the 500 hour exposure described in 5.2 to check the repeatability of the data.

## **6.2 Molybdenum addition test results**

This section details the results of the hot corrosion test including additions of Mo to the deposit. Section 3.4 describes how these data were derived.

Figure 6.1 shows the cumulative probability of metal loss data for PWA 1483 at exposure times of up to 500 hours. The blue data plotted shows the sample with no Mo added to the deposit. After 50 hours of exposure, the data exhibits no significant good metal loss at any measured point. After 100 hours, more significant metal loss can be observed with a median value of 6.6  $\mu\text{m}$  and 4%

exceedance probability of 27.1  $\mu\text{m}$ . The degree of good metal loss increases progressively over time with median and 4% exceedance probability values of 9 and 35.5  $\mu\text{m}$  respectively after 200 hours, and 36.8 and 95.9  $\mu\text{m}$  after 500 hours. The degree of good metal loss after 500 hours for the sample exposed without Mo added to the deposit is less than the equivalent sample exposed with Mo. In this case the median value was 27.5  $\mu\text{m}$  and the 4% exceedance probability value was 68.4  $\mu\text{m}$ .

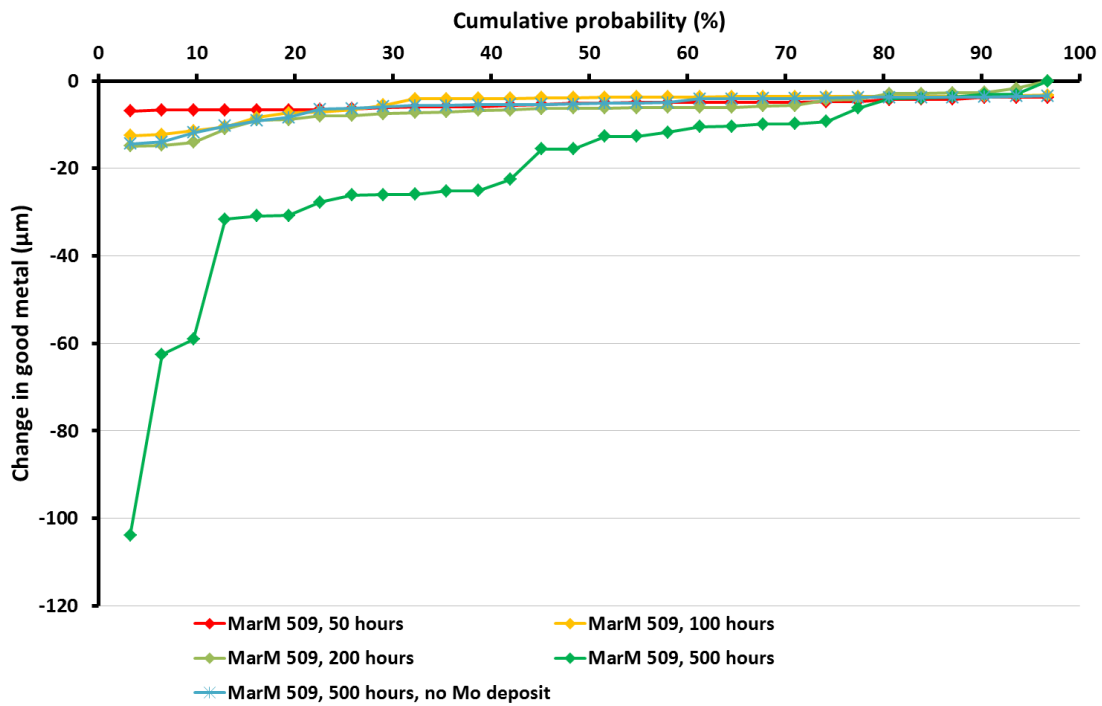


**Figure 6.1: Cumulative probability plot of metal loss for PWA 1483 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> followed by 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of molybdenum.**

The cumulative probability of good metal loss data for MarM 509 is presented in Figure 6.2. Data trends for 50, 100 and 200 hours with the Mo modified deposit, and 500 hours without Mo in the deposit, have relatively similar median metal loss values of between 3.8 and 6.2  $\mu\text{m}$ . The 4% probability of good metal loss exceedance data after 50 hours is 5.1  $\mu\text{m}$ . After 100 and 200 hours with the Mo

modified deposit, and 500 hours without Mo in the deposit, the 4% probability of metal loss exceedance data is between 12.5 and 14.8  $\mu\text{m}$ .

Compared to the shorter exposure times and the 500 hour exposure without Mo in the deposit, the data for MarM 509 after 500 hours with the Mo deposit exhibits much greater good metal loss. The median value in this case is 14.1  $\mu\text{m}$  while the 4% probability of metal loss exceedance value is 94  $\mu\text{m}$ .



**Figure 6.2:** Cumulative probability plot of metal loss for MarM 509 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> followed by 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of molybdenum.

### 6.3 Microscopy analysis

This section examines the changes in morphology occurring over time using backscattered electron SEM micrographs. The selected corrosion feature images do not necessarily indicate the average degree of metal loss.

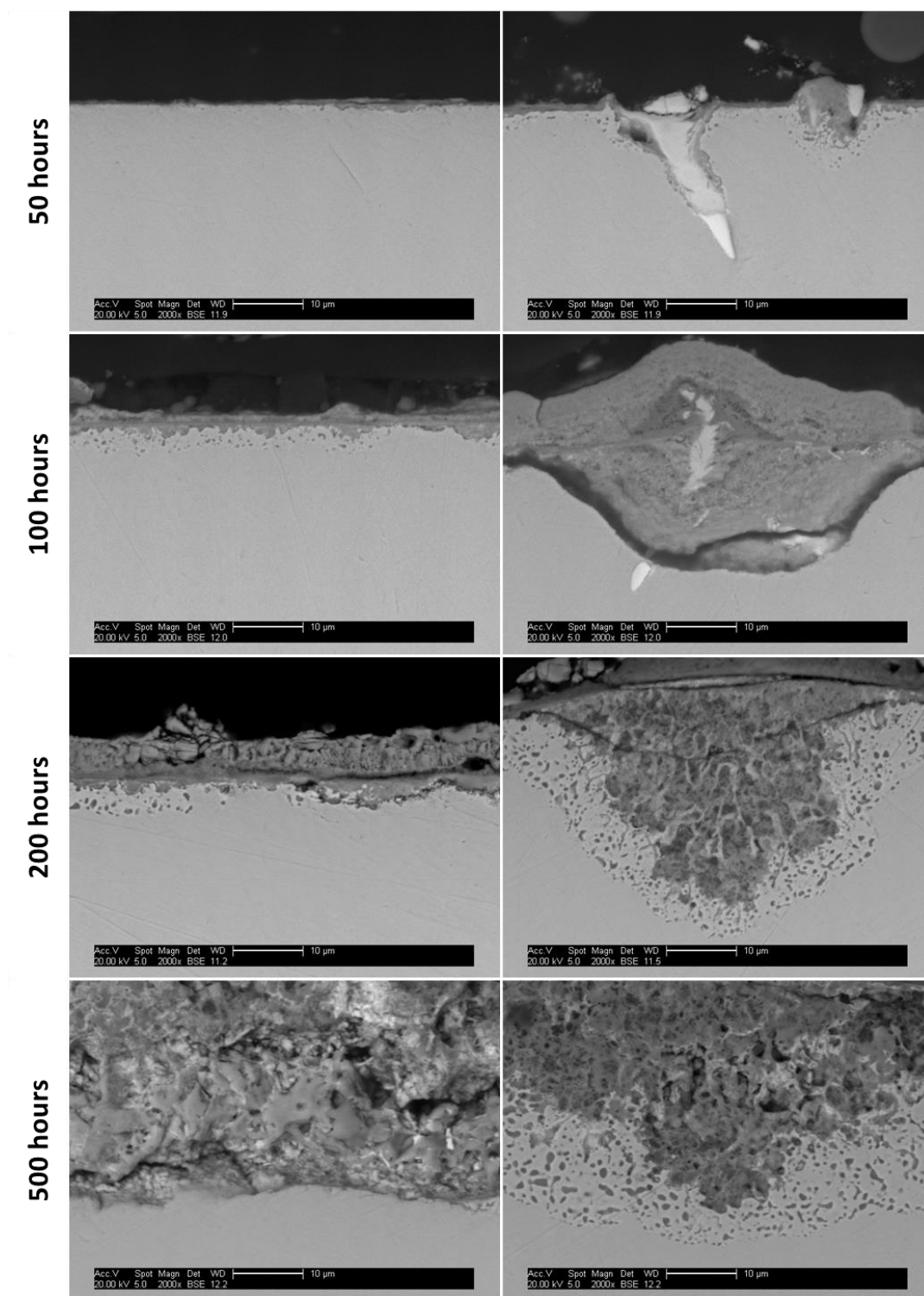
### **6.3.1 PWA 1483 morphology**

Figure 6.3 shows backscattered electron micrographs of PWA 1483 after exposures with the Mo modified deposit. After 50 hours of exposure the image representative of the majority of the sample (left side) shows negligible damage. Damage is observed to be localized around alloy precipitates located at the surface (right side). Here, internal damage can be observed adjacent to the remains of an alloy precipitate, extending up to 10  $\mu\text{m}$  into the alloy.

The corrosion features after exposure times between 100 and 500 hours appear to form two different types of morphology. One type (shown in Figure 6.3, 100 hours, right side image) does not exhibit internal damage within the metal and the corrosion product inner layer is a relatively consistent shade. The other type (shown for 200 and 500 hours, right side images) does feature internal damage within the metal and the corrosion product has a more mottled shade. Three possible explanations for the differences in morphology are: different corrosion mechanisms occurring; different stages of the same mechanism; or a combination of both.

**Representative damage**

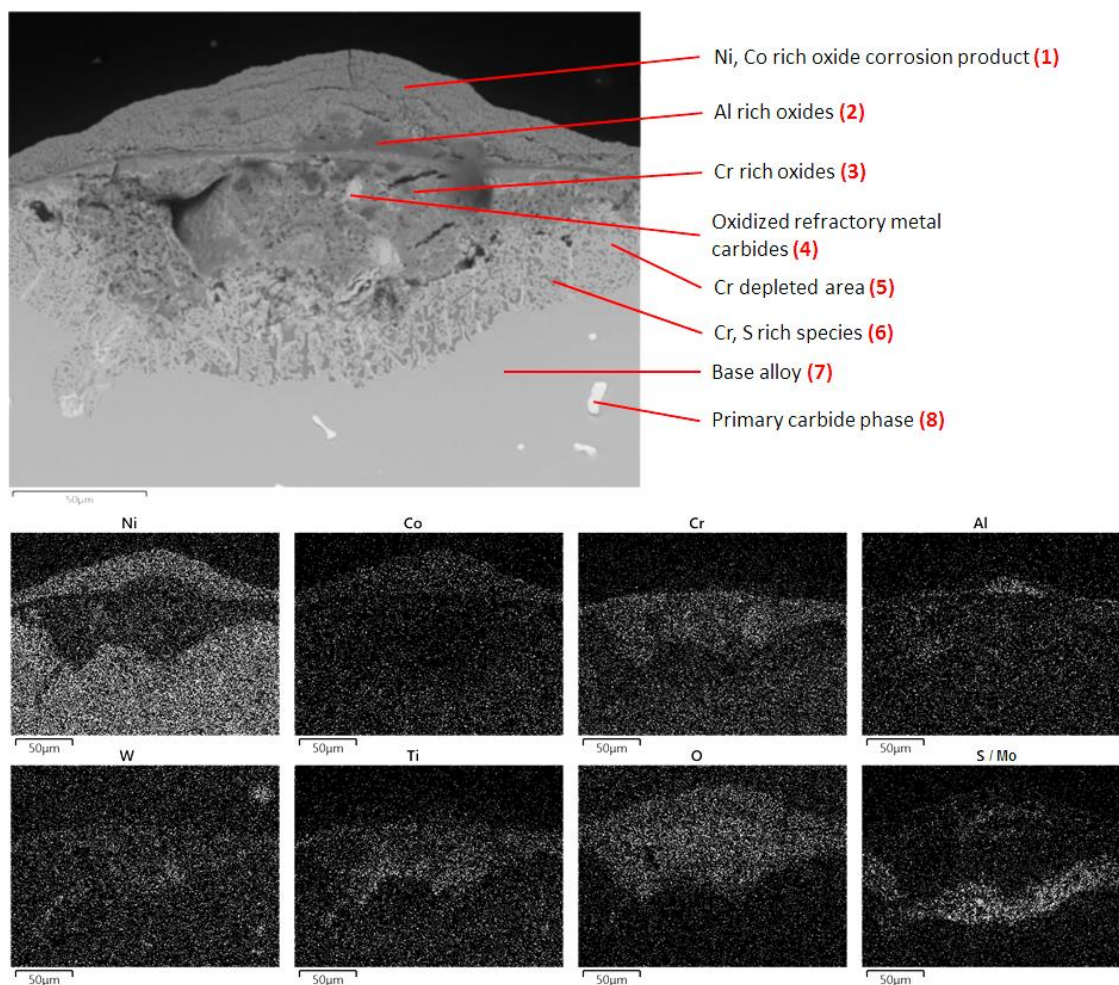
**Feature of interest**



**Figure 6.3: SEM Backscattered electron micrographs of PWA 1483 exposed for 500 hours in air and 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h each of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo. Left side images are representative of the majority of the surface, right side are selected corrosion features.**

Figure 6.4 shows a backscattered electron image with EDX point quantification and maps for a mixed mode corrosion feature on PWA 1483 after 500 hours of exposure with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo deposit. The outer-most layer of corrosion product is primarily comprised of Ni and Co-rich oxides; this layer is approximately 30 µm thick at the centre point of the feature. Beneath this Ni and Co-rich oxide layer, a relatively thin layer of Al-rich oxide can be observed, which shows up darker than the adjacent Ni and Co oxides. The Al-rich oxide layer is thicker towards the centre of the pit feature (8 µm) than at the edges of the pit (1-2 µm). An inner layer rich in Cr oxides, 60 µm thick at the centre point of the pit feature, is situated below the Al oxide layer. Within this layer, the oxidized remains of primary carbide phases rich in Ta can be observed. This kind of layering of corrosion product is a consequence of elements from the alloy dissolving in the melt and subsequently precipitating at the gas phase interface and is typical of type II hot corrosion [14], [32]. This should occur in order of the elements affinity for O<sub>2</sub>; in this case the Al oxide layer appears to have formed above the Cr oxide despite the free energy change for the formation for Al oxide being lower than that of Cr oxide (shown in Figure 2.8).

At the interface of the remaining good metal and the corrosion product, there exists a layer composed of Cr-rich sulphide species and Cr depleted metal. The depth of penetration of S-rich precipitates into the alloy in this region varies between 20 and 40 µm. Where a carbide precipitate extends through this region of internal damage deeper into the alloy (left side of the pit), so too does the penetration of S in the alloy extending a further 20 µm. The formation of sulphide species within the alloy adjacent to the surface is often associated with type I hot corrosion (described in Section 2.6.2) typically occurring approximately 200 °C hotter than this exposure (900 °C). Here basic fluxing causes the local activity of S in the melt to increase to the point at which sulphidation of the metal is possible.

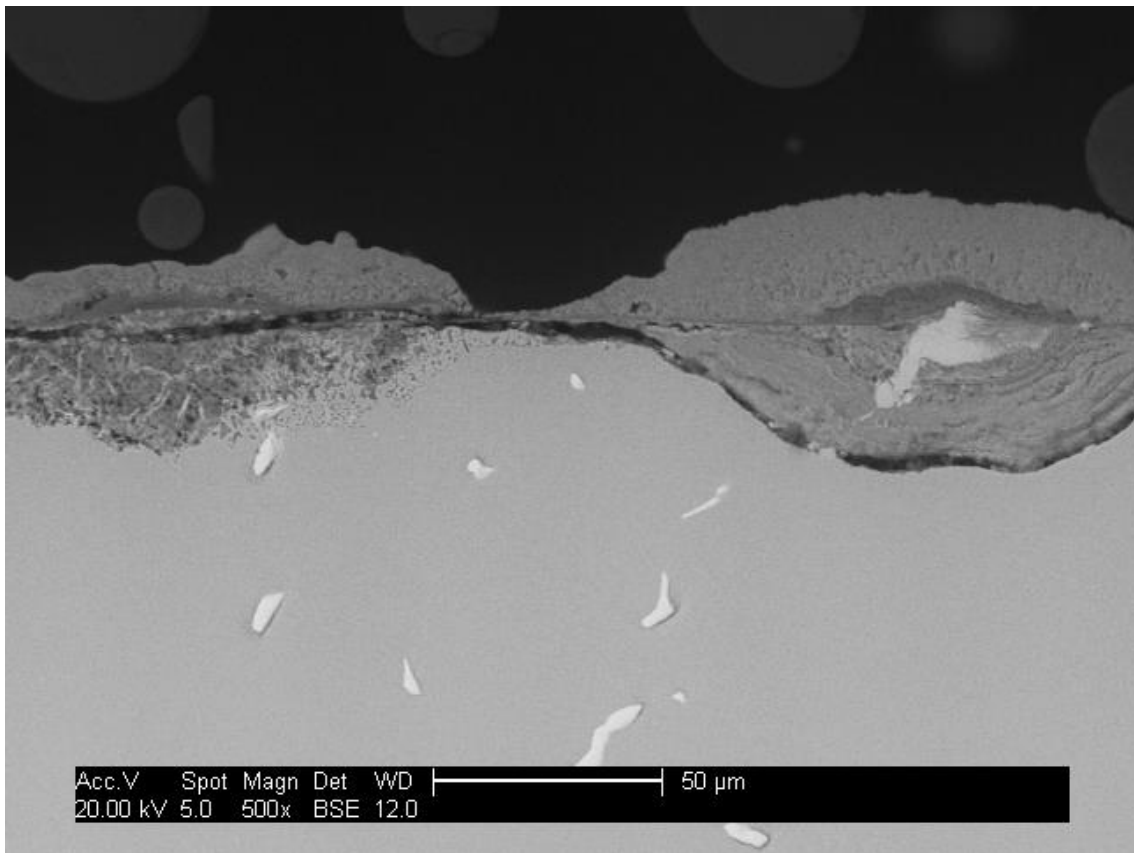


|     | Ni   | Co   | Cr   | Al   | Ti   | W   | Ta   | S/Mo | O    | Na  |
|-----|------|------|------|------|------|-----|------|------|------|-----|
| (1) | 56   | 11.5 | 2.3  | 1.4  | 1.1  |     |      | 1    | 21.6 |     |
| (2) | 22.8 | 11.3 | 9.4  | 15.9 | 3.1  |     |      | 1.8  | 30.2 | 1.8 |
| (3) | 21.8 | 4.4  | 14.1 | 2.3  | 4.5  | 2.8 | 3    | 5.8  | 30.3 | 8.2 |
| (4) | 17.6 | 3    | 7.9  | 1.4  | 10.5 |     | 28.8 | 1.4  | 23.5 | 1.3 |
| (5) | 68.9 | 6.9  | 4.4  | 2.4  | 1.5  | 3.9 |      | 2.1  | 4.8  |     |
| (6) | 33.9 | 3.9  | 17.5 | 6.5  | 2.6  |     |      | 27   | 5.6  |     |
| (7) | 61.1 | 8.5  | 11.2 | 4.5  | 4.6  | 2.8 |      | 0.8  | 3.2  |     |
| (8) | 23.9 | 3.3  | 5.2  | 1.1  | 12.6 | 6.1 | 38.1 | 2.4  | 3    |     |

Figure 6.4: BSE image with point analysis (wt%) and EDX element map of a corrosion feature on PWA 1483 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h each of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo. Atomic % EDX data given in Figure D.3.

Figure 6.5 shows the two types corrosion of features located adjacent to each other. Both features have two distinct outer layers of corrosion product indicating at least some similarities in the degradation mechanism.

The proximity of the two features (approximately 50  $\mu\text{m}$ ) suggests that conditions within the melt may be similar and given that both features have outer layers of corrosion product arranged in the same manner, it is likely that both features have experienced the same mechanisms but are at different stages of degradation.



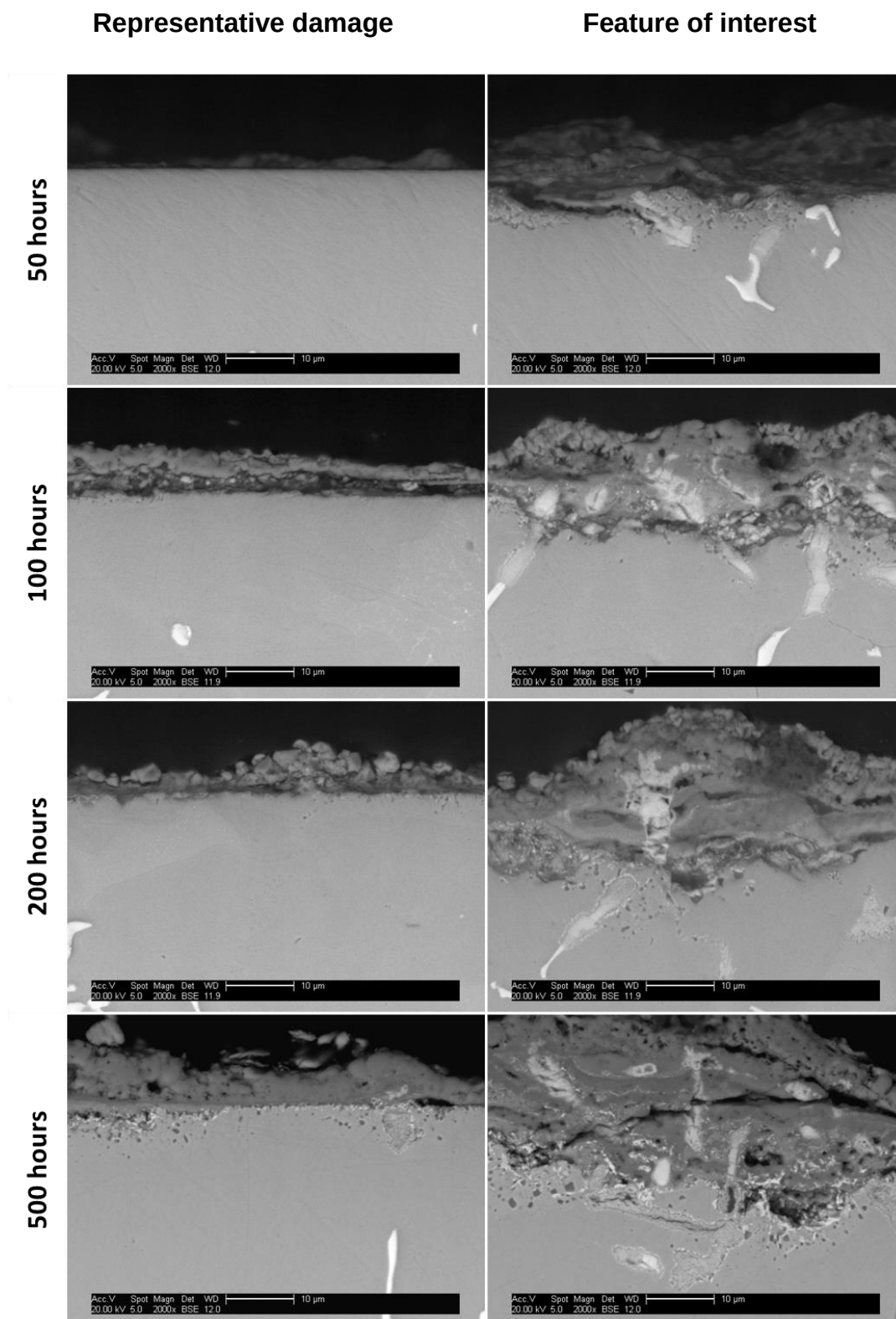
**Figure 6.5: SEM Backscattered electron micrographs of PWA 1483 exposed for 500 hours in air and 300 ppm  $\text{SO}_2$ . The deposit flux was 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  each of 80/20  $(\text{Na/K})_2\text{SO}_4$  and Mo.**

### 6.3.2 MarM 509 morphology

BSE micrographs representative of the majority of the sample (left side) and corrosion features (right side) for MarM 509 after exposures using the Mo modified deposit are shown in Figure 6.6. The amount of hot corrosion product visible in the images representative of the majority of the surface increases progressively with exposure time. Starting after 100 hours of exposure, internal damage caused by the formation of sulphide species can be observed and the frequency of these species also increases with exposure time.

The corrosion features shown in Figure 6.6 appear to have formed around carbide precipitates located at the surface of the sample. Exceptions for this were found on the sample after 500 hours of exposure and are discussed later. The carbide precipitates contacting the surface have oxidized inwardly in the manner described in Section 7.3. After 50, 100 and 200 hours of exposure, the formation of internal sulphide species appears mostly to be in areas of the alloy adjacent to the oxidized remains of carbide precipitates. After 500 hours this relationship is less obvious because relatively small phases of heavy elements (showing up brightly) with irregular shape are distributed around the surface of the metal and in the corrosion product adjacent to the surface.

At several points around the circumference of the MarM 509 sample exposed for 500 hours, pit features exhibiting significantly greater good metal loss and different morphology compared to other corrosion features on the sample can be observed. An example of these features is shown in Figure 6.7.



**Figure 6.6:** SEM backscattered electron micrographs of MarM 509 exposed for 500 hours in air and 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 μg/cm<sup>2</sup>/h each of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo. Left side images are representative of the majority of the surface, right side are selected corrosion features.

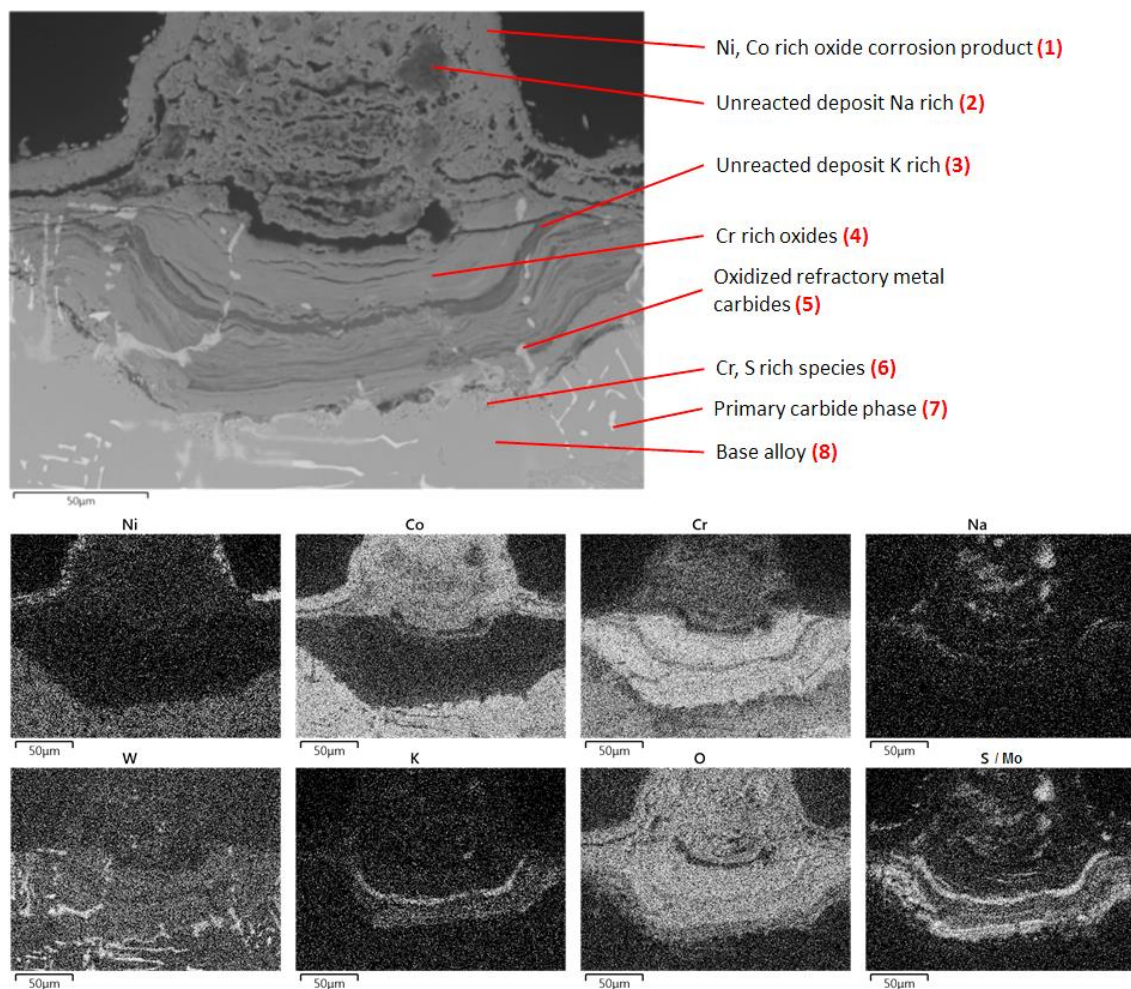
Figure 6.7 shows a backscattered electron image with EDX point quantification and maps of a corrosion pit feature on MarM 509 after 500 hours of exposure with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo deposit. Although the oxidized remains of carbide precipitates are visible in the pit's corrosion product, it does not appear that this pit feature has formed around such a precipitate.

The corrosion product is comprised of multiple phases arranged in layers. The outer most layer is relatively thin (approximately 10 to 15 µm) and rich in both Ni and Co. Beneath this layer is a thicker (up to 100 µm) Co-rich layer that exists towards the centre of the pit. Within this layer there are regions rich in Na and S which are likely to be unreacted Na<sub>2</sub>SO<sub>4</sub> deposit. This phase is a relatively dark shade in the BSE image and is therefore unlikely to be Mo, which is heavier than S and so would appear brighter.

Situated below the Co rich layers are two Cr rich layers bisected by a thin layer (10 µm) rich in K and S (likely unreacted K<sub>2</sub>SO<sub>4</sub> from the deposit). K and S are also shown in the element map to be present in the lower Cr rich layer. The corrosion product adjacent to the metal surface is rich in either S or Mo. This layer shows up brighter than the S containing species that is likely unspent deposit. It is possible that this layer is rich in Mo. Alternatively the abundance of Cr may explain why this layer of corrosion product is a lighter shade.

The metal adjacent to the surface of the alloy features internal damage, up to 15 µm of depth into the alloy, with an irregular distribution. EDX element map shows that the metal in this region is lean in Cr.

Although the corrosion feature shown in Figure 6.7 shows evidence of mixed mode corrosion, the depth of the pit and the thickness of the oxide corrosion product layers indicate the hot corrosion mechanism may have been dominated by acidic fluxing prior to the end of the test. This type of feature does not appear on MarM 509 samples exposed in the same conditions without Mo in the deposit (Figure 5.6); it is therefore likely that the chemistry of the melt has been altered by the Mo to become more acidic.



|     | Ni  | Co   | Cr   | Ti  | W    | Ta   | S/Mo | O    | Na  | K   |
|-----|-----|------|------|-----|------|------|------|------|-----|-----|
| (1) | 5.8 | 57.3 | 4.6  |     | 1.4  | 1.3  | 0.7  | 23.1 | 2.3 |     |
| (2) | 4.3 | 23.9 | 7.3  |     |      | 0.9  | 15.2 | 29.5 | 12  | 2.1 |
| (3) | 2.2 | 12.7 | 24.2 |     | 4.3  | 2.1  | 13.9 | 31.7 | 1.2 | 6.6 |
| (4) | 2.1 | 12.5 | 42.1 | 0.4 | 12.7 | 1.6  | 1.5  | 25.1 | 1.4 | 0.4 |
| (5) | 3.9 | 23.3 | 13.3 | 2.9 | 6.2  | 32.2 | 0.8  | 5.9  | 0.6 |     |
| (6) | 7.3 | 38.5 | 25.8 |     | 5.2  | 2.3  | 13.2 | 5.4  | 0.8 |     |
| (7) | 4.7 | 23.3 | 13.3 | 2.9 | 6.6  | 36.3 | 0.7  | 5.9  | 0.6 |     |
| (8) | 10  | 51   | 24.2 | 0.3 | 8    | 1.6  | 0.3  | 2.9  | 0.9 |     |

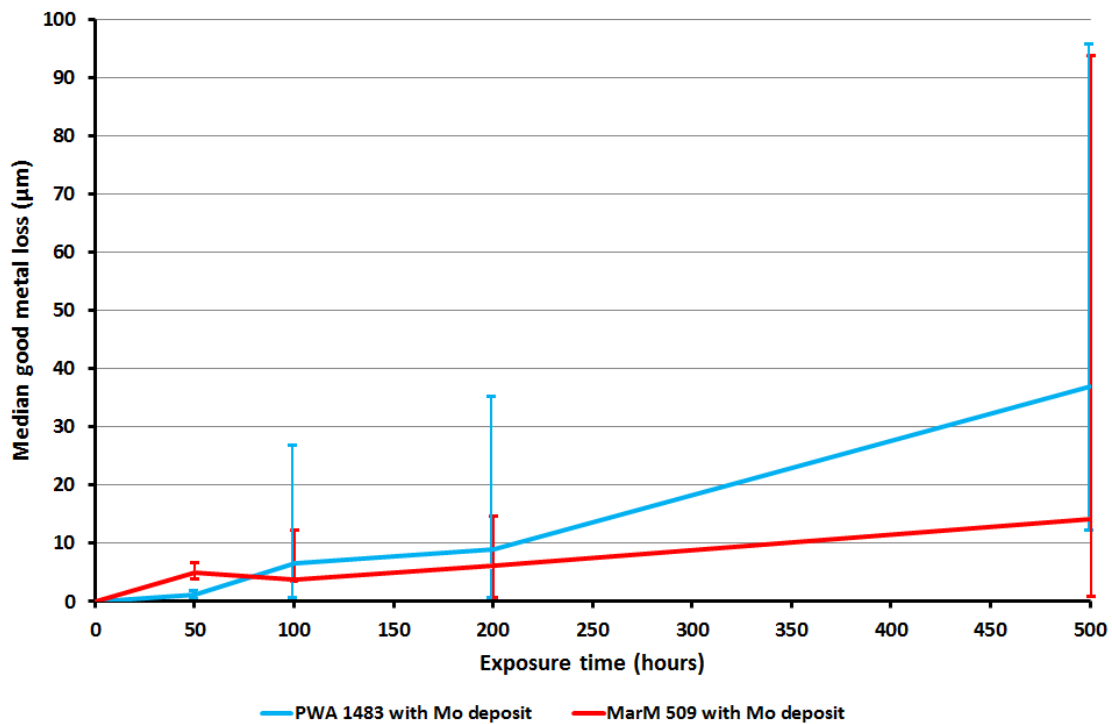
Figure 6.7: BSE image with point analysis (wt%) and EDX element map of a corrosion feature on MarM 509 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h each of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo. Atomic % EDX data given in Figure D.4.

#### **6.4 Effect of molybdenum additions on hot corrosion kinetics**

The median good metal loss values of data in Figures 6.1 and 6.2 are presented in Figure 6.8 with the data range bars indicating 4 and 96% probability of metal loss exceedance values. The median metal loss value of PWA 1483 and MarM 509 remains similar (within 4  $\mu\text{m}$ ) up until 200 hours of exposure. After 500 hours, the median metal loss value of PWA 1483 is significantly greater (37  $\mu\text{m}$ ) compared to MarM 509 (14  $\mu\text{m}$ ). This indicates that the incubation period for the majority of the surface of both alloys lies between 200 and 500 hours.

The 4% probability of metal loss exceedance value, indicated by the upper range limit bars, show that parts of both PWA 1483 and MarM 509's surfaces have transitioned from incubation to propagation at a point between 50 and 100 hours of exposure. The difference between 4% probability of metal loss exceedance values of PWA 1483 and MarM 509 is greater after 100 and 200 hours of exposure (15 and 21  $\mu\text{m}$  respectively) than after 500 hours (2  $\mu\text{m}$ ). This may be a consequence of a possible change in mechanism that has allowed for morphological features such as those observed in Figure 6.7 to occur after 500 hours of exposure.

The 96% probability of metal loss exceedance value, indicated by the lower range limit bars, show that parts of both PWA 1483 and MarM 509's surfaces have remained in incubation during exposures. The exception to this is for PWA 1483 after 500 hours which has suffered a minimum of 12  $\mu\text{m}$  of metal loss.



**Figure 6.8:** Median good metal loss values with data range bars for PWA 1483 and MarM 509 exposed for 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 4/1 (Na/K)<sub>2</sub>SO<sub>4</sub> followed by 1.5 µg/cm<sup>2</sup>/h of molybdenum.

Figures 6.9 and 6.10 compare the median and 4% probability of good metal loss exceedance for PWA 1483 and MarM 509 both with the Mo modified deposit and with the un-modified deposit. Data for exposures using the unmodified deposit is taken from Section 5.2.1, with the full distributions shown in Figures 5.1 and 5.2. The difference in median good metal loss values (Figure 6.9) for the two deposit compositions is small, 3 µm for PWA 1483 after 500 hours of exposure, and 2 µm for MarM 509. These differences in median good metal loss are small enough to be considered not significant.

The differences in the hot corrosion damage become more significant when comparing the 4% probability of good metal loss exceedance values after 500 hours of exposure (Figure 6.10). Here PWA 1483 has suffered a further 22 µm of good metal loss when the deposit has been modified with Mo while MarM 509 has lost 61 µm more metal.

Cracks in turbine component material systems can be induced by the formation of hot corrosion pits [103], [120]. The relatively high good metal loss values at a low level of cumulative probability (corresponding to pit features) for exposures with a Mo modified deposit can be therefore said to be significant for the lifetime of a turbine component.

These data presented in this chapter confirms that additions of Mo to the deposit increases metal loss due to hot corrosion. This thought to be due to alloy induced hot corrosion mechanism described in the literature [84]. Further research could include the modification of the deposit with other refractory metals. Ta in particular is a common addition to superalloy material systems. BSE micrographs of both PWA 1483 and MarM 509 (Figures 6.3 and 6.6) exhibit the oxidized remains of carbide precipitates rich in Ta within the corrosion product. It is therefore unclear if these species are able to react with the deposit as Mo appears to.

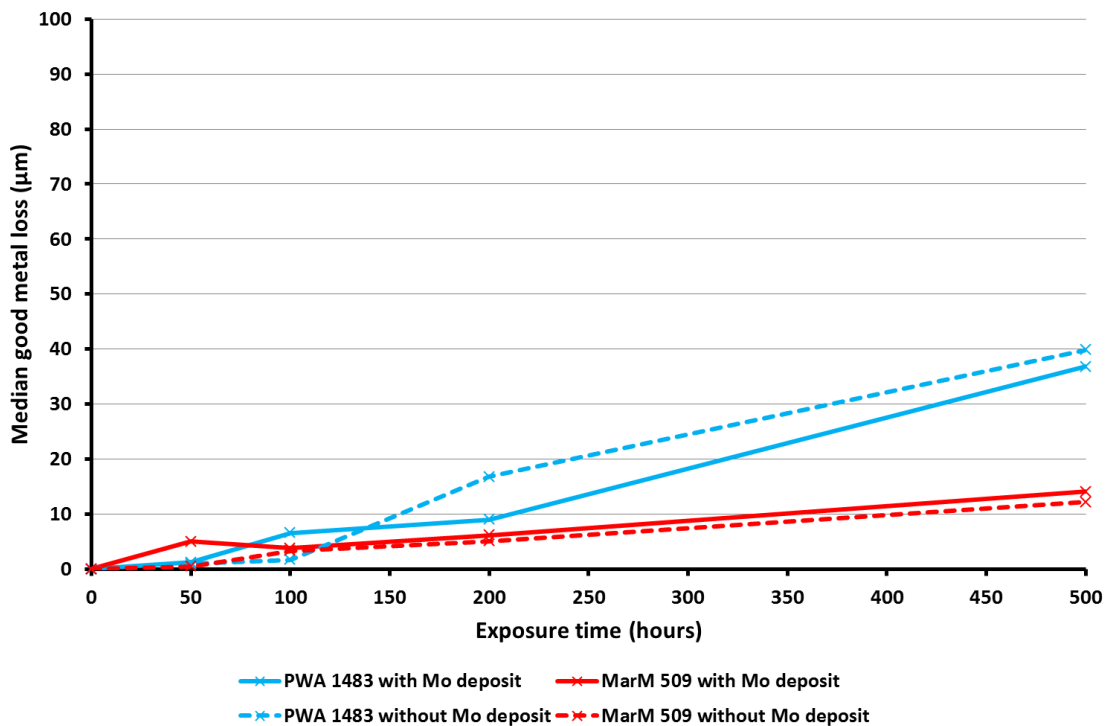


Figure 6.9: Median good metal loss data for PWA 1483 and MarM 509 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> either modified with 1.5 µg/cm<sup>2</sup>/h of molybdenum or unmodified.

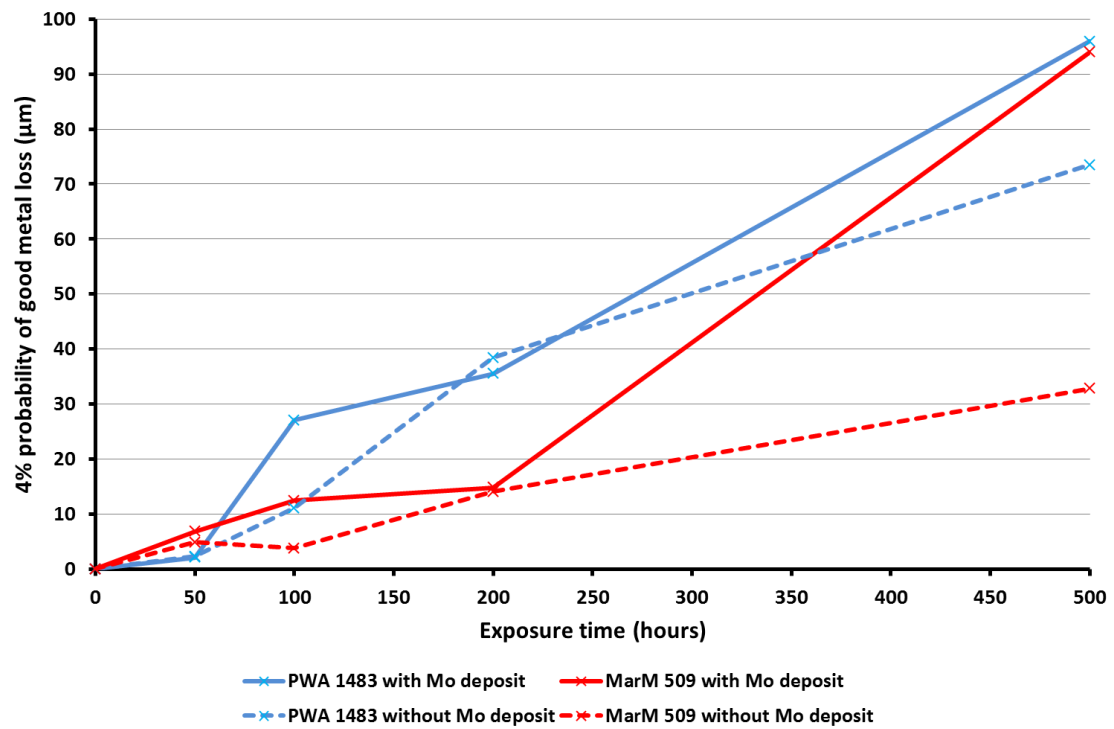


Figure 6.10: 4% probability of good metal loss data for PWA 1483 and MarM 509 exposed for up to 500 hours at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 μg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> either modified with 1.5 μg/cm<sup>2</sup>/h of molybdenum or unmodified.



## 7. General discussion

This chapter brings together the discussion of the findings of Chapters 4 to 6. This includes an estimate of error in the methodology in the next Section (Section 7.1). Also discussed are the effects of novel atmospheres associated with industrial turbines fired on H<sub>2</sub>-rich syngas (tests A to C), the effect of increasing water vapour (tests D to F) and the effect of Mo added to the deposit (test G). The industrial implications of this research are highlighted in Section 7.6.

### 7.1 Error analysis

This section first lists the sources of error inherent in the methodology then, where possible, determines a statistical value for the error. Sources of error have been grouped into three categories; pre-exposure metrology, operational error and post-exposure metrology. A more detailed explanation of how error values were calculated is given in Appendix C.

Pre-exposure metrology error includes the following:

- Micrometer resolution ( $\pm 1 \mu\text{m}$ )
- Micrometer quantizing (analogue to digital) ( $\pm 1 \mu\text{m}$ )
- Micrometer user error ( $\pm 1.3 \mu\text{m}$ )

The pre-exposure metrology errors combined amount to  $\pm 1.9 \mu\text{m}$ .

Operational errors are related to aspects of the methodology that don't involve direct dimensional measurement. These errors are difficult to quantify in terms of metal loss and rely on correlation to empirical data. Operational errors include the following:

- Deposit application ( $\pm 0.8 \mu\text{m}$ )
- Exposure temperature ( $\pm 1 \mu\text{m}$ )
- Atmosphere composition (Specifically SO<sub>2</sub> content)
- Water vapour content
- Spallation through sample handling and unloading temperature

- Sample composition
- Sample roughness

The quantified operational errors combined amount to  $\pm 1.3 \mu\text{m}$

Post-exposure error includes the following:

- Image analyser stage movement ( $\pm 1 \mu\text{m}$ )
- User error in plotting metal coordinates ( $\pm 0.5 \mu\text{m}$ )
- Sample mounting angle ( $+0.7 \mu\text{m}$ )

The post-exposure errors combined amount to  $+1.3$  and  $-1.1 \mu\text{m}$ .

Based on the error values calculated for pre-exposure metrology, operation and post-exposure metrology, a total error of  $+2.6$  and  $-2.5 \mu\text{m}$  can be derived.

## 7.2 The influence of water vapour on corrosion kinetics

Tests A to C, that were described in Chapter 4, investigated hot corrosion in industrial gas turbines three novel simulated atmospheres produced when firing on  $\text{H}_2$ -rich syngas. Two of these atmospheres had a low  $\text{SO}_2$  content (3.6 ppm) and differed most significantly in their  $\text{H}_2\text{O}$  contents (10 and 20 vol.%). In these exposure conditions, higher corrosion rates were observed in the test atmosphere with a higher  $\text{H}_2\text{O}$  content.

Chapter 5 investigated the effect of increasing water vapour in an atmosphere of 300 ppm  $\text{SO}_2$  in air. In these test atmospheres, the corrosion rates were generally observed to decrease as the water content increased (from 0 to 20 vol.%). Selected samples from the hot corrosion tests described in Chapters 4 and 5 both used the same deposit (80%  $\text{Na}_2\text{SO}_4$ , 20%  $\text{K}_2\text{SO}_4$ ) and deposit flux ( $1.5 \mu\text{g}/\text{cm}^2/\text{h}$ ). Median good metal loss data from these tests are presented in Figure 7.1 for comparison.

A number of studies described in the literature [55]–[60], [62], [63] (Section 2.5.1) observed increases in oxidation rates for chromia forming alloys as the concentration of water vapour in air atmospheres increased. Some of these

studies [59], [60], [62], [63] hypothesize that water vapour is able to volatilize the protective chromia scale (to form  $\text{CrO}_2(\text{OH})_2$  and  $\text{Cr}(\text{OH})_3$  species) rendering it non-protective. The volatilization of the chromia scale provides one explanation for why hot corrosion rates were observed to increase with increasing water vapour content in a test atmosphere containing 3.6 ppm  $\text{SO}_2$  (shown in Figure 7.1).

If the volatilization of the chromia scale is accepted as the mechanistic reason for the increasing corrosion rates with higher levels of water vapour in a 3.6 ppm  $\text{SO}_2$  atmosphere, then a second mechanism is required to explain the decrease in corrosion rates with higher levels of water vapour observed in the 300 ppm  $\text{SO}_2$  atmosphere. One such mechanism could involve the interaction of water vapour and  $\text{SO}_2$  creating an environment where the  $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$  deposit becomes less stable, possibly by affecting the  $\text{SO}_2/\text{SO}_3$  equilibrium. Further research could investigate the effects of water vapour on salt stability at high temperatures.

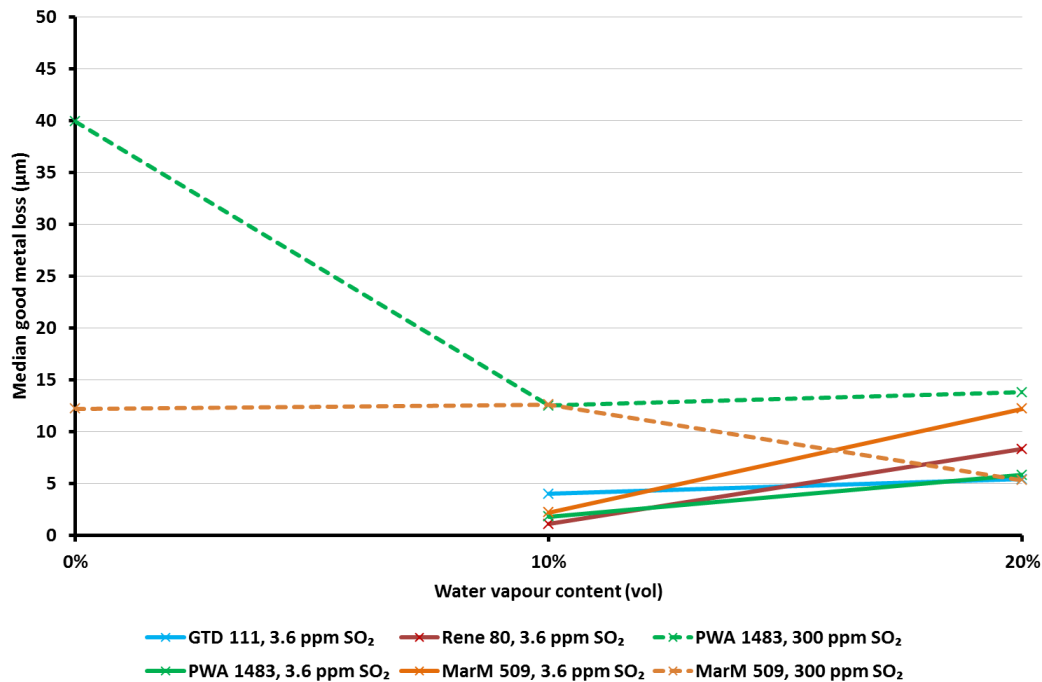
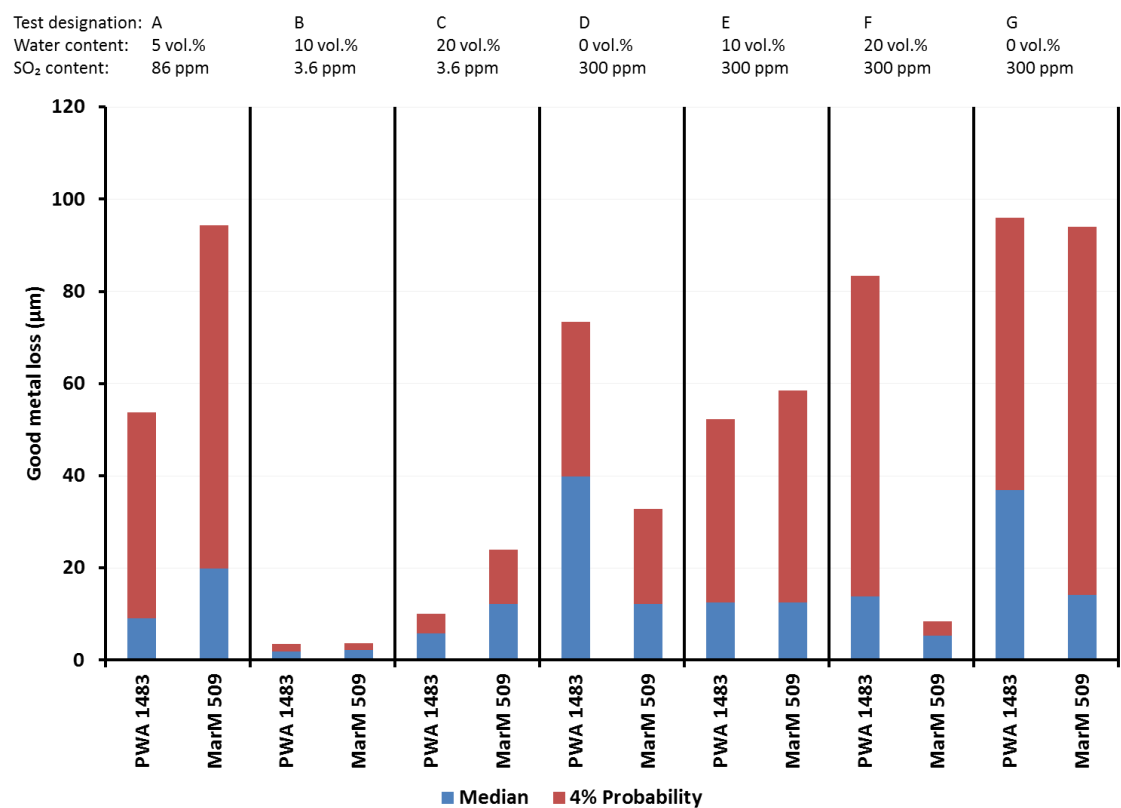


Figure 7.1: Median good metal loss values after 500 hours of exposure at 700 °C in atmospheres containing 3.6 or 300 ppm  $\text{SO}_2$ , and 0, 10 or 20 vol.% water vapour. The deposit was 80%  $\text{Na}_2\text{SO}_4$ , 20%  $\text{K}_2\text{SO}_4$  with a flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$ .

### 7.3 Relative corrosion performance of MarM 509 and PWA 1483

Good metal loss data produced by the hot corrosion tests A to C (described in Chapter 4) generally show greater degradation for MarM 509 than GTD 111, Rene 80 or PWA 1483 when exposed under the same conditions. In contrast to this, good metal loss data acquired from hot corrosion tests D to F (Chapter 5) and test G (Chapter 6) generally show greater degradation for PWA 1483 when compared to MarM 509. Selected data from tests A to G exposed with the same deposit flux ( $1.5 \mu\text{g}/\text{cm}^2/\text{h}$ ) are presented in Figure 7.2.



**Figure 7.2: Median and 4% good metal loss exceedance values for PWA 1483 and MarM 509 for tests A to G after 500 hours of exposure with a deposit flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$  80% Na<sub>2</sub>SO<sub>4</sub> & 20% K<sub>2</sub>SO<sub>4</sub>.**

Three significant differences between PWA 1483 and MarM 509 are shown in Table 7.1. These include the superalloy's base element (Ni or Co respectively), Cr content and the area percentage of carbide precipitates.

**Table 7.1: Summary of selected key differences between PWA 1483 and MarM 509 that may influence degradation rates and mechanisms.**

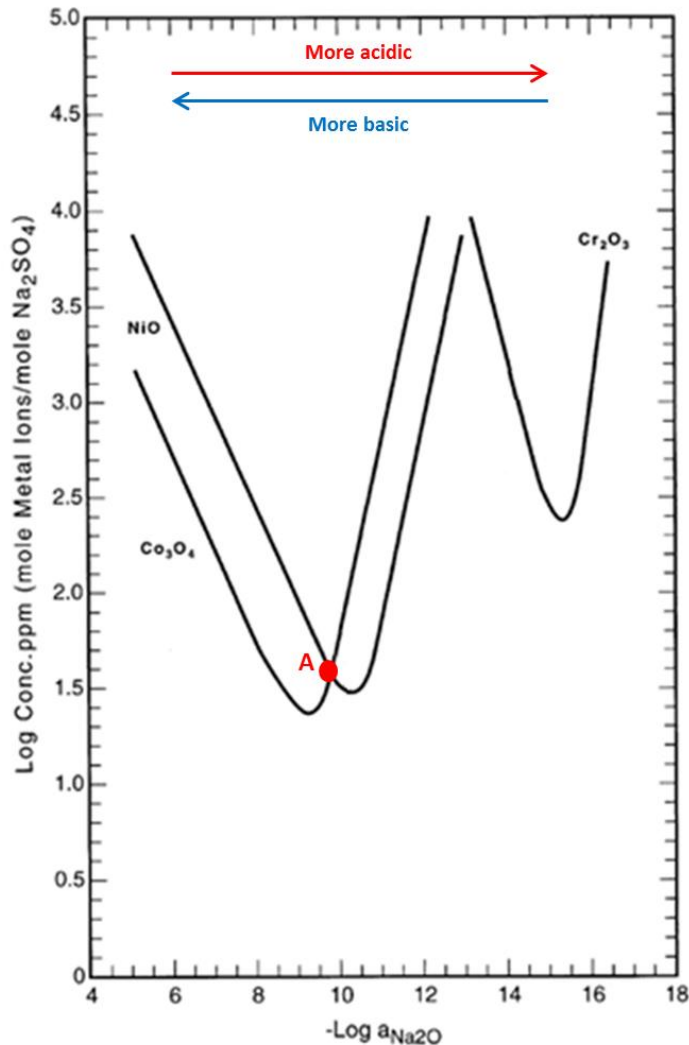
|          | Base element | Cr content (% wt) | Precipitate (area %) |
|----------|--------------|-------------------|----------------------|
| PWA 1483 | Nickel       | 12.2              | 0.9                  |
| MarM 509 | Cobalt       | 23.5              | 6.2                  |

The Cr content of  $\text{Cr}_2\text{O}_3$ -forming alloys has been identified as a key factor influencing hot corrosion kinetics [14], [15] with increasing Cr content leading to reduced oxidation rates and lengthened hot corrosion incubation times. If Cr content was the sole or overwhelmingly dominant factor in determining the hot corrosion rates then one may expect to consistently see greater good metal loss values for PWA 1483 than MarM 509 for all corrosion tests (A to G). Figure 7.2 shows this not to be the case; therefore other possible explanations should be explored.

One significant difference between tests A to C, where the degradation of MarM 509 exceeds PWA 1483, and tests D to F, where the degradation of PWA 1483 exceeds MarM 509, is the  $\text{SO}_2$  content in the test atmosphere.  $\text{SO}_3$  (in equilibrium with  $\text{SO}_2$ ) from the gas phase is thought to stabilise the acidity of the molten deposit [66], therefore test environments with a higher concentration of  $\text{SO}_2$  should remain in an acidic fluxing regime for longer. A body of work [78], [82] determining the solubility curve of various metal oxides in fused  $\text{Na}_2\text{SO}_4$  at 927 °C (plotted in Figure 7.3) shows that  $\text{Co}_3\text{O}_4$  has a solubility minimum at a point more basic than  $\text{NiO}$ . As a deposit becomes more acidic than the point at which the solubility curve of  $\text{Co}_3\text{O}_4$  bisects the curve of  $\text{NiO}$  (Figure 7.3 point A),  $\text{Co}_3\text{O}_4$  may be considered more soluble than  $\text{NiO}$ . Since the base element of MarM 509 is Co and for PWA 1483 it is Ni, one could therefore expect greater degradation of MarM 509 relative to PWA 1483 in tests D to F (300 ppm  $\text{SO}_2$ ) than tests A to C (90 to 3.6 ppm  $\text{SO}_2$ ). The opposite trend is observed in Figure 7.2 therefore the solubility curve differences of  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$  does account for the difference.

The solubility curve of  $\text{Cr}_2\text{O}_3$  is positioned to the right of the  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$  curves in Figure 7.3.  $\text{Cr}_2\text{O}_3$  could potentially dissolve in  $\text{Na}_2\text{SO}_4$  through basic fluxing while  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$  dissolve through acidic fluxing. In a regime of basic

dissolution,  $\text{Cr}_2\text{O}_3$  is more soluble than  $\text{Co}_3\text{O}_4$  and  $\text{NiO}$ . MarM 509 has a higher Cr content (23.5 wt.%) than PWA 1483 (12.2 wt.%) and could therefore be more susceptible to the more basic conditions of tests A to C than the more acidic conditions of tests D to G. This is consistent with the data shown in Figure 7.2.



**Figure 7.3:** Measured solubility curves of  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$  and  $\text{Cr}_2\text{O}_3$  in fused  $\text{Na}_2\text{SO}_4$  at 927 °C [78], [82].

The area percentage of the alloy that is made up of carbide precipitates is much greater for MarM 509 compared to PWA 1483 (6.2 and 0.9% respectively). These carbide precipitates may allow alloy induced fluxing mechanisms to occur alongside gas phase induced fluxing. In this case, alloy induced fluxing is likely a more dominant mechanism where the concentration of  $\text{SO}_2$  in the gas phase is

lower (tests A to C), and less dominant where the concentration of SO<sub>2</sub> in the gas phase is higher (tests D to G). Alternatively, or additionally, the carbide precipitates may disrupt the formation of protective oxide scales. This is discussed in the next section (7.4).

## 7.4 Carbide precipitate degradation

This section describes how the refractory metal carbides present in the alloys oxidise more rapidly than the surrounding alloy matrix and has been published as part of an article in the journal *Materials at High Temperature* [17]. Carbide precipitates may also disrupt the formation of a continuous protective chromia scale by causing a localised area lean in Cr. It is not clear if the effect of carbide precipitates should be more influential for hot corrosion occurring in atmospheres with a lower SO<sub>2</sub> content, however the possibility should not be disregarded.

BSE micrographs in Chapter 4 show hot corrosion degradation often distributed around refractory metal carbides that contact the alloy surface. This effect appears to be particularly severe in the case of MarM 509, which has a greater proportion of precipitate phases than the other alloys investigated and, according to good metal loss data reported in Chapter 4, a worse corrosion performance in the H<sub>2</sub>-IGCC derived gas turbine environments (tests A to C). In this section the role alloy precipitates play during type II hot corrosion attack is explored in greater detail.

The main phases present in the alloys GTD 111, Rene 80, PWA 1483 and MarM 509 were described in detail in Section 3.6; these included  $\gamma$ - $\gamma'$  alloy matrix and refractory metal carbide phases. Figure 7.4 shows BSE images of the large carbide phases at locations away from the alloy surfaces. EDX point analyses show the elemental composition of these phases (Table 7.2). It should be noted that the electron beam has a diameter of approximately 1  $\mu$ m and penetrates up to 5  $\mu$ m into the surface of the substrate, therefore the EDX signal may pick up elements from adjacent phases and so the compositions produced may include contributions from multiple phases.

In Figure 7.4 and Table 7.2, point one is representative of the bulk alloy matrices. All four alloys are described in the literature as able to form a  $\gamma$ - $\gamma'$  matrix [113], [116]–[118], however it can be seen in Figure 7.4 that only Rene 80 has been supplied featuring this binary phase.

Point two is the primary carbide phase, identified in the literature as MC type carbides containing refractory metals [113], [116]–[118]. These are of irregular shape and typically 10-100  $\mu\text{m}$  in size. Point analysis (Table 5.1) shows that, for GTD 111, PWA 1483 and MarM 509, this carbide phase is particularly rich in Ta. By contrast, in the case of Rene 80, the primary carbide phase is rich in Ti and W.

Point three is secondary carbide phases described as  $\text{M}_{23}\text{C}_6$  and  $\text{M}_6\text{C}$  type in the literature [113], [116]–[118]. For GTD 111, Rene 80 and PWA 1483, these phases are relatively small (approximately 1  $\mu\text{m}$ ) and of a more regular shape. These secondary carbides appear to have higher Mo content than the primary carbides. The MarM 509 secondary carbide phase appears to be a binary phase which has a similar size and shape to the primary carbide phase and is particularly rich in Cr.

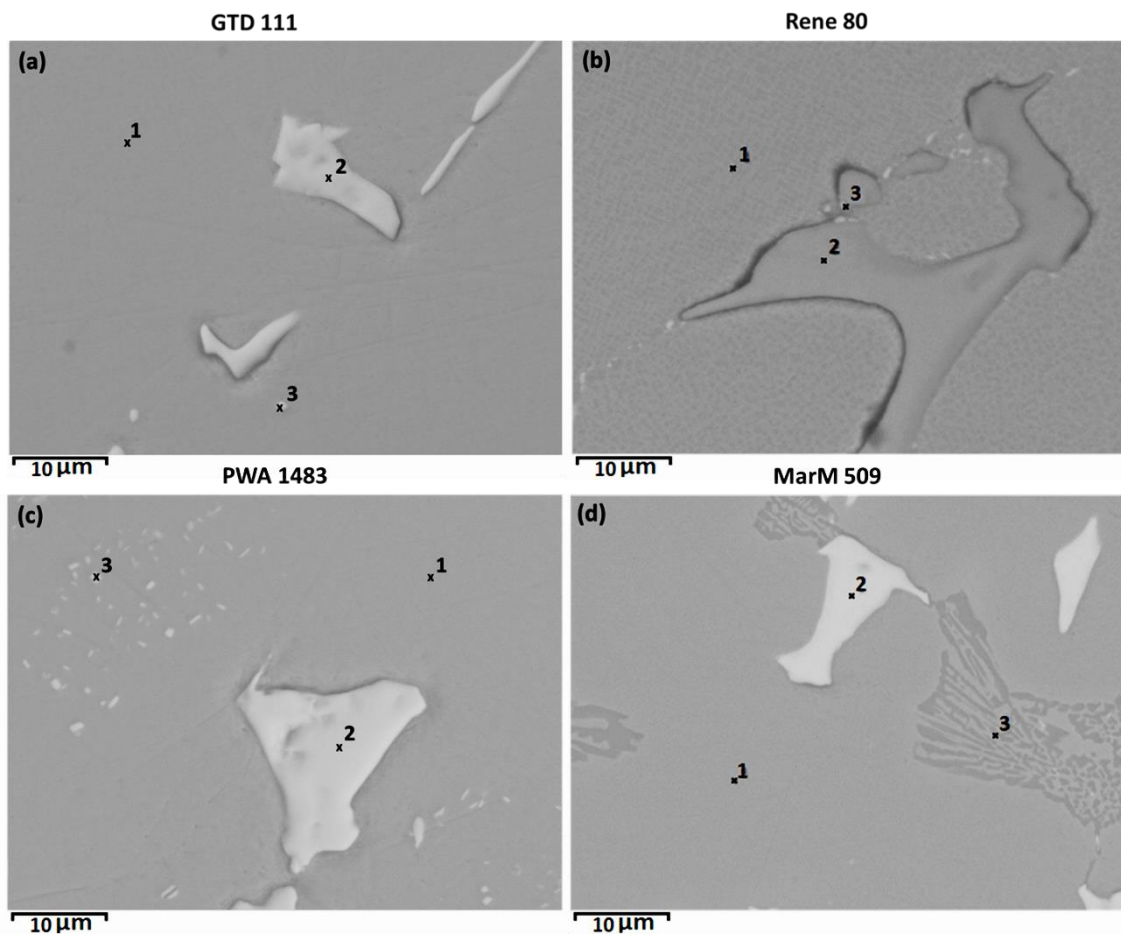


Figure 7.4: BSE images of selected points showing the larger carbide phases present in (a) GTD 111, (b) Rene 80, (c) PWA 1483 and (d) MarM 509.

Table 7.2: Element compositions (Wt.%) of selected points in Figure 7.4 for (a) GTD 111, (b) Rene 80, (c) PWA 1483 and (d) MarM 509. Atomic % data given in Figure D.5.

| (a) GTD 111 |     |      |      |      |      |     |     |     | (b) Rene 80 |     |      |      |      |      |      |     |
|-------------|-----|------|------|------|------|-----|-----|-----|-------------|-----|------|------|------|------|------|-----|
|             | Co  | Ni   | Cr   | Ta   | Ti   | W   | Mo  | Al  |             | Co  | Ni   | Cr   | Mo   | Ti   | W    | Al  |
| Point 1     | 9.8 | 59.5 | 13.9 | 3.8  | 3.6  | 5.5 | 1.3 | 2.7 | Point 1     | 9   | 58.4 | 13.3 | 4.1  | 6.3  | 5.1  | 2.4 |
| Point 2     | 4.8 | 33.3 | 8.9  | 26.3 | 15   | 9.6 | 0.7 | 1.2 | Point 2     | 4.9 | 30.1 | 7.9  | 10.2 | 27.2 | 17.5 | 1   |
| Point 3     | 6.7 | 44.8 | 9.7  | 16.5 | 9.19 | 8.5 | 2.7 | 2   | Point 3     | 6.4 | 39.3 | 14.2 | 17.2 | 8.4  | 11.9 | 1.4 |

| (c) PWA 1483 |     |      |      |      |      |     |     |     | (d) MarM 509 |      |     |      |      |     |     |     |
|--------------|-----|------|------|------|------|-----|-----|-----|--------------|------|-----|------|------|-----|-----|-----|
|              | Co  | Ni   | Cr   | Ta   | Ti   | W   | Mo  | Al  |              | Co   | Ni  | Cr   | Ta   | Ti  | W   | Zr  |
| Point 1      | 8.6 | 60.4 | 10.8 | 5.6  | 4.9  | 4.5 | 1.6 | 3.7 | Point 1      | 52.1 | 9.8 | 23.9 | 4.7  | 0.2 | 9   | 0.4 |
| Point 2      | 4.6 | 30.8 | 6.7  | 36.5 | 12.5 | 5.7 | 1.9 | 1.3 | Point 2      | 27.8 | 5.4 | 13.8 | 38.3 | 2.4 | 7.9 | 4.3 |
| Point 3      | 7.9 | 47.9 | 11.8 | 15.8 | 7    | 4.9 | 2.4 | 2.4 | Point 3      | 41.6 | 7.8 | 34.7 | 5.2  | 0.2 | 9.9 | 0.5 |

#### 7.4.1 The early stages of precipitate degradation

To show the development of carbide precipitate degradation during the early stages of oxidation, samples of MarM 509 and Rene 80 were exposed in air at 700 °C for 100 hours with no deposit.

Figure 7.5 shows a BSE image and associated EDX elemental maps for MarM 509. Two large precipitate phases are shown in contact with the sample's surface while a third may also contact the surface out of the imaging plane. It is apparent that these precipitates are undergoing a change in chemistry moving inward from the surface and that they have a disrupted region near the surface that protrudes outwards.

The O EDX map shows that the metal carbide precipitates at the alloy surface have oxidized approximately 20 µm inwardly along the precipitate. This oxidation is associated with the diffusion of specific elements to the metal surface and formation of metal oxides at the surface. These changes have created an area of the surface that is devoid of a protective oxide scale and would therefore be vulnerable to further environmental attack. Additionally, the boundary between the oxidized precipitate and the main alloy matrix appears well defined and may provide an inwards transport route for O that may allow lateral oxidation of the bulk alloy.

Figure 7.6 shows a typical BSE image and associated elemental maps of Rene 80 after 100 hours of exposure to air at 700 °C. In contrast to MarM 509, in Rene 80 the metal carbide precipitate is not vulnerable to rapid oxidation and remains relatively unaffected by this exposure. This carbide precipitate is shown to be Ti-rich in Table 7.2 and does not feature Ta, such a composition therefore appears to be more stable in O<sub>2</sub> than the Ta-rich primary carbide phase of MarM 509.

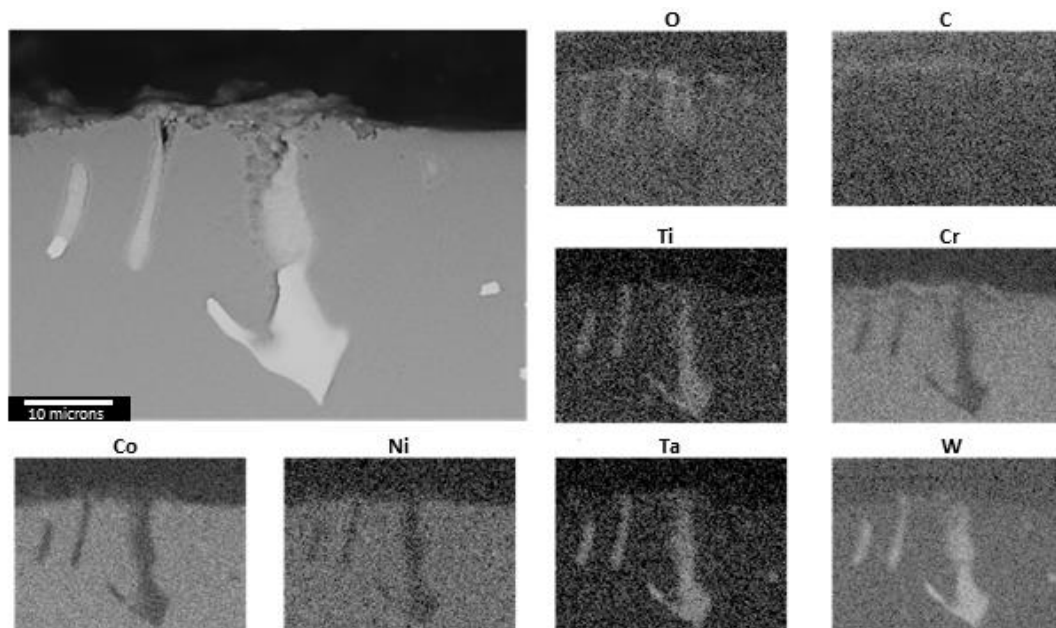


Figure 7.5: BSE image and EDX elemental maps of MarM 509 after exposure at 700 °C for 100 hours in air with no deposit.

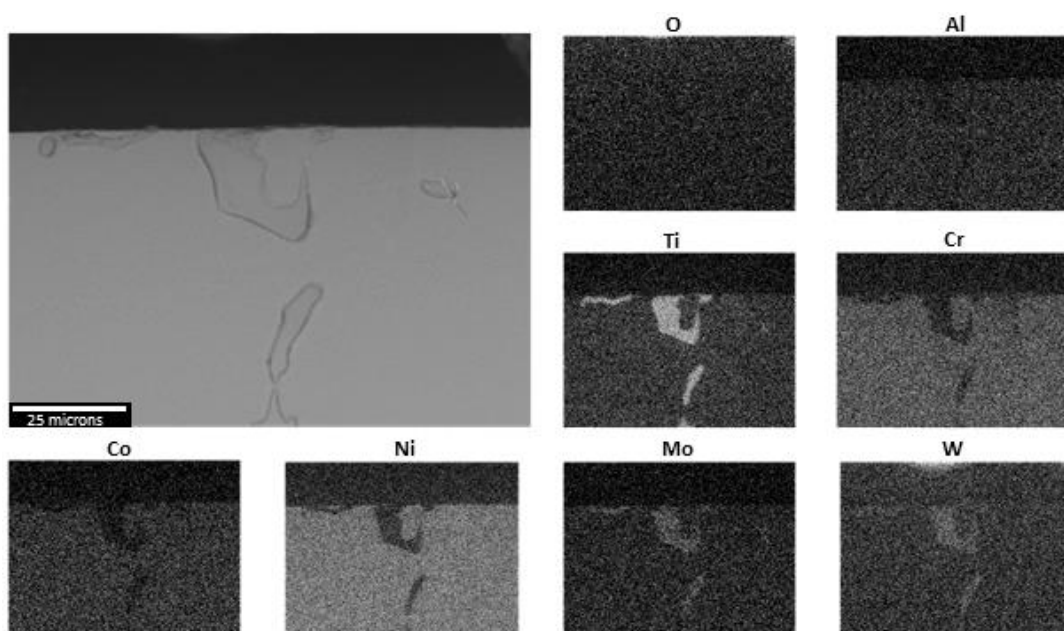


Figure 7.6: BSE image and EDX elemental maps of Rene 80 after exposure at 700 °C for 100 hours in air with no deposit.

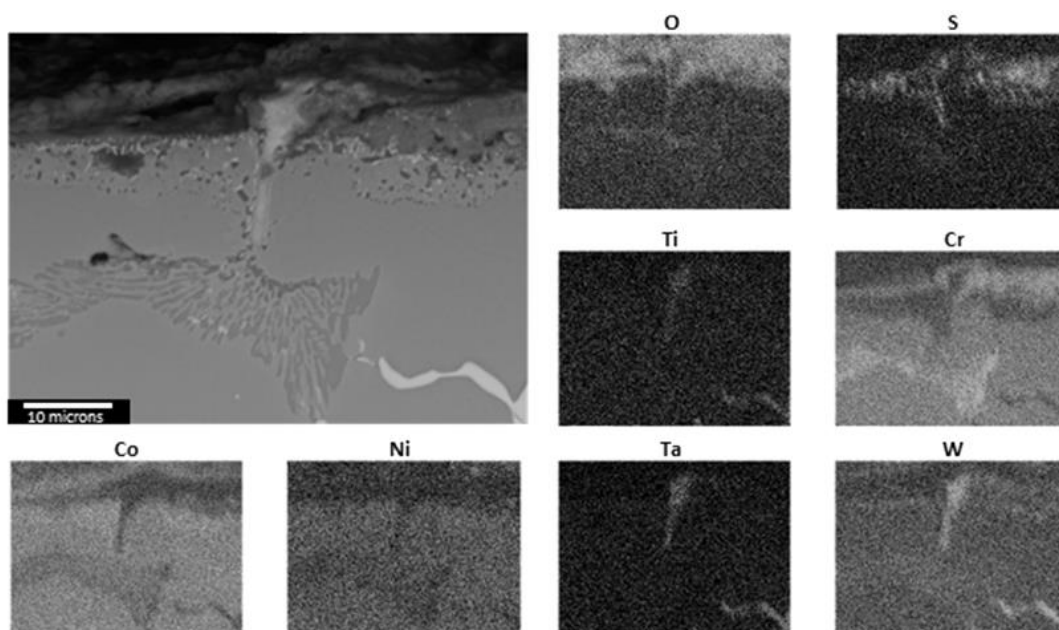
#### 7.4.2 Carbide precipitates and type II hot corrosion

Figure 7.7 shows a selected BSE image and associated elemental maps for MarM 509 after exposure for 100 hours at 700 °C to an atmosphere of 86 ppm SO<sub>2</sub>, 10 vol.% CO<sub>2</sub>, 8 vol.% O<sub>2</sub> and 5 vol.% H<sub>2</sub>O balanced in N<sub>2</sub> with a deposit flux of 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> (results of these conditions given in Chapter 4). The precipitate intersecting the surface has fully oxidized and new phases have formed in the alloy adjacent to the alloy/precipitate phase boundary (such phases are also observed near the alloy's surface). The EDX maps show these phases to be rich in S (as such, they may be sulphide precipitates); a feature more commonly associated with type I hot corrosion. Internal sulphidation has also occurred below the surface scale on the bulk alloy, although only to a depth of approximately 5 µm, which is less than the 15 µm observed when adjacent to the precipitate. The presence of deeper S-rich species close to the alloy/carbide phase boundary suggests that the corrosive species are able to use this phase boundary to transport more rapidly into the alloy.

The light gray precipitate which is Ta-rich and W-rich in Figure 7.7 extends down to a two phase region rich in Cr (of the type shown in Figure 7.4 (d) point 3). The carbide species within this zone have oxidized laterally from the point where this dark gray Cr-rich carbide meets the Ta carbide phase that intersects the surface. This again suggests that the Ta/W precipitates, or their interface with the alloy matrix can allow the transport of deleterious species deeper into the alloy matrix than precipitate free regions.

Figure 7.8 shows an example BSE image and associated elemental maps of Rene 80 after 100 hours of exposure at 700 °C to an atmosphere of 86 ppm SO<sub>2</sub>, 10 vol.% CO<sub>2</sub>, 8 vol.% O<sub>2</sub> and 5 vol.% H<sub>2</sub>O balanced in N<sub>2</sub> and deposit flux of 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>. The degradation shown in this micrograph has some typical type II hot corrosion features: e.g. a form of (in this case broad) pit with a corrosion product made up of an outer layer consisting of Ni and Co rich oxides, and an inner layer made up of Cr and Al oxides. The structure of this multi-layered corrosion product is based on the alloy elements' affinities for O<sub>2</sub>. The BSE image also indicates some internal sulphidation close to the alloy

surface (to a depth of approximately 2  $\mu\text{m}$ ) at the extremes of the image, albeit to a much lesser extent than that shown in Figure 7.7 for MarM 509 (approximately 5  $\mu\text{m}$ ). Rene 80 is a Mo-containing alloy, with that element being shown in Figure 7.4 to preferentially partition to the precipitate phases. Due to an overlap of X-ray energy peaks, Mo and S can be difficult to differentiate in these EDX maps, however, differences in atomic weight means that Mo shows up as lighter in BSE images. In this case there appears to be S containing precipitates in the alloy adjacent to the carbide precipitate visible on the micrograph, but again these are present to a lesser extent than those adjacent to the MarM 509 carbide precipitate shown in Figure 7.7. The metal carbide precipitate itself appears to have partially oxidized, with the lower region remaining unreacted.



**Figure 7.7: BSE image and EDX elemental maps of MarM 509 after exposure for 100 hours at 700 °C to an atmosphere of 86 ppm SO<sub>2</sub>, 10% CO<sub>2</sub>, 8% O<sub>2</sub> and 5% H<sub>2</sub>O balanced in N<sub>2</sub> and deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.**

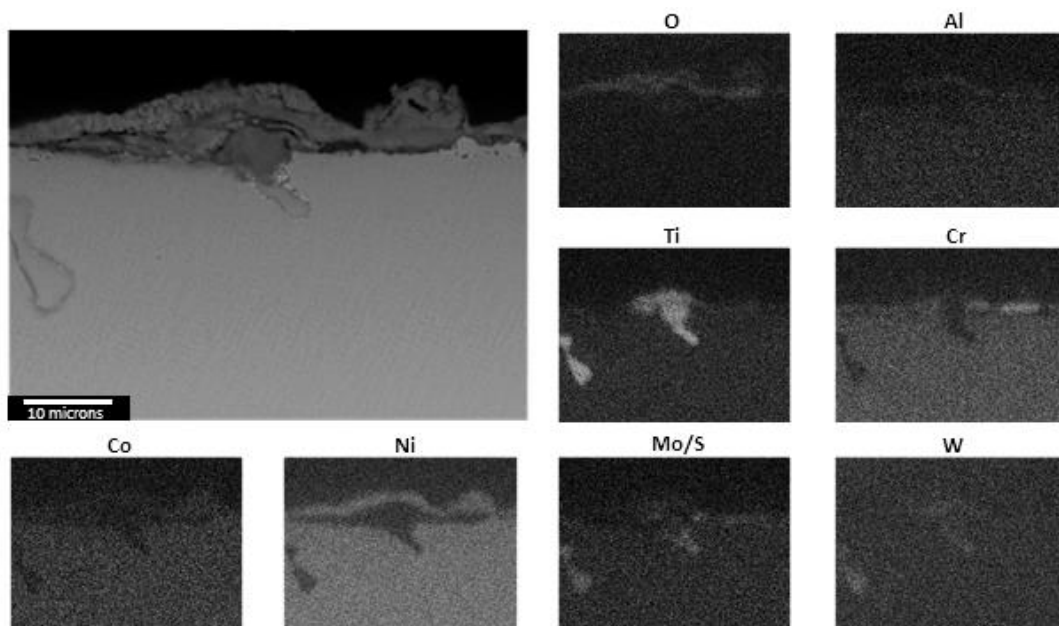


Figure 7.8: BSE image and EDX elemental maps of Rene 80 after exposure for 100 hours at 700 °C to an atmosphere of 86 ppm SO<sub>2</sub>, 10.% CO<sub>2</sub>, 8.% O<sub>2</sub> and 5% H<sub>2</sub>O balanced in N<sub>2</sub> and deposit flux of 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.

## 7.5 Mixed mode corrosion mechanisms

Degradation that exhibits features associated with both type I (internal sulphide species) and type II hot corrosion (pitting) is described as mixed mode hot corrosion. When exposed with the alkali sulphate deposits, the uncoated materials all exhibited at least some evidence of mixed mode corrosion after a sufficiently long exposure time in tests A to G.

The formation of internal sulphide species is brought about through a sufficiently high S activity below the metal interface. The basic fluxing mechanism is thought to bring about such a situation by removing the basic constituents of the melt through reactions with the metal [14], [85], [86] resulting in a higher concentration of S. Studies by Otsuka et al. [83] show that the acidity/basicity of a molten deposit varies over time during hot corrosion. It is possible that the molten deposit enters a basic fluxing regime in a localised area, allowing sulphidation to occur.

Figure 7.9 uses data on the solubility of metal oxide in fused  $\text{Na}_2\text{SO}_4$  (determined by Rapp et al. [78], [82]) to show how the acidity/basicity of the melt could possibly change over time as the hot corrosion reactions progress. Initially (Figure 7.9 left), reactions at the metal surface are dominated by the basic fluxing of chromia by the melt. Consumption of the basic constituent of the melt ( $\text{Na}_2\text{O}$ ), results in a greater concentration of the acidic constituent ( $\text{SO}_3$ ). As the hot corrosion reaction progresses from incubation to propagation, the chromia scale becomes compromised and acidic fluxing of the alloy base elements can occur (Figure 7.9 right). Examples of basic and acidic fluxing reactions are given in Section 2.6.2. It should be noted that the solubility curves calculated by Rapp et al. were determined at  $927^\circ\text{C}$  while exposures in the experimental work of this thesis were carried out at  $700^\circ\text{C}$ . Therefore details of the curves could be different.

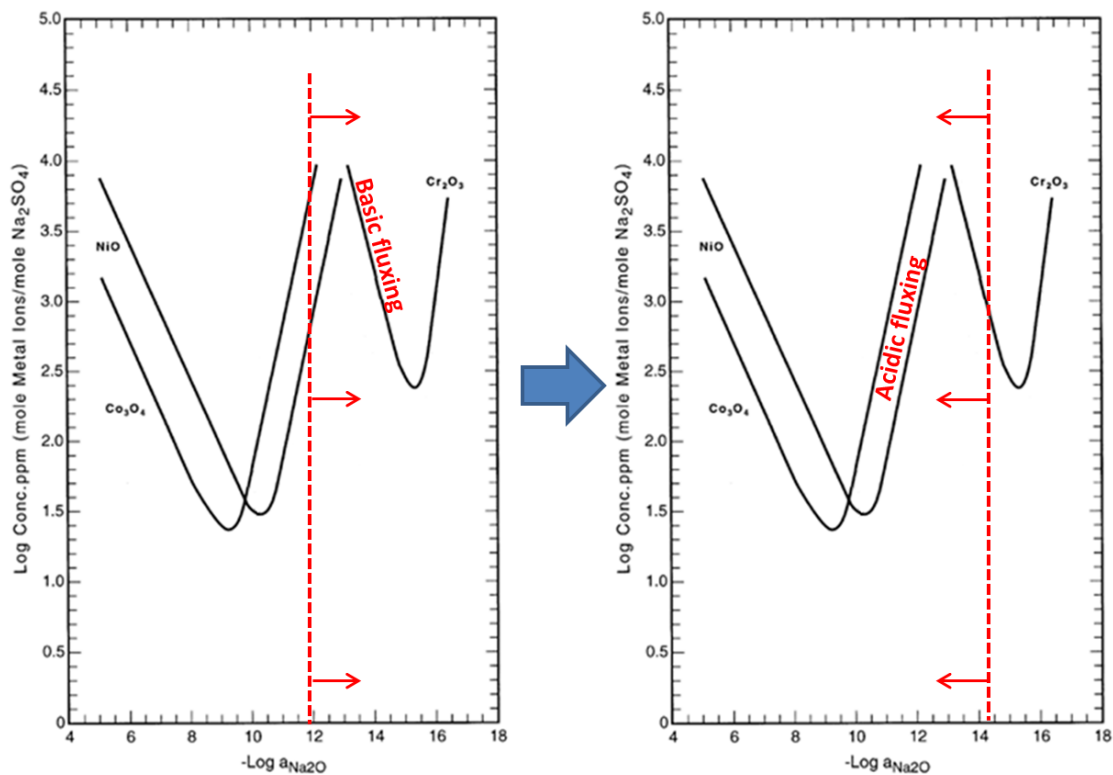


Figure 7.9: Illustration of how the acidity/basicity of the melt (dashed red line) may change during hot corrosion superimposed on solubility curves of selected metal oxides at  $927^\circ\text{C}$  determined by Rapp et al [78], [82].

Interactions with carbide precipitates of refractory metals may provide another method for altering the acidity/basicity of the deposit melt. When molten,  $\text{Na}_2\text{SO}_4$  can be broken down into a basic constituent ( $\text{Na}_2\text{O}$ ) and an acidic constituent ( $\text{SO}_3$ ). Refractory metals such as Mo and W are thought to react with the basic constituent of the melt; the reactions for this, using Mo as an example, are given in Section 2.6.3. This results in an increase in the acidity of the melt (in Figure 7.8 this would be shown by moving the dashed red line further to the right). The mechanism for this is the removal of the basic constituent and the generation of a second acidic species ( $\text{Na}_2\text{MoO}_4$  in the case of reactions with Mo). If the acidic species deriving from the refractory metal is the species that attacks the alloy, then the activity of  $\text{SO}_3$  in the melt could increase, possibly resulting in substrate sulphidation.

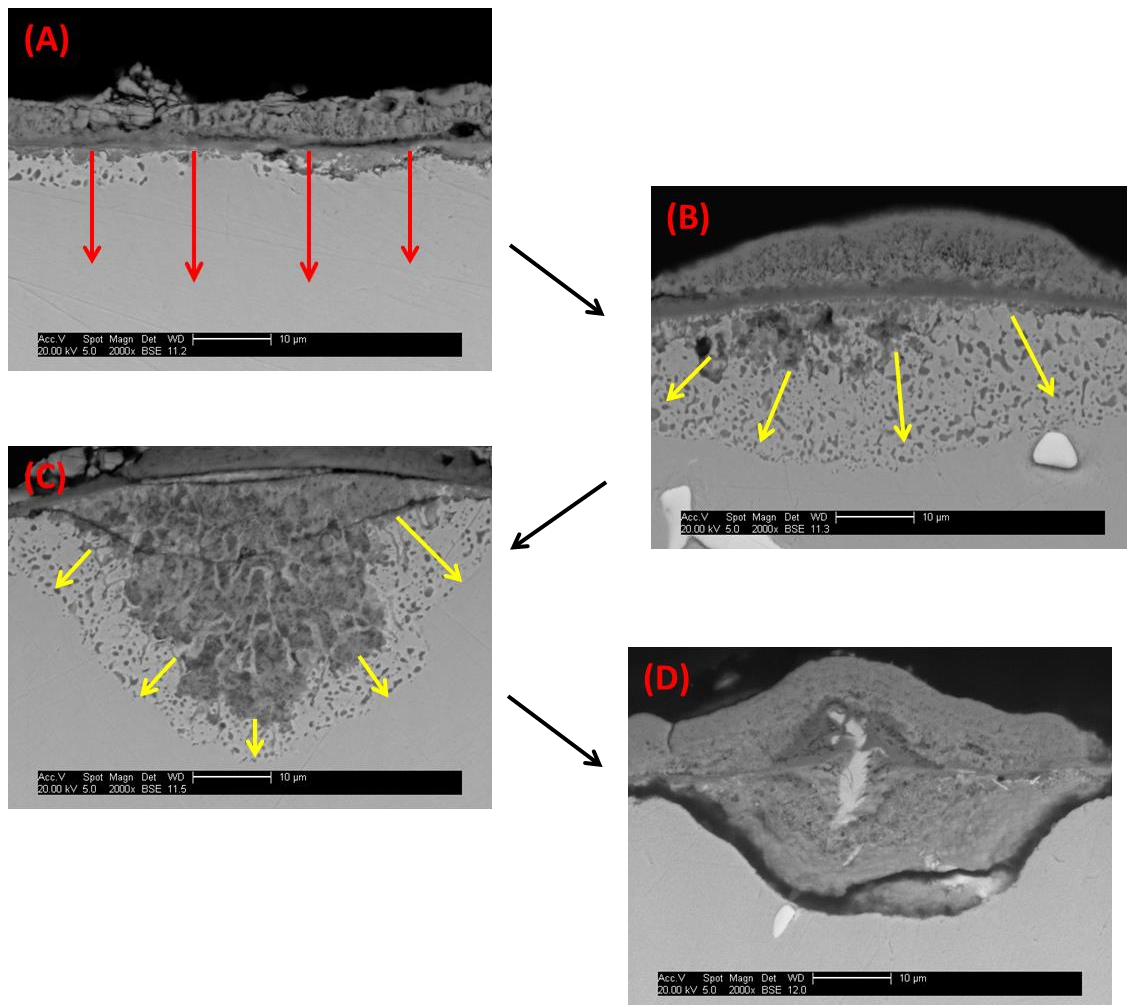
Figure 7.10 shows BSE micrographs of PWA 1483 arranged in an order to show the possible development of a pit feature through mixed mode hot corrosion. The pit development process may be governed by the local chemistry of the melt with new pits forming and progressing at different times and at different locations on the sample. For this reason the images presented in Figure 7.10 are not necessarily in chronological order.

When the surface of the alloy has passed the incubation stage and the local chemistry of the melt has a sufficiently high activity of S, S is able to dissolve into the alloy to create a distribution of sulphide species up to a certain depth. This is shown in Figure 7.10 moving from images A to B.

The formation of CrS precipitates within the alloy depletes the Cr content of the nearby metal making it more susceptible to hot corrosion attack. As the chemistry of the melt changes into a regime where acidic fluxing is more favourable, the areas of the sample affected by sulphidation, and therefore depleted in Cr, dissolve into the melt. This is shown in Figure 7.10 moving from images B to C.

The acidic fluxing corrosion front progresses either to the limit of the sulphidation front or beyond it when moving from images C to D in Figure 7.10. At this point evidence of the original sulphidation has been completely removed.

Hot corrosion could continue degrading good metal through acidic fluxing, this could be at a reduced rate compared to degradation of metal affected by sulphidation. Alternatively, the chemistry of the melt may re-enter a regime of basic fluxing for one or more elements in the alloy allowing further sulphidation to occur and the cycle (of A to D) to start again.



**Figure 7.10: BSE images showing the possible progression of mixed mode hot corrosion on PWA 1483 exposed at 700 °C in an atmosphere of 300 ppm SO<sub>2</sub> in air and with an 80% Na<sub>2</sub>SO<sub>4</sub>, 20% K<sub>2</sub>SO<sub>4</sub> deposit with a flux of 1.5 µg/cm<sup>2</sup>/h. The red arrows in image A shows the progression of sulphidation, the yellow arrows in images B and C show the progression of the acidic fluxing hot corrosion front.**

The literature pertaining to hot corrosion (Section 2.6) does not clearly define type I and type II hot corrosion. Descriptions of these phenomena are most often

based on typical observations such as temperature regime, fluxing type and hot corrosion morphology [14], [34], [66].

Mixed mode corrosion features were observed in all exposure conditions described in this thesis that allowed hot corrosion to progress from incubation to propagation (tests A and C to G). Given the prevalence of mixed mode hot corrosion morphology, especially in the early stages of hot corrosion, and how that is derived from the fluxing type, fluxing type and hot corrosion morphology may be misleading characteristics to use when distinguishing type I and type II hot corrosion.

## **7.6 Industrial implications**

The research presented in this thesis has several industrial implications. Chapter 4 shows that if an industrial gas turbine is to have the capability to operate with failure of the SO<sub>x</sub> removal sub-system then bare alloys should be expected to suffer enhanced hot corrosion rates. Maintaining component lives would require an environmentally resistant coating to avoid hot corrosion degradation.

Greater degradation should be expected firing the gas turbine on H<sub>2</sub>-rich syngas compared to natural gas and therefore environmentally resistant coating should be considered for that application. This increased level of degradation is not as severe as in the SO<sub>x</sub> removal failure scenario.

Data regarding the degradation of material in atmospheres with differing levels of water vapour have implications on the desired gas turbine operating atmosphere. With low levels of SO<sub>x</sub> in the turbine atmosphere, water vapour is detrimental, whereas in higher concentrations of SO<sub>x</sub>, there may be benefits.

Insights into the degradation of carbide precipitates at the surface of alloys contribute to the discussion on superalloy design. Certain carbide precipitate compositions may prove less detrimental to the material's corrosion performance than others and their adoption could extend component lifetimes.

## 8. Conclusions

Type II hot corrosion in industrial gas turbines has been investigated and scientific understanding of the effects of variables such materials selection, SO<sub>2</sub> content and water vapour on hot corrosion kinetics and mechanics has been furthered. This Chapter summarizes the findings of Chapters 4 to 7 and highlights their contribution to knowledge.

### 8.1 Type II hot corrosion in combusted hydrogen-rich syngas environments

A series of laboratory hot corrosion tests based on three possible operating conditions hydrogen-rich syngas fuelled industrial gas turbines have been carried out at 700°C. These conditions were based on the following; by-pass of syngas desulphurization (test A); combustion of natural gas (test B); combustion of hydrogen rich syngas (test C) and had variables including test atmosphere, deposit flux and materials.

- The environment of test A had the highest concentration of SO<sub>2</sub> (86 ppm) and produced the greatest degree of good metal loss. This confirms previous observations made in the literature [66], [121] and highlights the requirement for an effective desulphurization stage in the power plant. Materials exposed in test B did not progress beyond the incubation stage of hot corrosion. Greater degrees of metal loss were observed in test C compared to test B. These tests both had SO<sub>2</sub> contents of 3.6 ppm while the water vapour contents were 10 vol.% (test B) and 20 vol.% (test C), thus the increase in good metal loss in test C is attributed to the increase in water vapour content.
- Of the materials tested, MarM 509 consistently exhibited the greatest degree of metal loss while PWA 1483 showed the least. The hot corrosion performance of GTD 111 and Rene 80 were comparable to each other.

After 500 hours of exposure in test A with a deposit flux of  $5 \mu\text{g}/\text{cm}^2/\text{h}$ , the median good metal loss values of these alloys were: GTD 111,  $32.2 \mu\text{m}$ ; Rene 80,  $31.1 \mu\text{m}$ ; PWA 1483,  $9.5 \mu\text{m}$ ; and MarM 509,  $40.4 \mu\text{m}$ . One factor that may have contributed to the greater metal loss of MarM 509 is the higher vol. fraction of refractory metal carbides within the alloy matrix.

- The metallic coatings RT22 and SC2464 had a lower degree of metal loss than the uncoated alloys. After 500 hours of exposure in test A with a deposit flux of  $5 \mu\text{g}/\text{cm}^2/\text{h}$ , the median metal loss values of these metallic coatings were: RT22,  $10.9 \mu\text{m}$ ; and SC2464,  $21.3 \mu\text{m}$ . For the normal operating condition of the proposed  $\text{H}_2$ -IGCC turbine (test C) such coatings may be necessary to prolong the working lifetime of gas turbine blades and vanes.

## 8.2 The effect of water vapour

A series of laboratory type II hot corrosion tests investigated the effects of increasing water vapour. Tests were carried out at  $700^\circ\text{C}$  in an atmosphere of 300 ppm  $\text{SO}_2$  with 0, 10 and 20% water vapour contents, and a 80%  $\text{Na}_2\text{SO}_4$  20%  $\text{K}_2\text{SO}_4$  deposit with a flux of  $1.5 \mu\text{g}/\text{cm}^2/\text{h}$ .

- Lower metal loss values were observed with increasing levels of water vapour in the test atmosphere. After 500 hours of exposure at water vapour levels of 0, 10 and 20% vol. respectively, the median metal loss values of PWA 1483 were:  $39.9 \mu\text{m}$ ,  $12.5 \mu\text{m}$  and  $13.8 \mu\text{m}$ . For MarM 509 the median metal loss values were:  $12.2 \mu\text{m}$ ,  $12.6 \mu\text{m}$  and  $5.3 \mu\text{m}$ .
- The hot corrosion performance of MarM 509 is better than PWA 1483 in the 300 ppm  $\text{SO}_2$  test atmosphere at all three tested levels of water vapour. This is the opposite of the observations made in test A (86 ppm  $\text{SO}_2$ , 5% vol.  $\text{H}_2\text{O}$ ) and C (3.6 ppm  $\text{SO}_2$ , 20% vol.  $\text{H}_2\text{O}$ ). It is proposed that at lower levels of  $\text{SO}_2$  in the environment, alloy induced fluxing mechanisms of

refractory metal carbides (of which MarM 509 has more than PWA 1483) become more important than gas phase fluxing mechanisms.

### **8.3 Effect of molybdenum additions to the deposit**

Understanding of alloy induced acidic fluxing was enhanced through a laboratory corrosion test using either a standard deposit or one with additions of Mo to the deposit. Two methods by which carbide precipitates in the alloy matrix could exacerbate hot corrosion degradation: by disrupting the formation of a protective oxide scale, and a lot induced acidic fluxing. This method of testing eliminated the disruption of the protective scale as a factor in increasing corrosion rates that had been observed occur.

- Additions of Mo to the test deposit were found to increase metal loss values. This is attributed to alloy induced acidic fluxing. The effect was observed to be greater for MarM 509 than PWA 1484.

### **8.4 General conclusions**

- Mixed mode corrosion features (where both pits and the formation of internal sulphide precipitates occur) were observed in all tests with the exception of test B. Test B did not progress into hot corrosion propagation and so would not form any hot corrosion features. A model for how the acidity/basicity of the hot corrosion deposit melt may change over time was presented based on metal oxide solubility in molten  $\text{Na}_2\text{SO}_4$  curves derived by Rapp et al [78], [82], [77]. Switching between basic fluxing and acidic fluxing mechanisms provides one explanation for the prevalence of mixed mode hot corrosion features.
- Carbide precipitates at the alloy surface were degraded more quickly than the surrounding alloy matrix. These precipitates acted as nucleation sites

for hot corrosion and their oxidised remains were commonly observed within hot corrosion features. A mechanism by which refractory metal carbide precipitates may allow the transport of deleterious species into the alloy has been suggested.

## 9. Future work

Section 7.1 discusses the effect of water vapour on hot corrosion at 700 °C. It was found that under, certain atmospheres (featuring SO<sub>2</sub> levels between 3.6 and 86 ppm), good metal loss increased with increasing water vapour content. In contrast, in an atmosphere containing 300 ppm SO<sub>2</sub>, increasing levels of water vapour were found to reduce the amount of good metal loss. This relationship between SO<sub>2</sub> concentration, water vapour content and hot corrosion should be further explored.

Another avenue of research investigating the effect of water vapour could look at how the effects may differ at different temperatures. Different types of hot corrosion are thought to peak at both 700 and 900 °C; it is possible that water vapour could affect these hot corrosion reactions by different mechanisms or to a different extent at 900 °C compared to 700 °C.

Chapter 6 used additions of Mo within the deposit to investigate the role that alloy precipitates may have on hot corrosion at 700 °C. To further this research, additions of other refractory metal elements (such as Ta or W) could be used in place of Mo. This may determine which elements commonly added to superalloys affect hot corrosion degradation and to what degree. This avenue of research could lead to the development of refractory metal carbide precipitates with an optimal composition for oxidation and hot corrosion resistance while also meeting required mechanical properties.

All the exposures described in Section 3.6 (Table 3.1) had a maximum duration of 500 hours. The accurate determination of hot corrosion reaction kinetics through empirical testing relies on the generation of sufficient data. Extending exposures to 1000 hours would allow more data points from within the propagation stage of hot corrosion. Such data could be used to determine the length of hot corrosion incubation which corresponds to the effective lifetime of a component in terms of hot corrosion. Building a library of hot corrosion empirical kinetic data could facilitate future gas turbine materials selection.



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## Appendix A. Tests A to G weight change data

This chapter presents the cumulative weight change data for tests A to G. Weight change data is not as accurate as dimensional metal loss measurements for quantifying hot corrosion damage since both positive and negative weight change can occur during hot corrosion. Test parameters are given in Section 3.6.

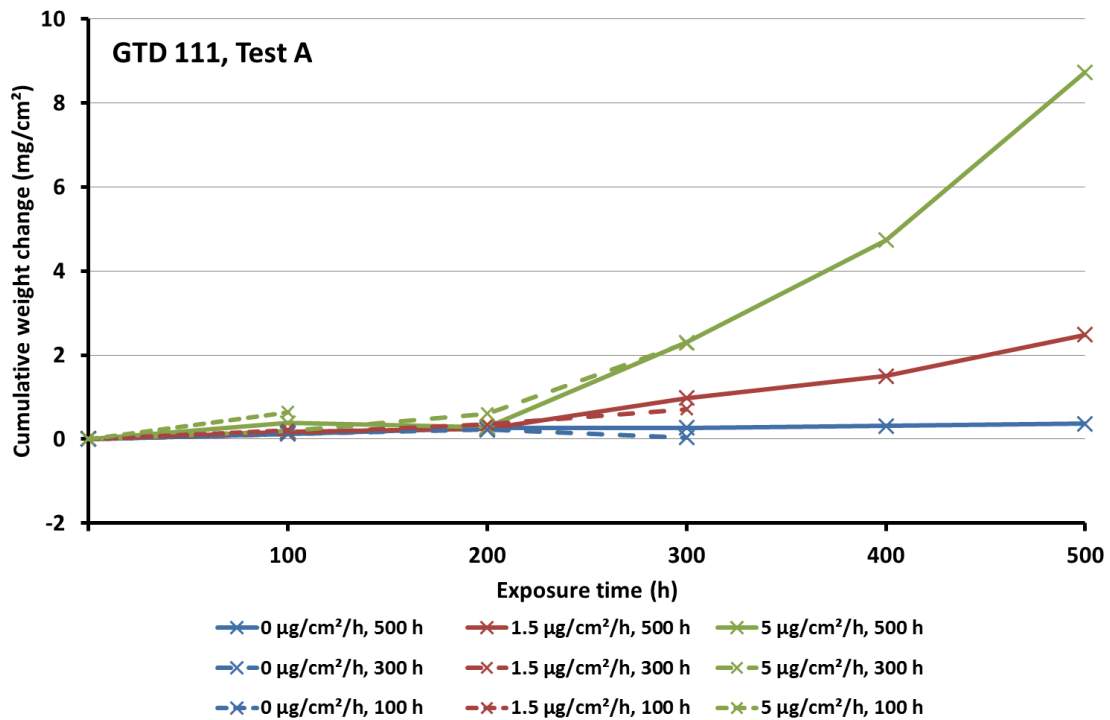


Figure A.1: Cumulative weight change data for GTD 111 exposed in test A at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

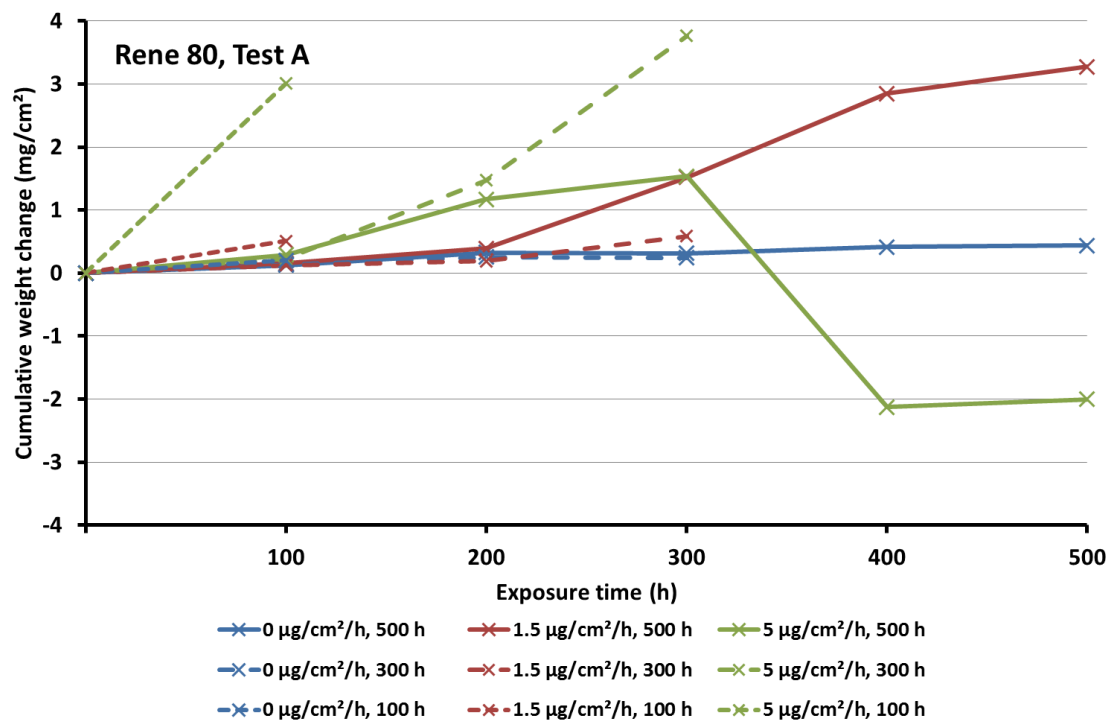


Figure A.2: Cumulative weight change data for Rene 80 exposed in test A at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

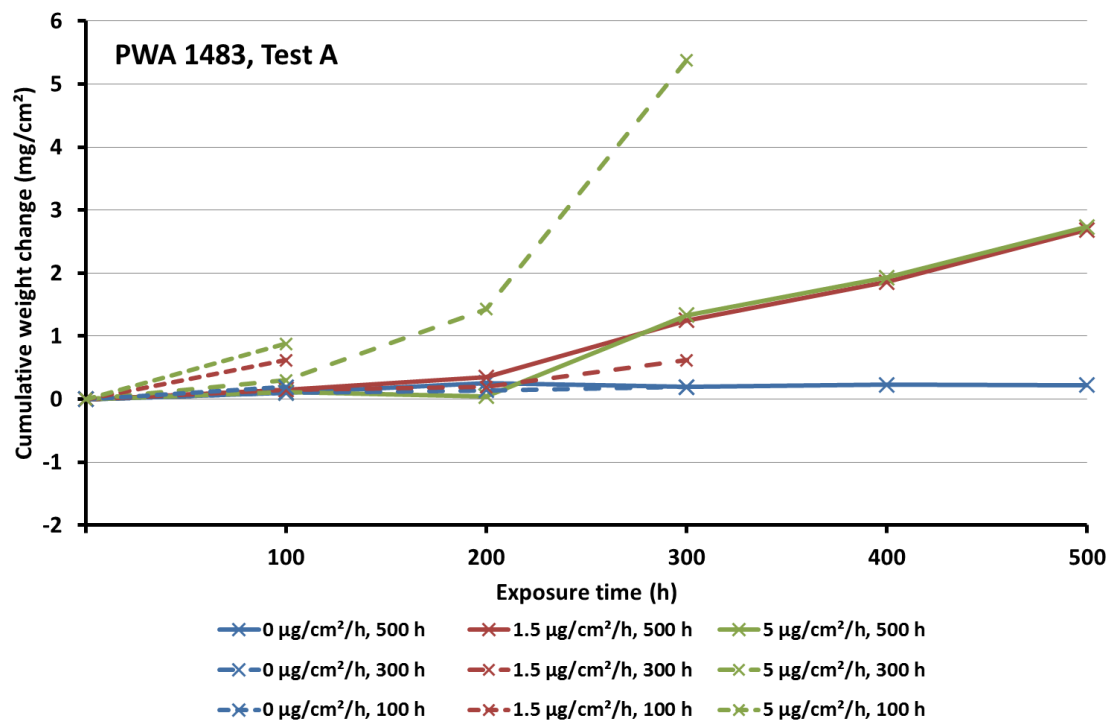


Figure A.3: Cumulative weight change data for PWA 1483 exposed in test A at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

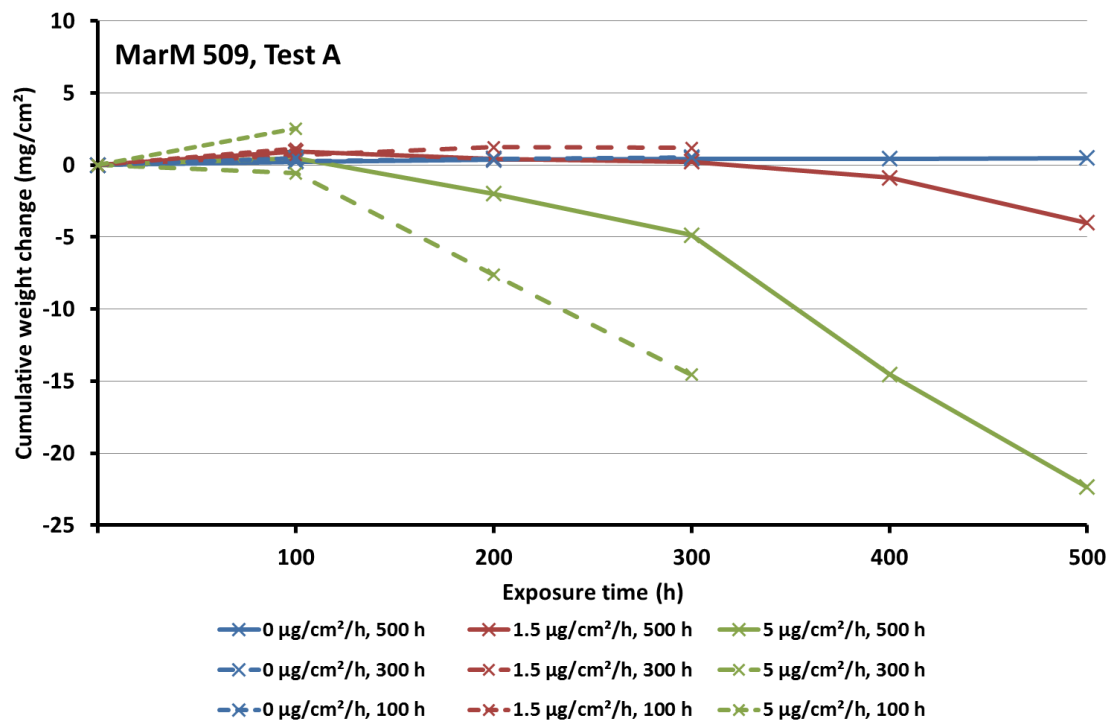


Figure A.4: Cumulative weight change data for MarM 509 exposed in test A at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

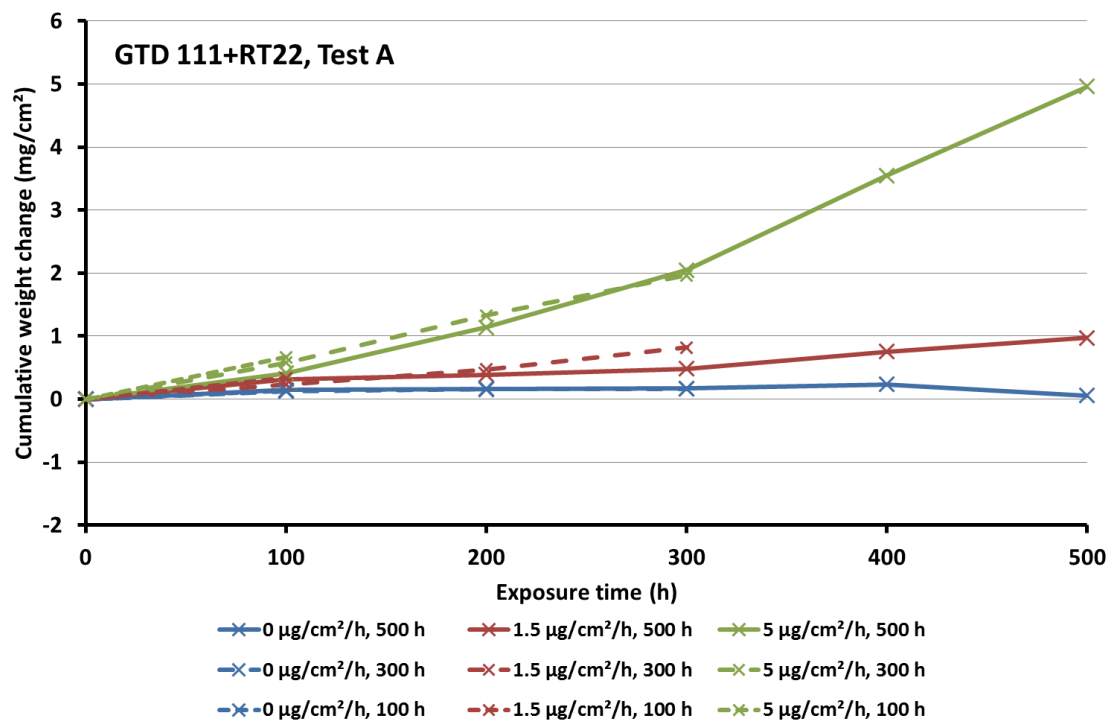


Figure A.5: Cumulative weight change data for RT22 coated GTD111 exposed in test A at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

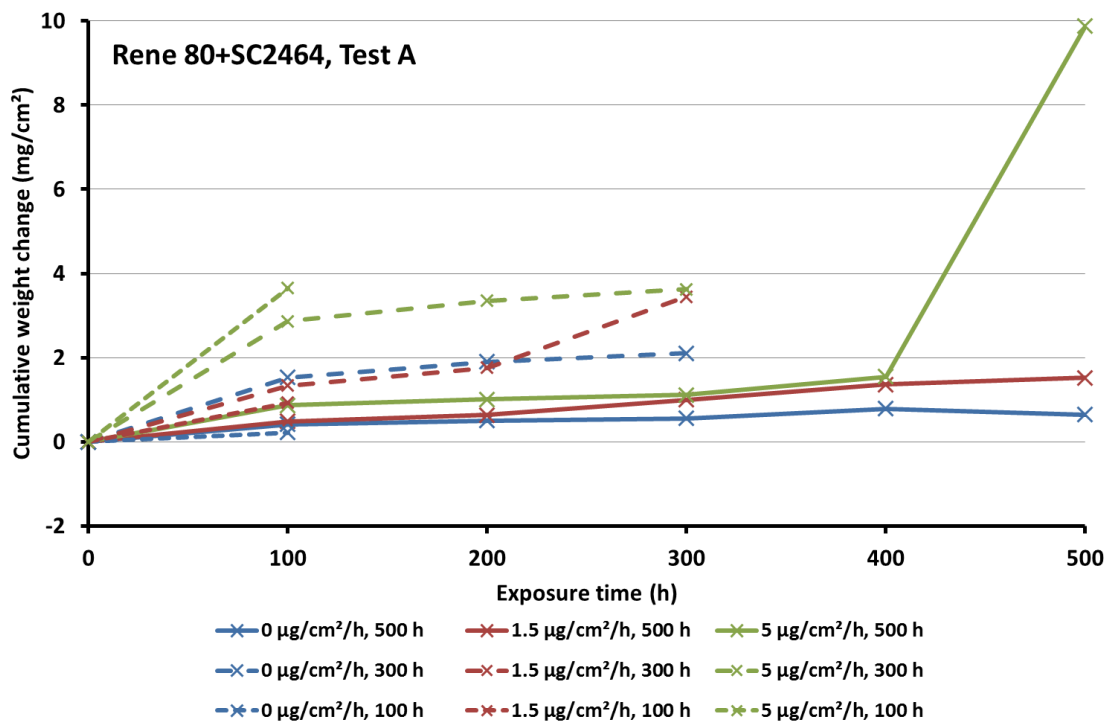


Figure A.6: Cumulative weight change data for SC2464 coated Rene 80 exposed in test A at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

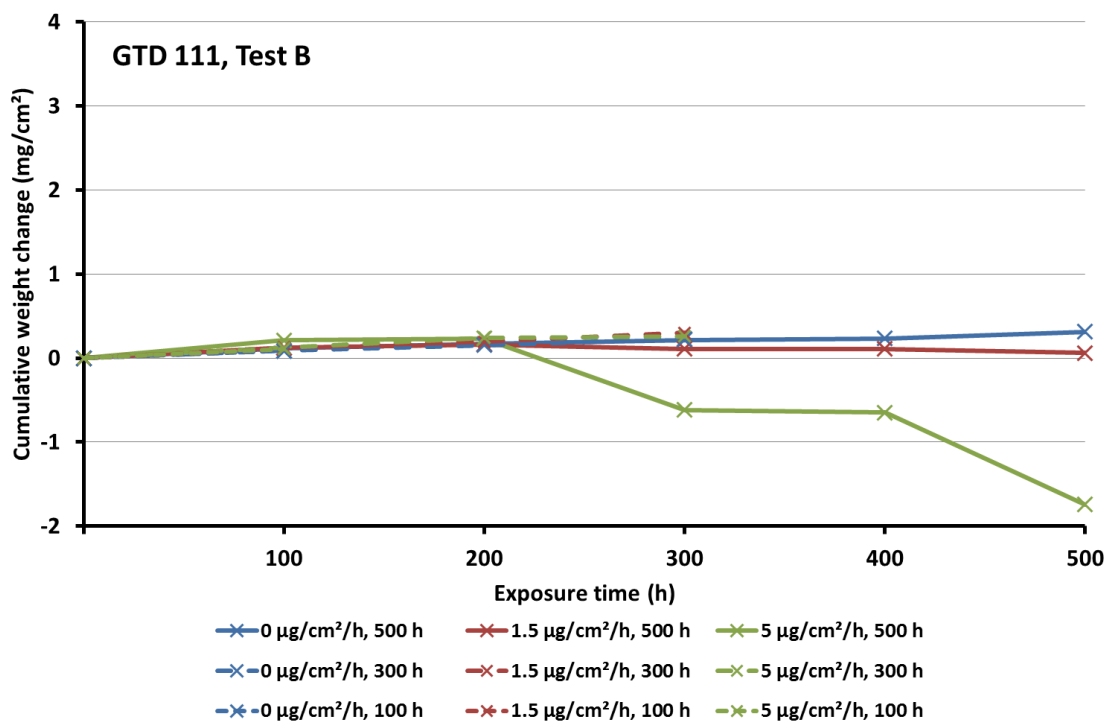


Figure A.7: Cumulative weight change data for GTD 111 exposed in test B at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

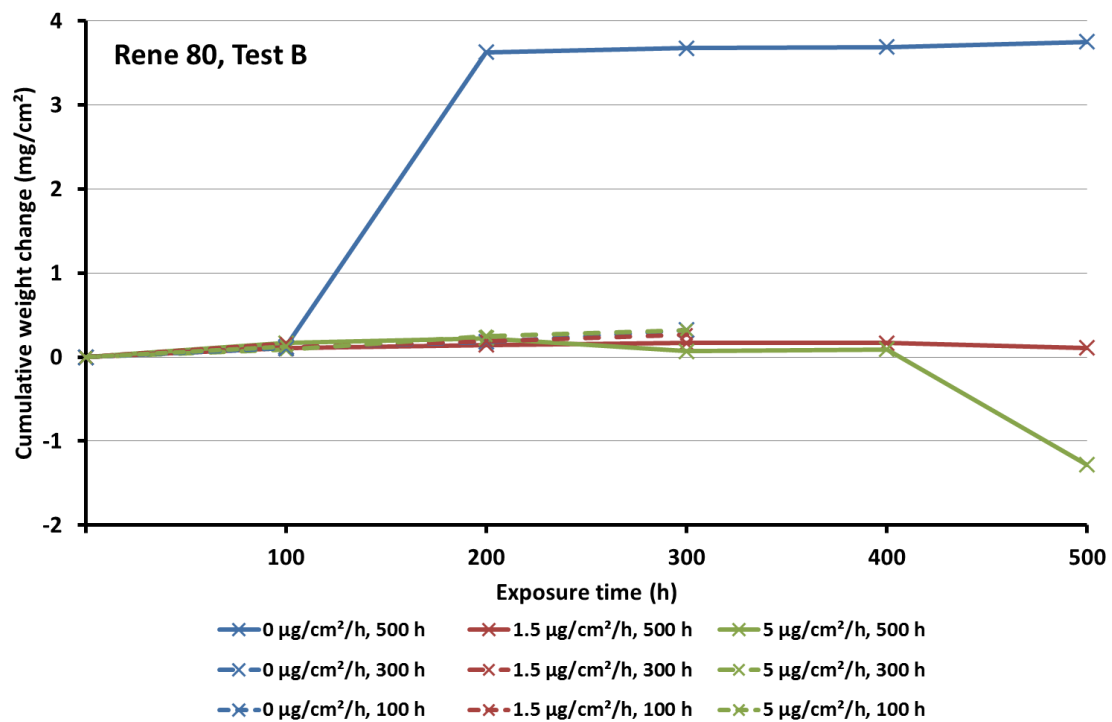


Figure A.8: Cumulative weight change data for Rene 80 exposed in test B at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

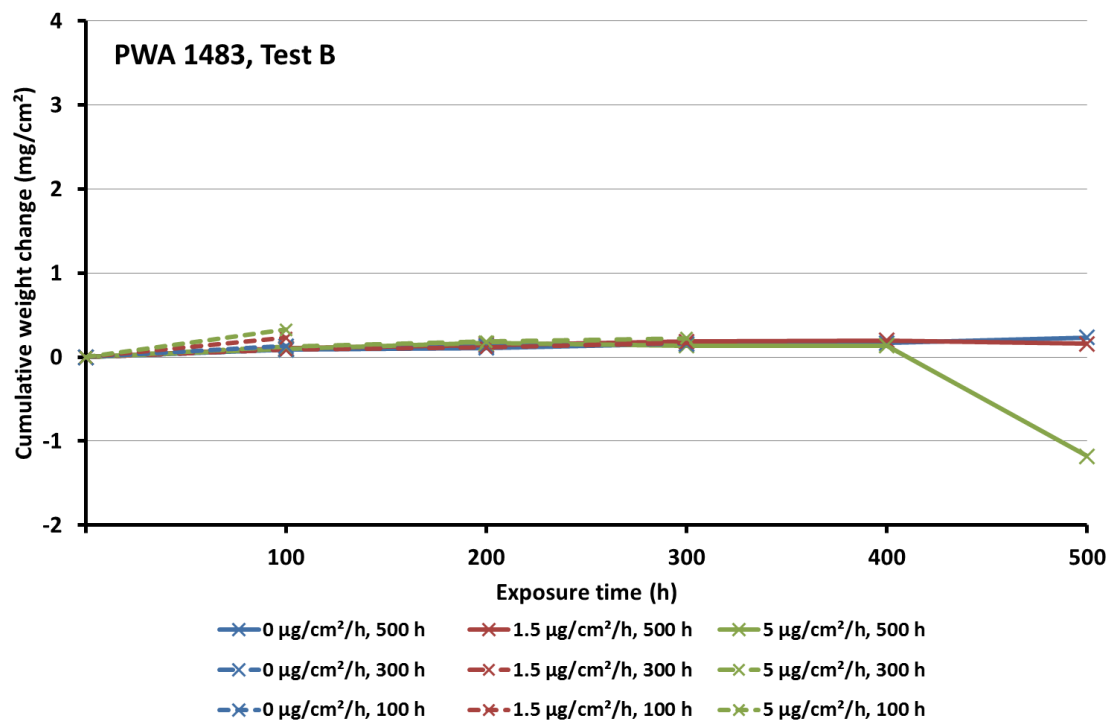


Figure A.9: Cumulative weight change data for PWA 1483 exposed in test B at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

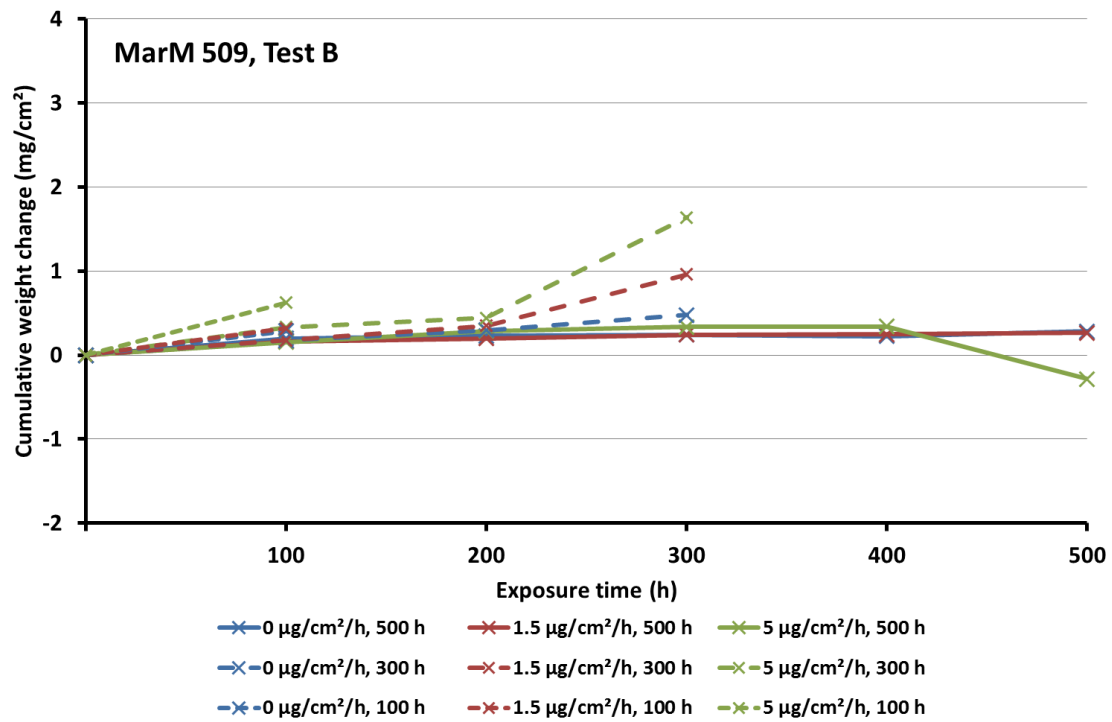


Figure A.10: Cumulative weight change data for MarM 509 exposed in test B at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

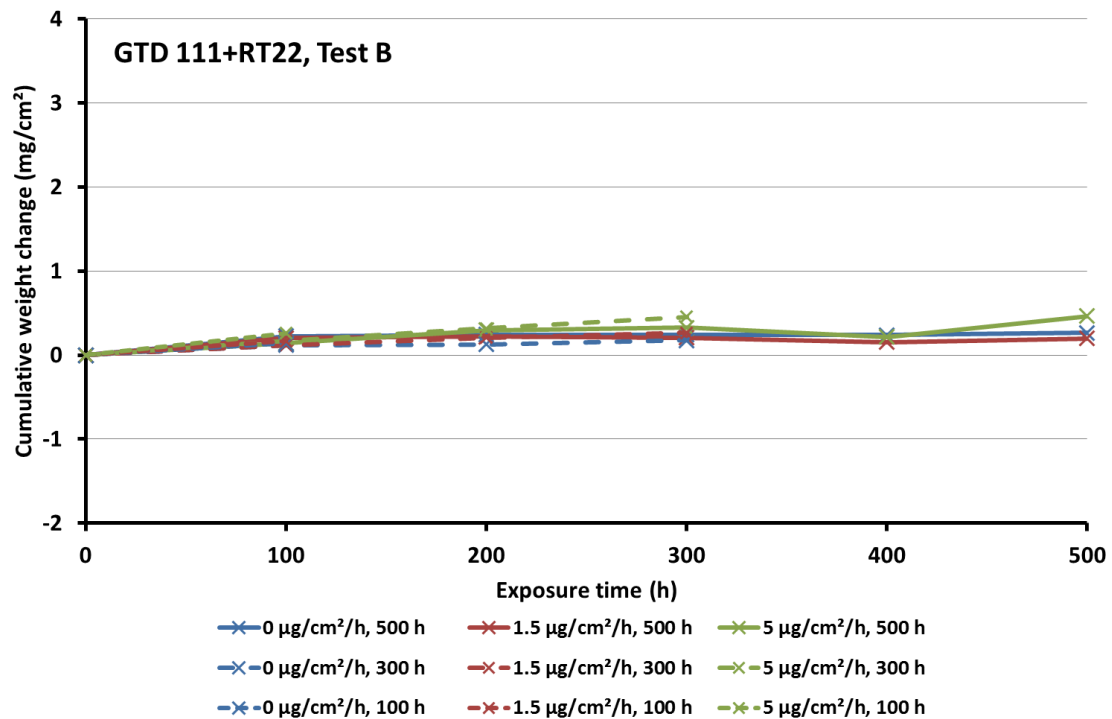


Figure A.11: Cumulative weight change data for RT22 coated GTD 111 exposed in test B at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

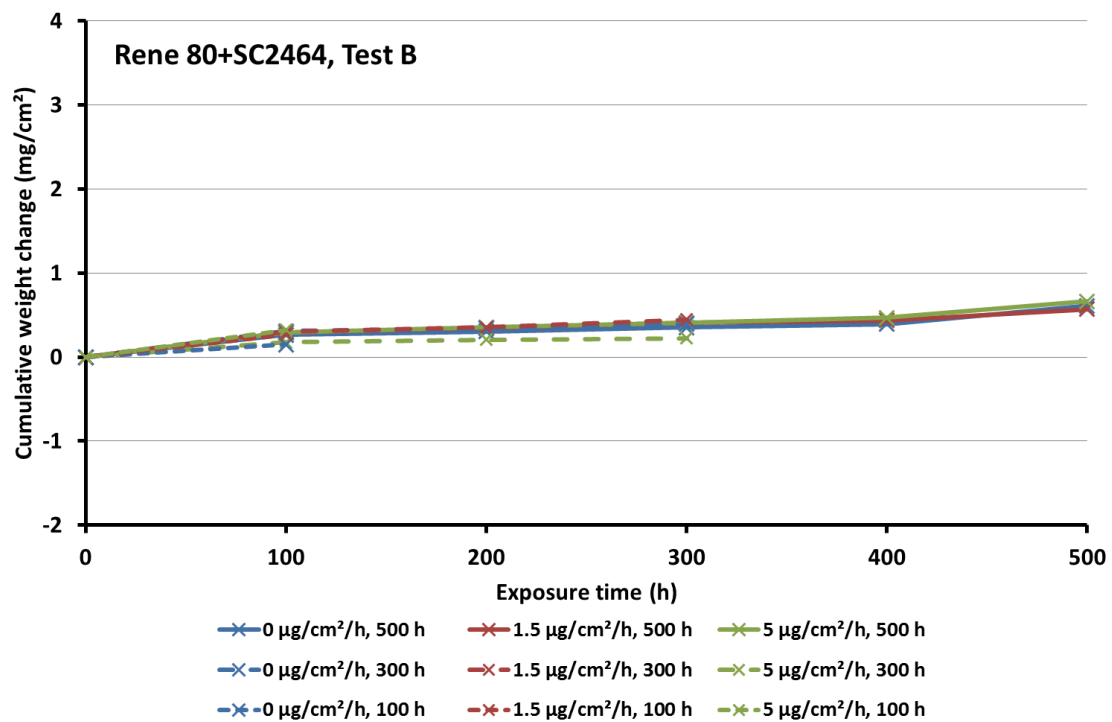


Figure A.12: Cumulative weight change data for SC2464 coated Rene 80 exposed in test B at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

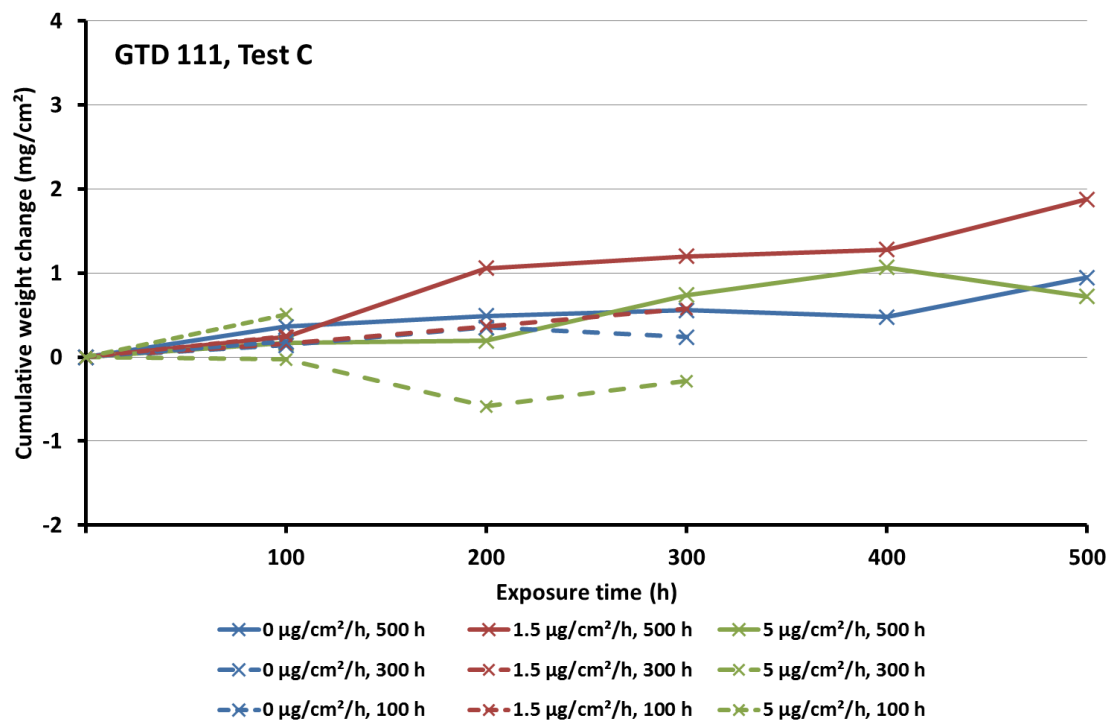


Figure A.13: Cumulative weight change data for GTD 111 exposed in test C at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

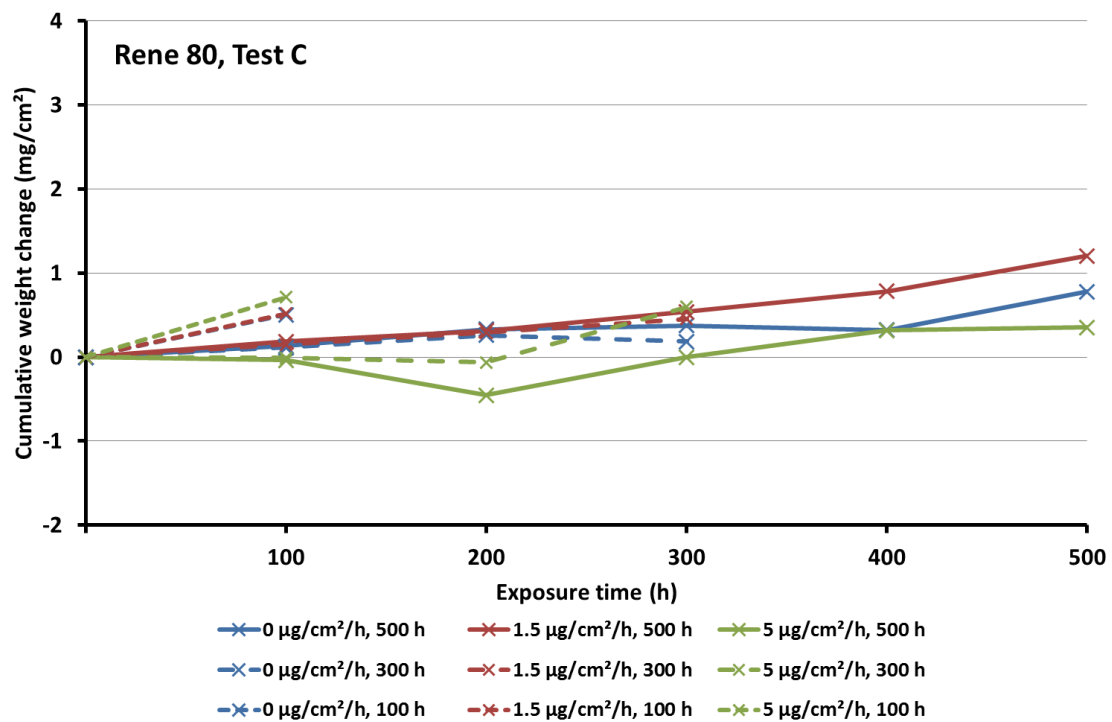


Figure A.14: Cumulative weight change data for Rene 80 exposed in test C at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

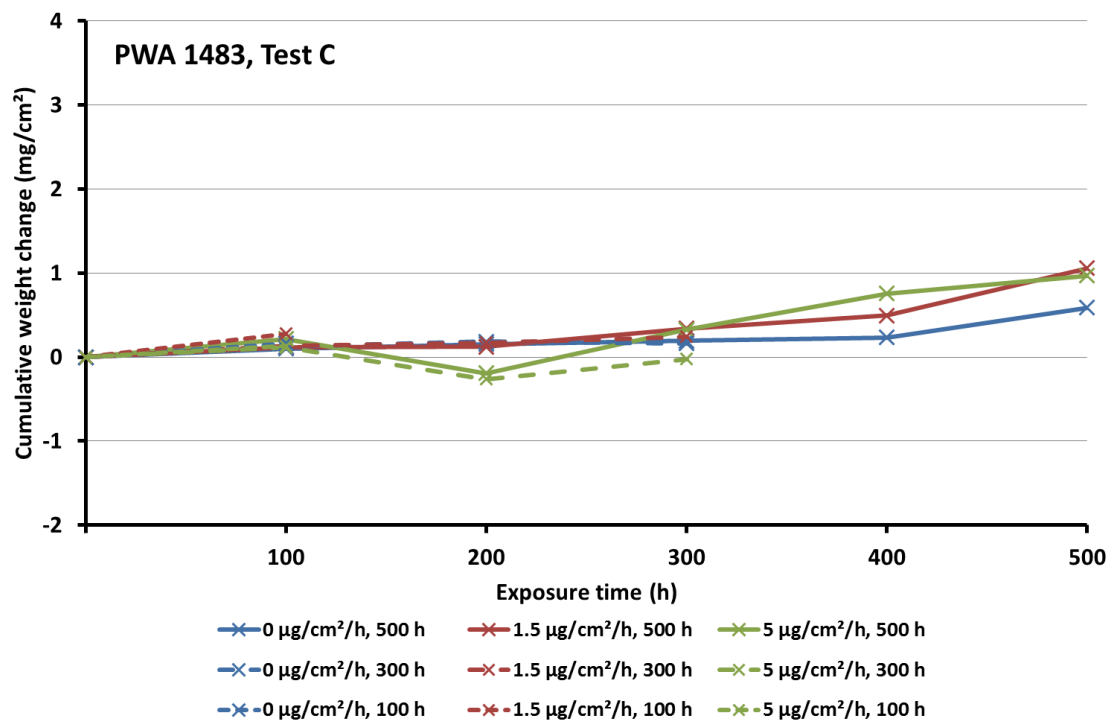


Figure A.15: Cumulative weight change data for PWA 1483 exposed in test C at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

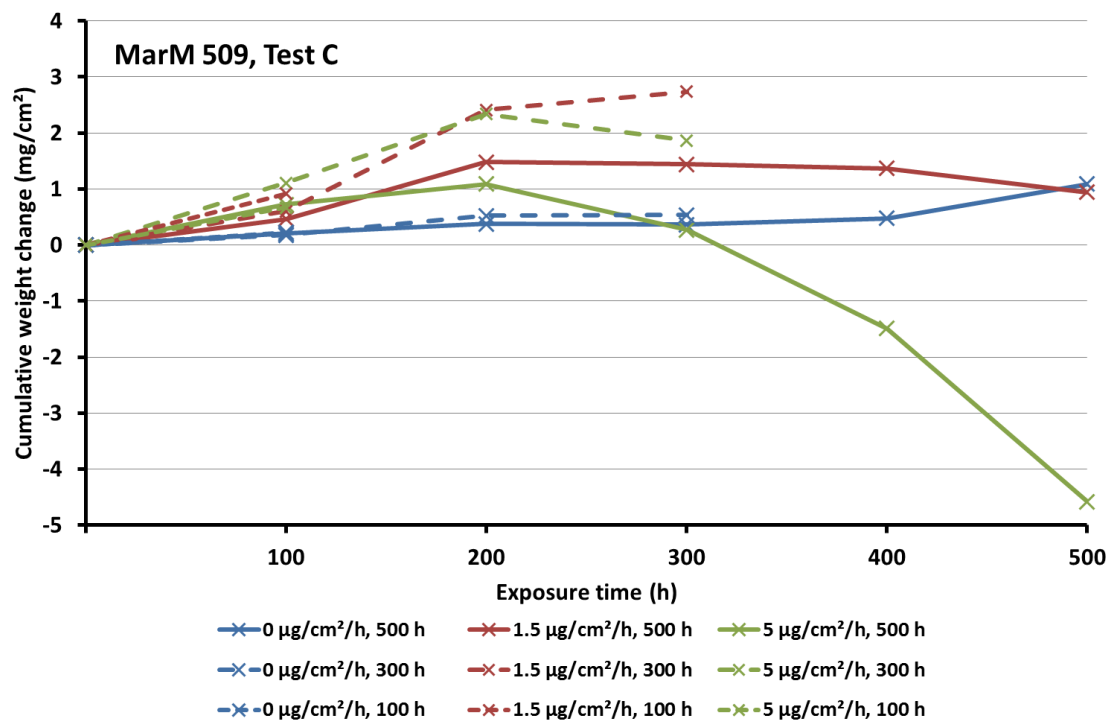


Figure A.16: Cumulative weight change data for MarM 509 exposed in test C at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

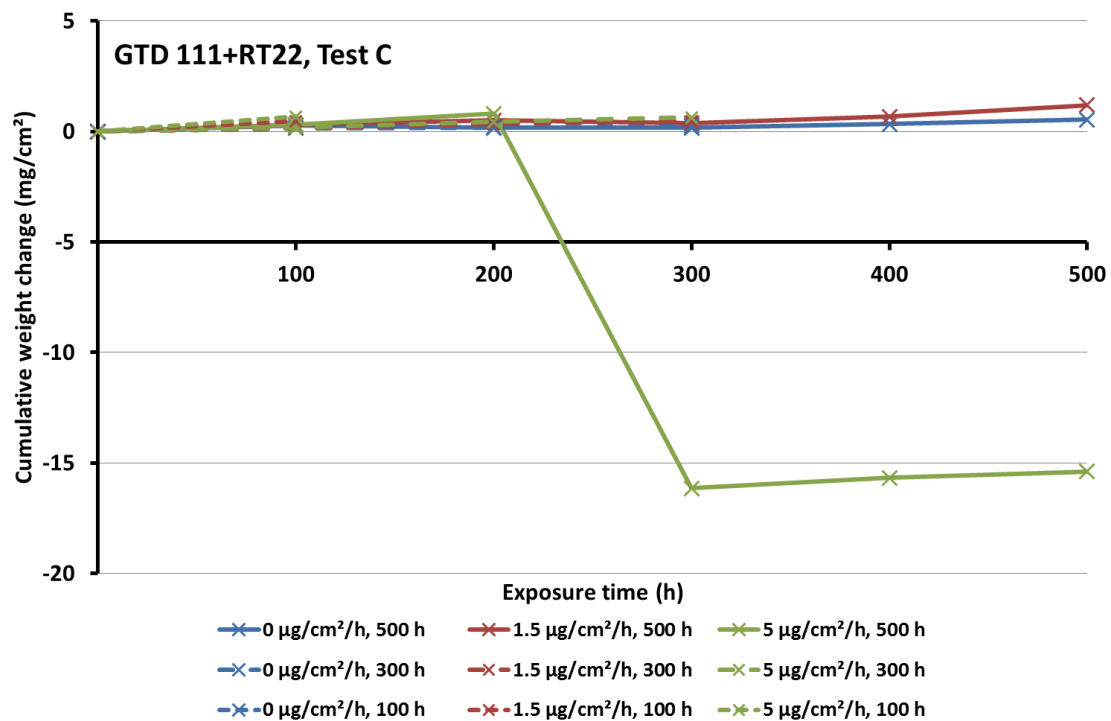


Figure A.17: Cumulative weight change data for RT22 coated GTD 111 exposed in test C at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

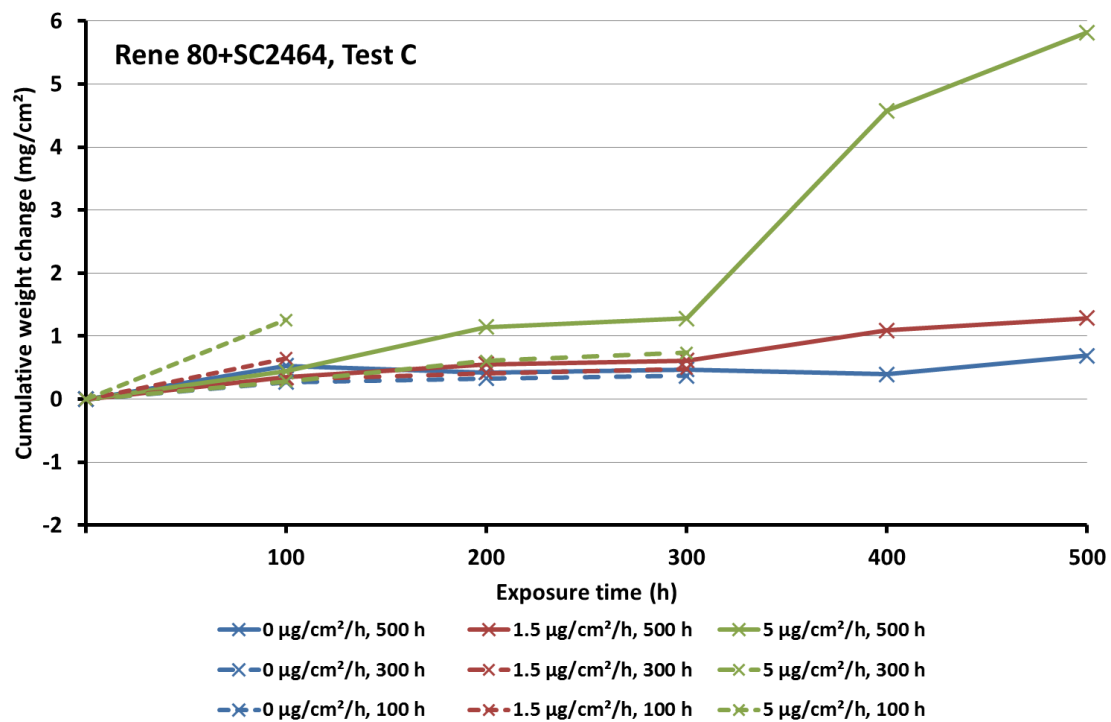


Figure A.18: Cumulative weight change data for SC2464 coated Rene 80 exposed in test C at 700 °C for up to 500 hours with an 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

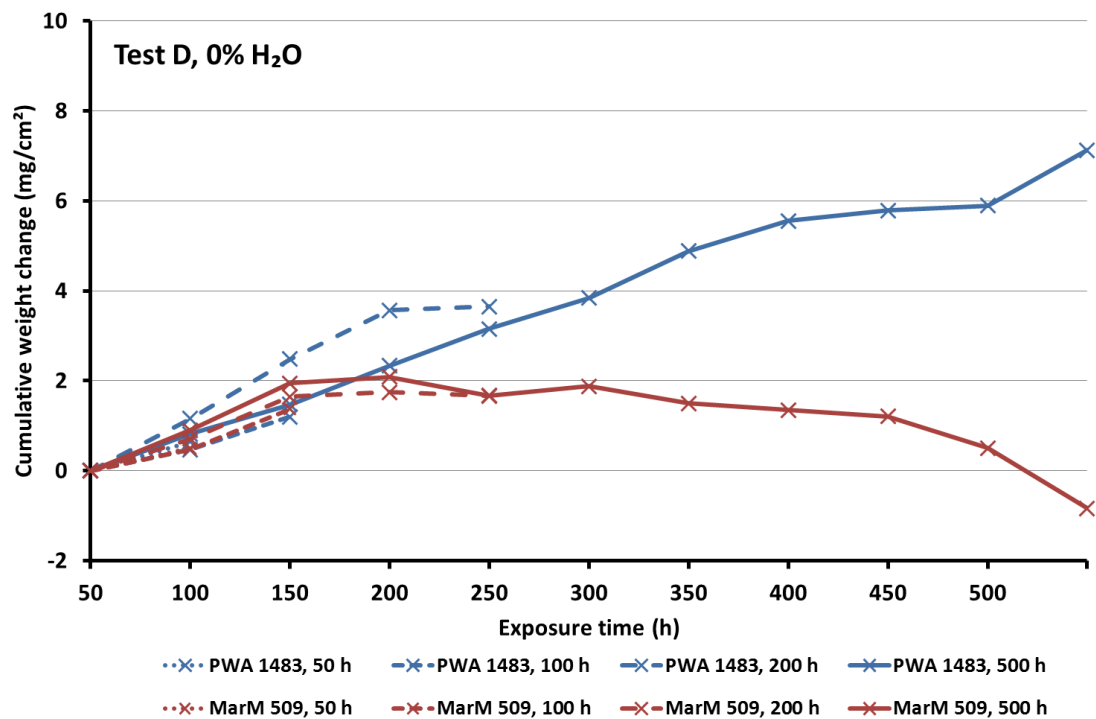


Figure A.19: Cumulative weight change data for PWA 1483 and MarM 509 exposed in test D at 700 °C for up to 500 hours with a 1.5µg/cm²/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

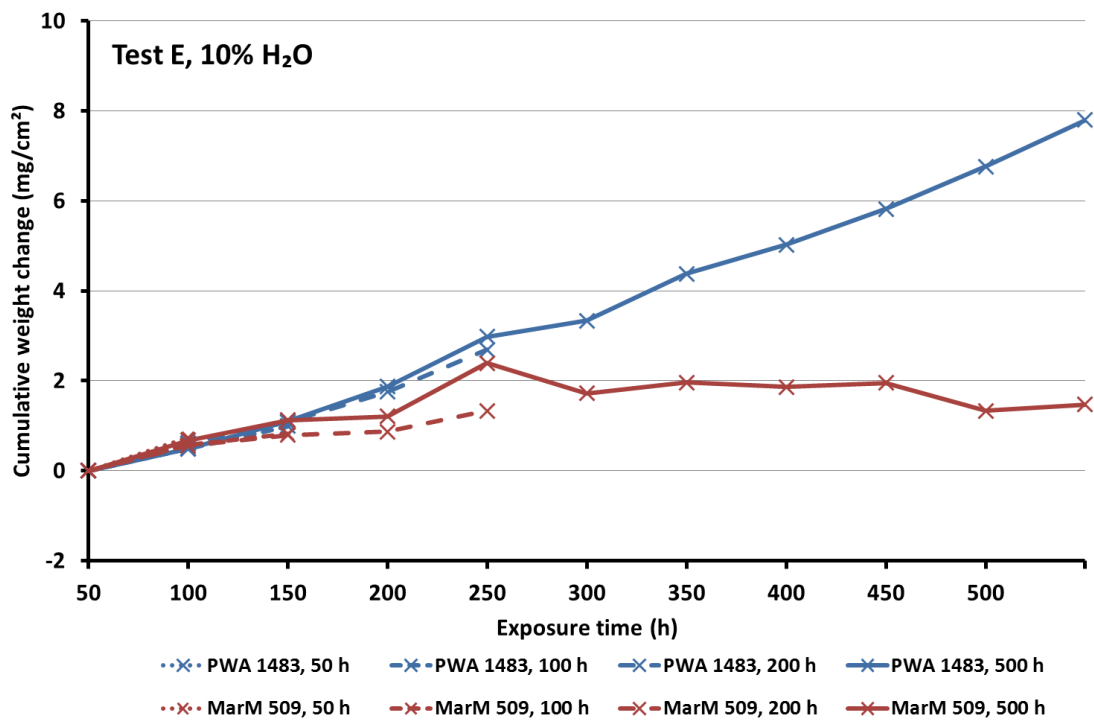


Figure A.20: Cumulative weight change data for PWA 1483 and MarM 509 exposed in test E at 700 °C for up to 500 hours with a 1.5µg/cm<sup>2</sup>/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

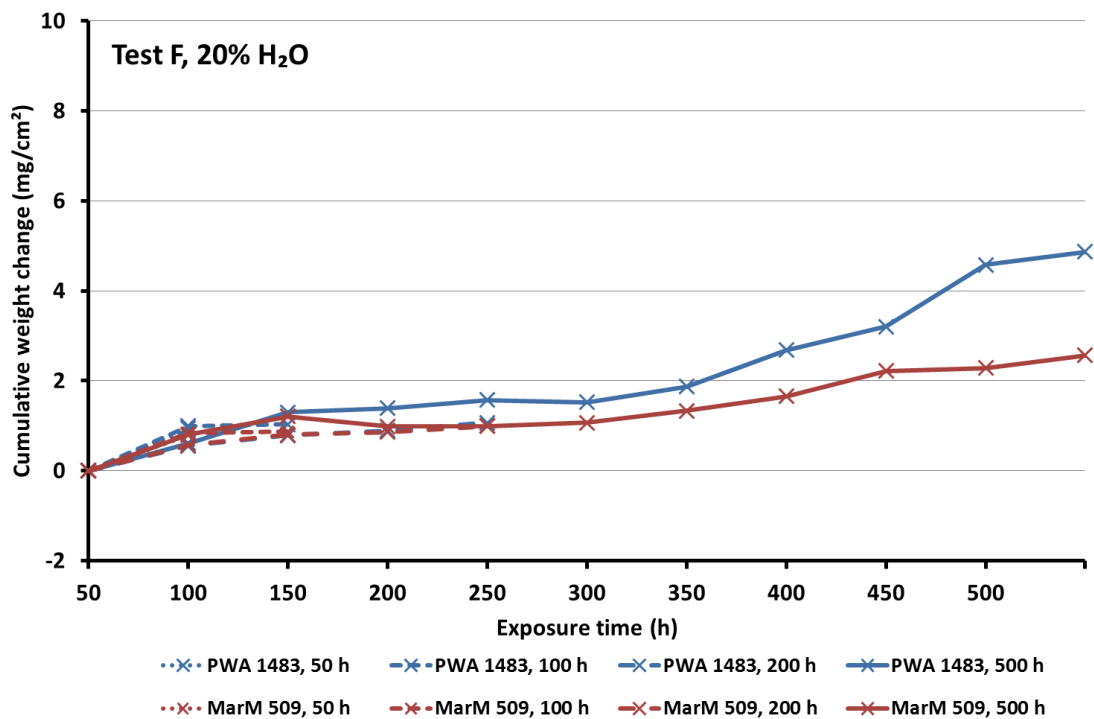
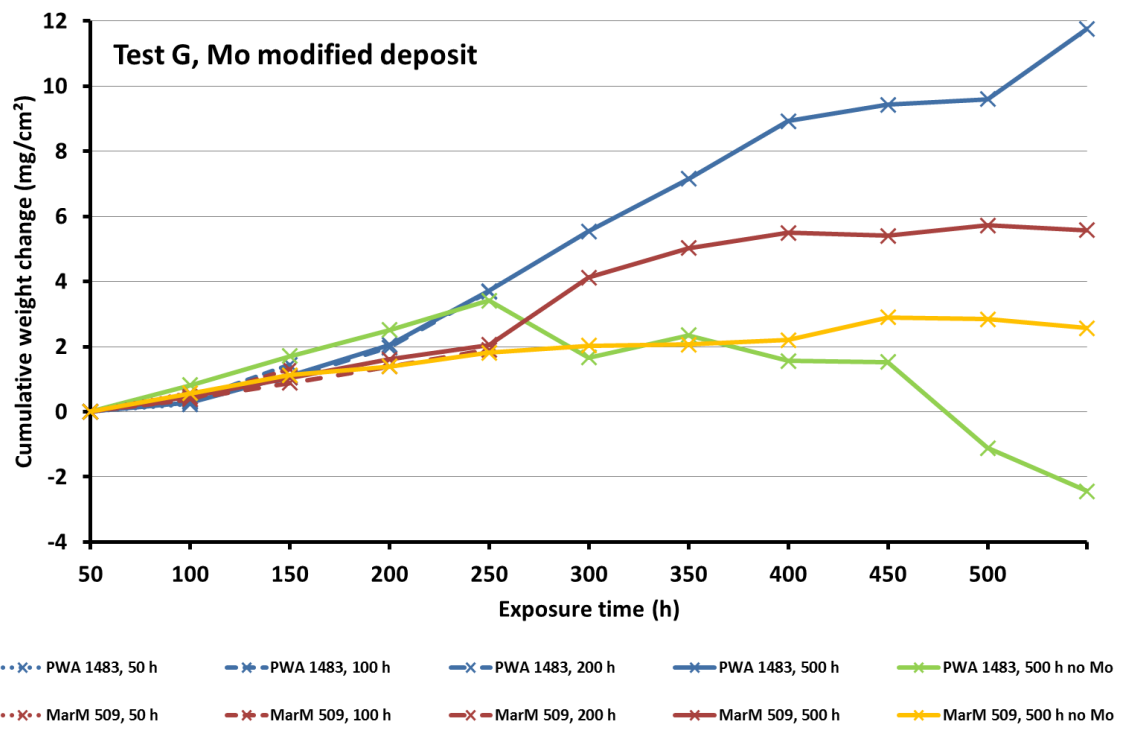


Figure A.21: Cumulative weight change data for PWA 1483 and MarM 509 exposed in test F at 700 °C for up to 500 hours with a 1.5µg/cm<sup>2</sup>/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.



**Figure A.22: Cumulative weight change data for PWA 1483 and MarM 509 exposed in test D at 700 °C for up to 500 hours with a 1.5µg/cm²/h 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.**

## Appendix B. Tests A to C good metal loss distributions

This chapter presents the dimensional good metal loss distributions for tests A to C. Test parameters are given in Section 3.6.

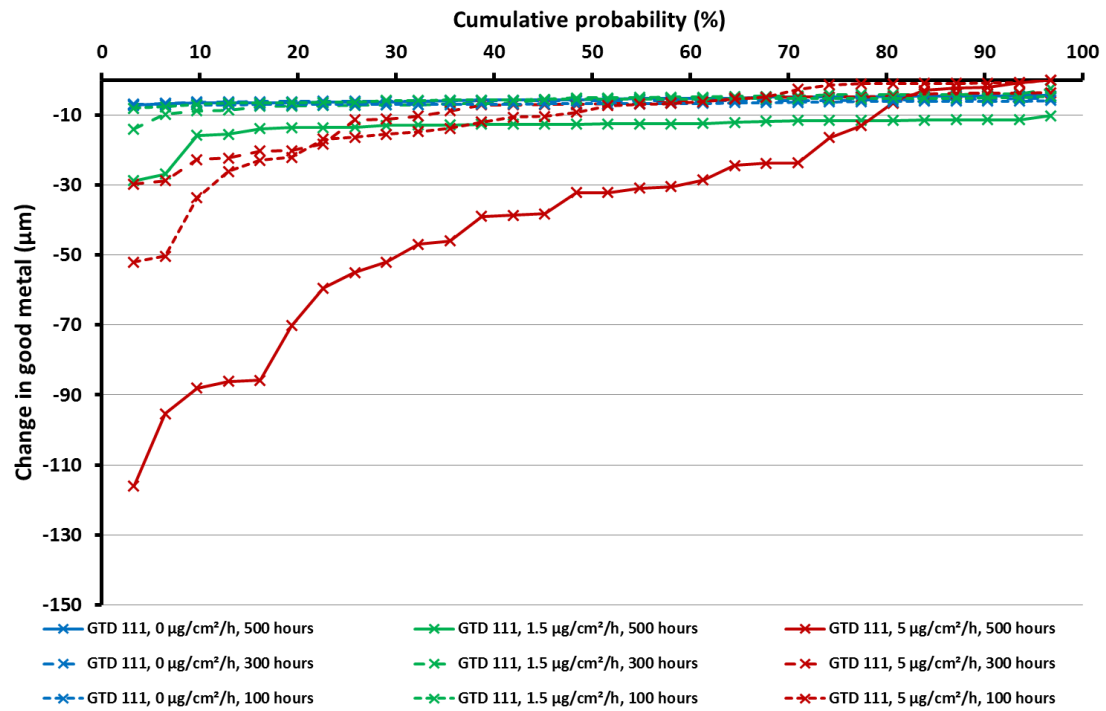


Figure B.1: Probability plot of good metal loss for GTD 111 exposed at 700 °C in test A with a 80/20  $(\text{Na/K})_2\text{SO}_4$  deposit.

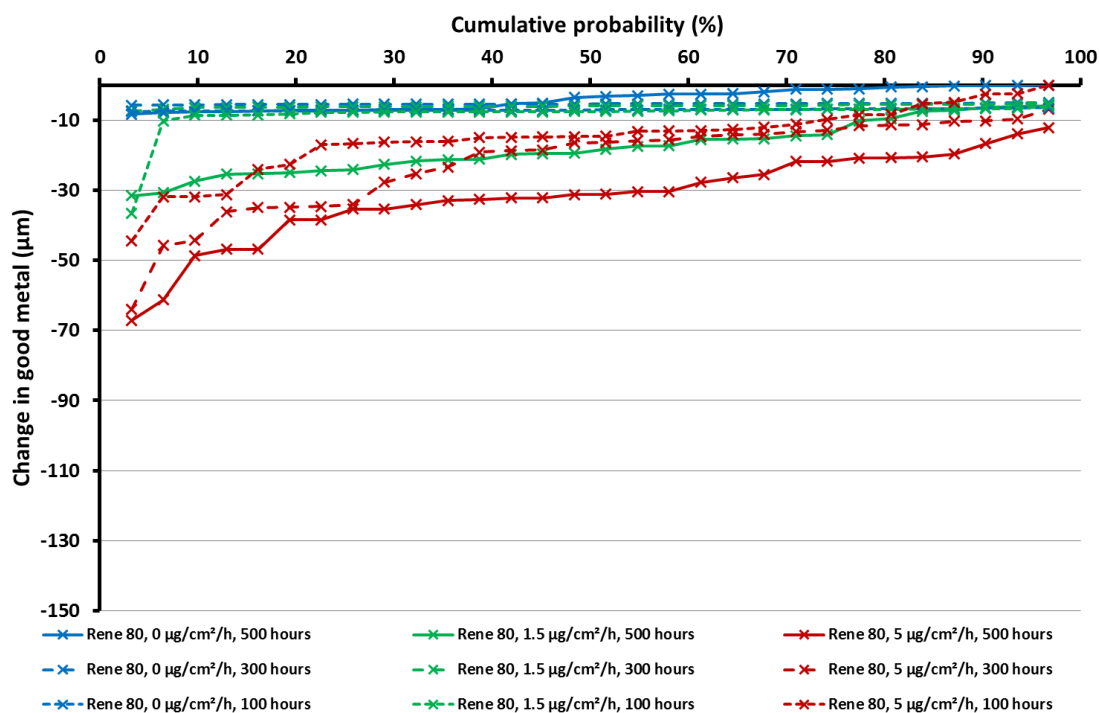


Figure B.2: Probability plot of good metal loss for Rene 80 exposed at  $700^\circ\text{C}$  in test A with a  $80/20 (\text{Na/K})_2\text{SO}_4$  deposit.

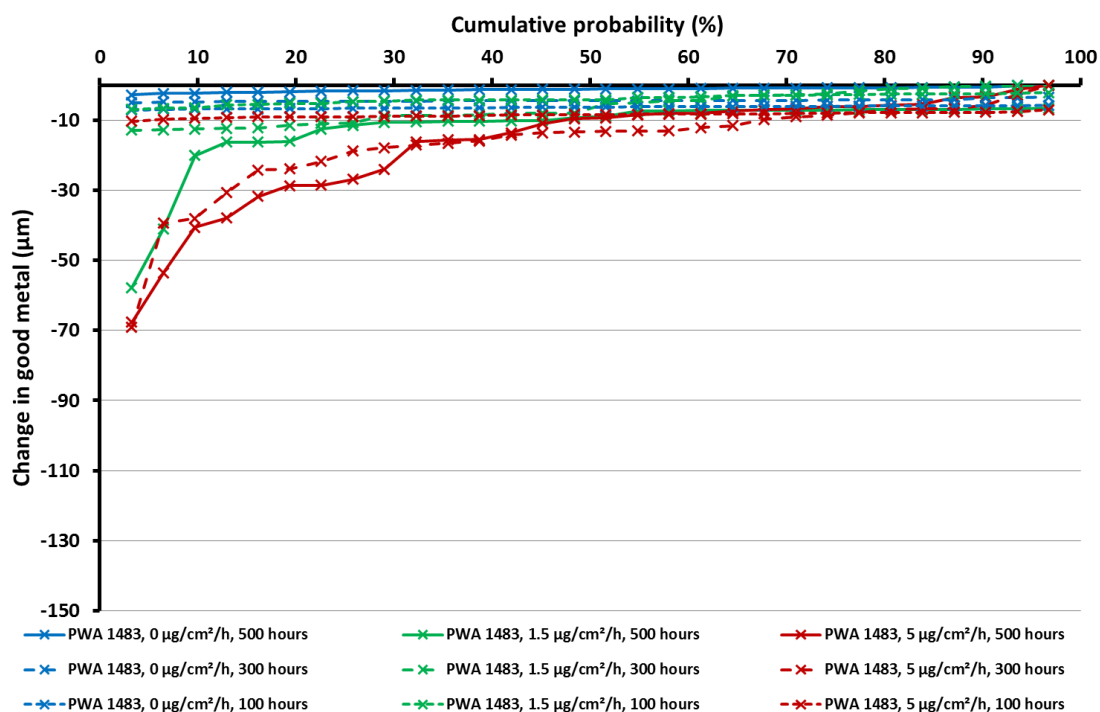


Figure B.3: Probability plot of good metal loss for PWA 1483 exposed at  $700^\circ\text{C}$  in test A with a  $80/20 (\text{Na/K})_2\text{SO}_4$  deposit.

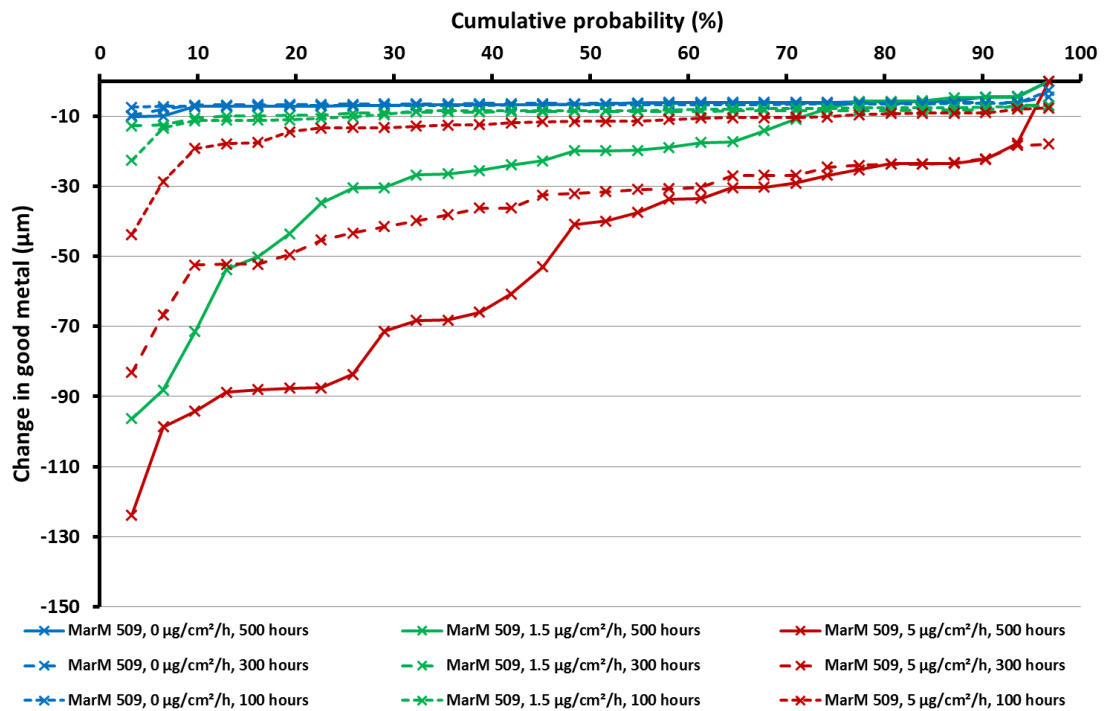


Figure B.4: Probability plot of good metal loss for MarM 509 exposed at 700 °C in test A with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

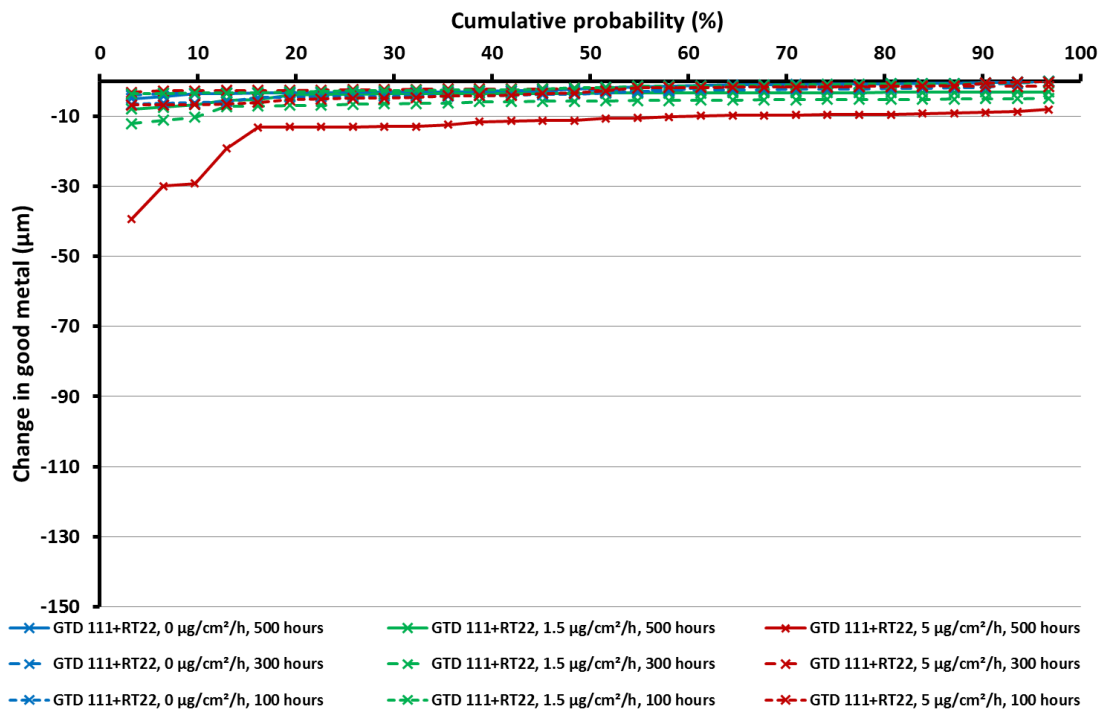


Figure B.5: Probability plot of good metal loss for SC2464 coated GTD 111 exposed at 700 °C in test A with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

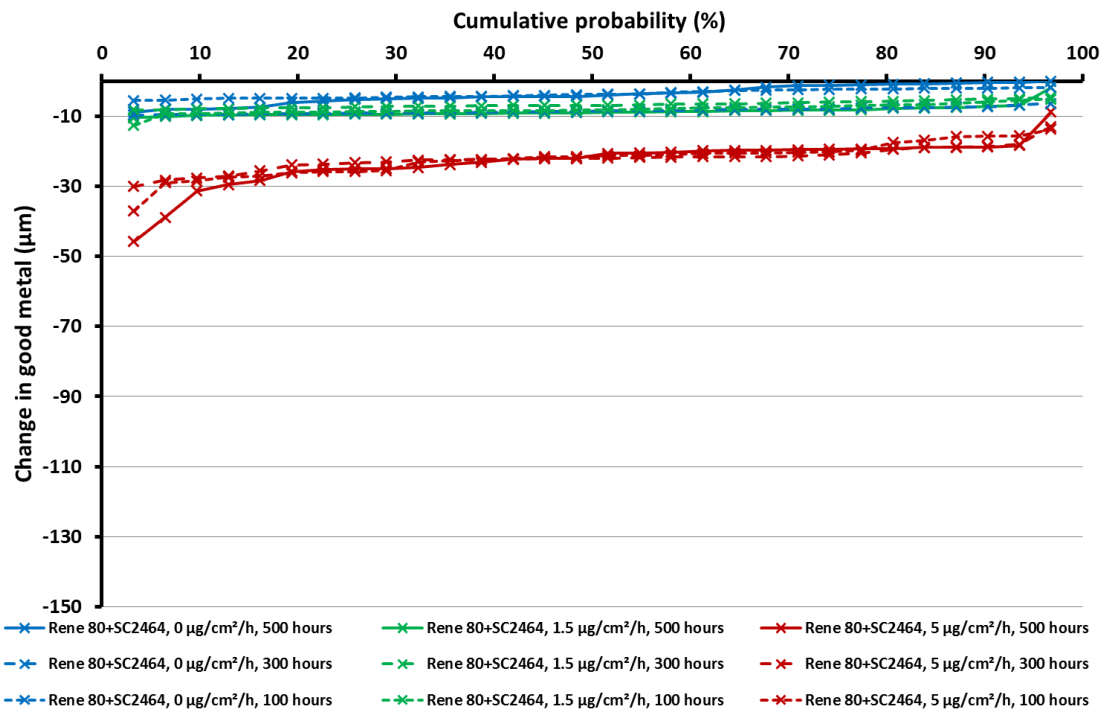


Figure B.6: Probability plot of good metal loss for SC2464 coated Rene 80 exposed at 700 °C in test A with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

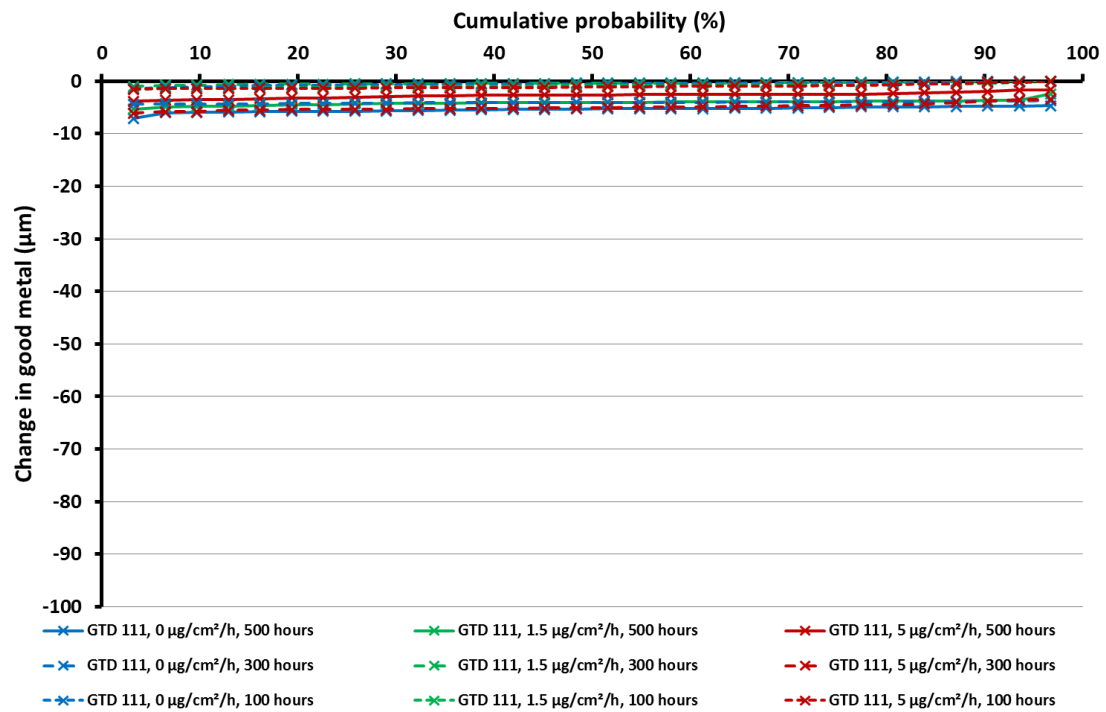


Figure B.7: Probability plot of good metal loss for GTD 111 exposed at 700 °C in test B with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

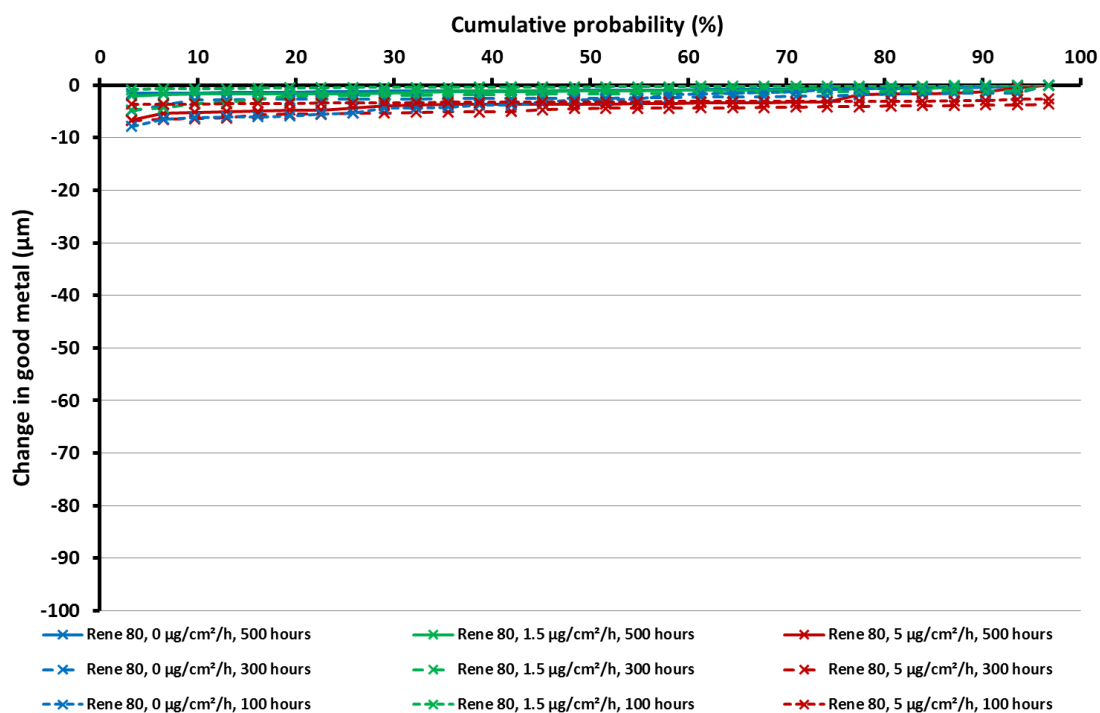


Figure B.8: Probability plot of good metal loss for Rene 80 exposed at 700 °C in test B with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

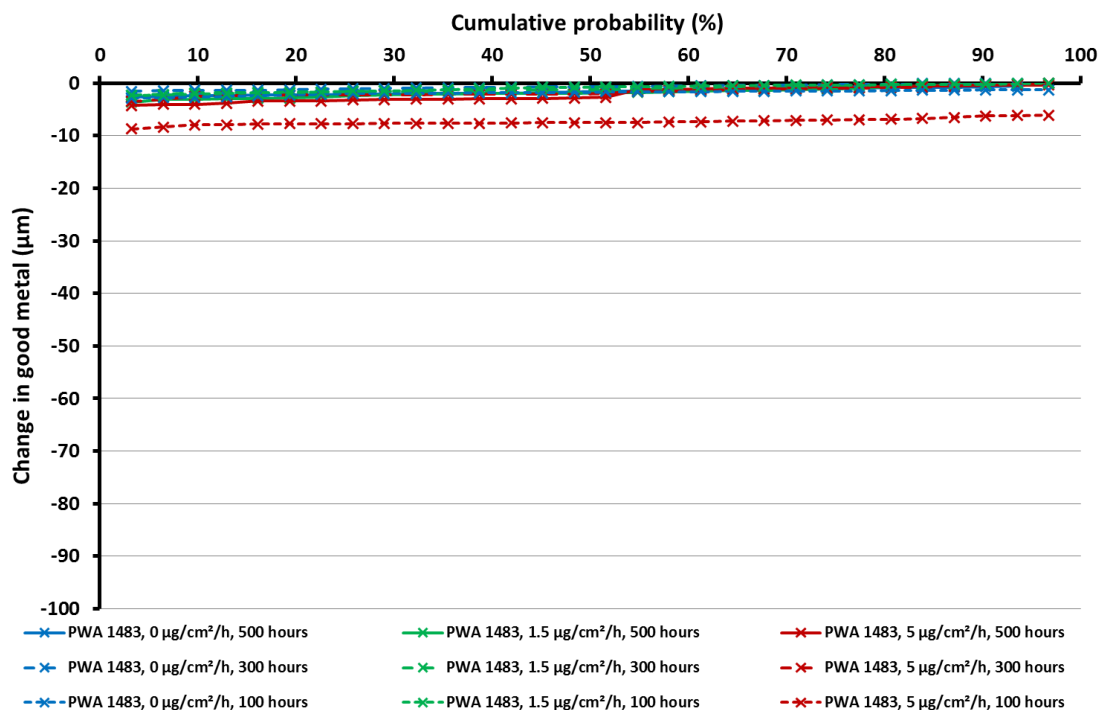


Figure B.9: Probability plot of good metal loss for PWA 1483 exposed at 700 °C in test B with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

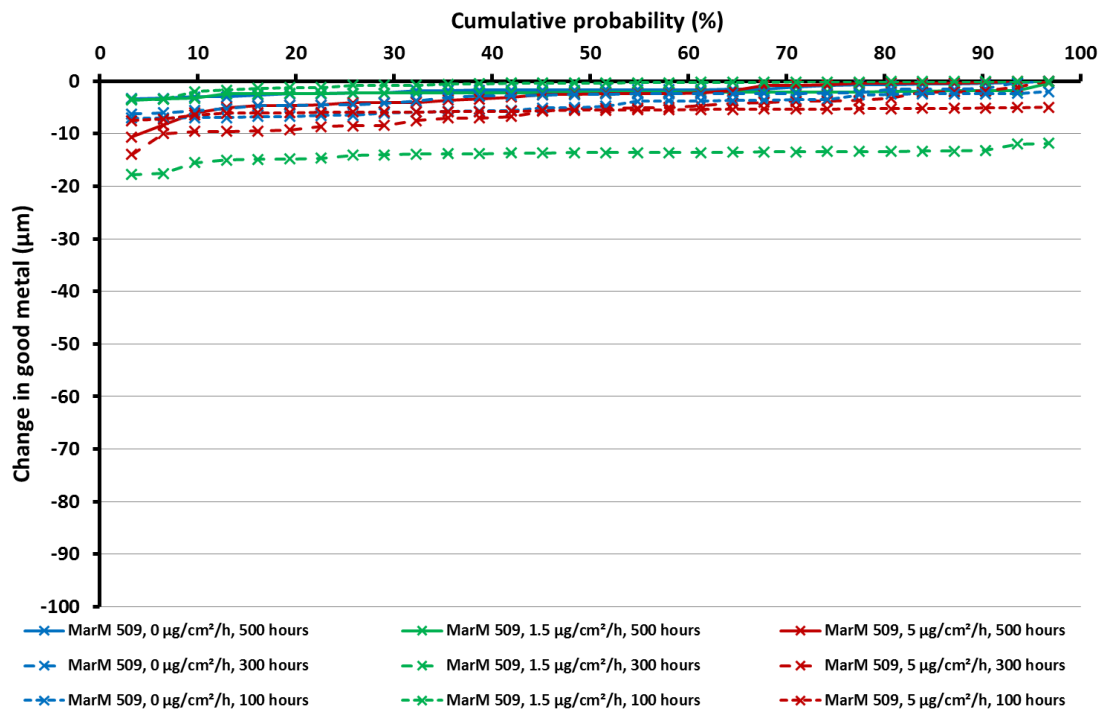


Figure B.10: Probability plot of good metal loss for MarM 509 exposed at 700 °C in test B with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

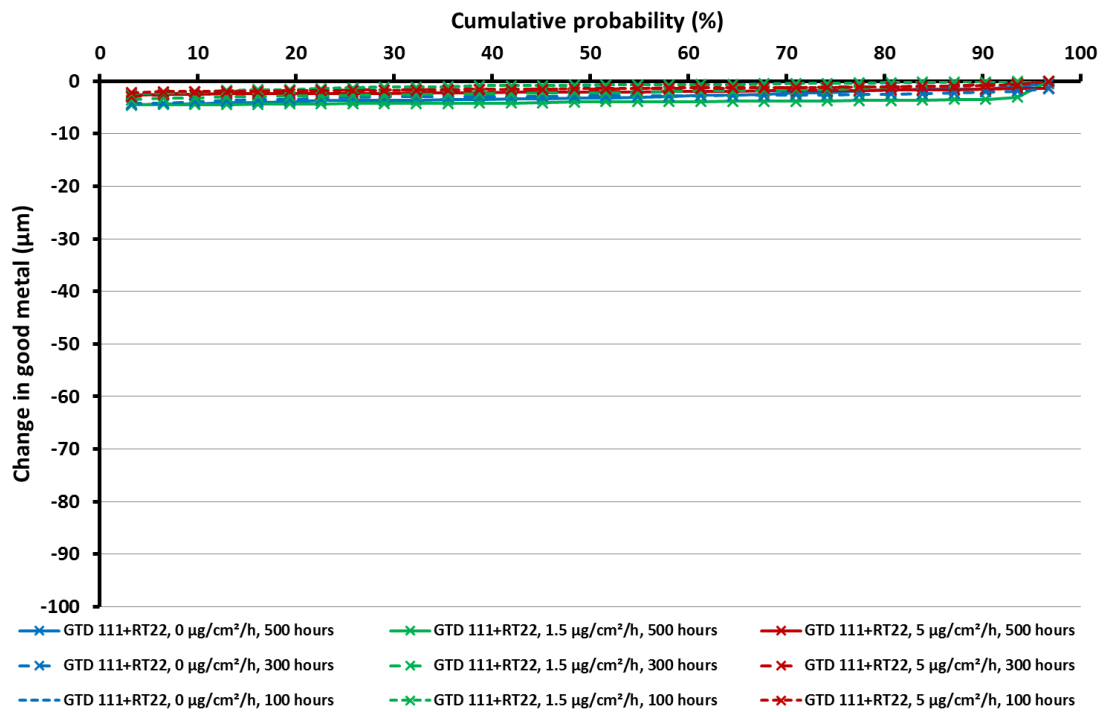


Figure B.11: Probability plot of good metal loss for RT22 coated GTD 111 exposed at 700 °C in test B with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

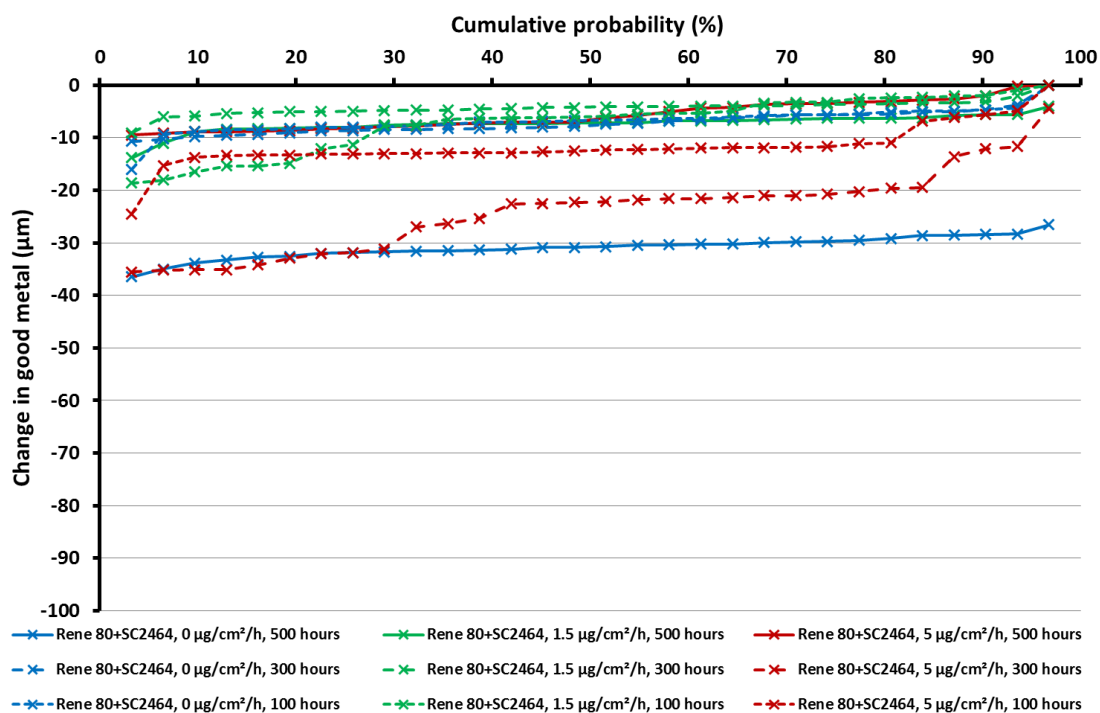


Figure B.12: Probability plot of good metal loss for SC2464 coated Rene 80 exposed at 700 °C in test B with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

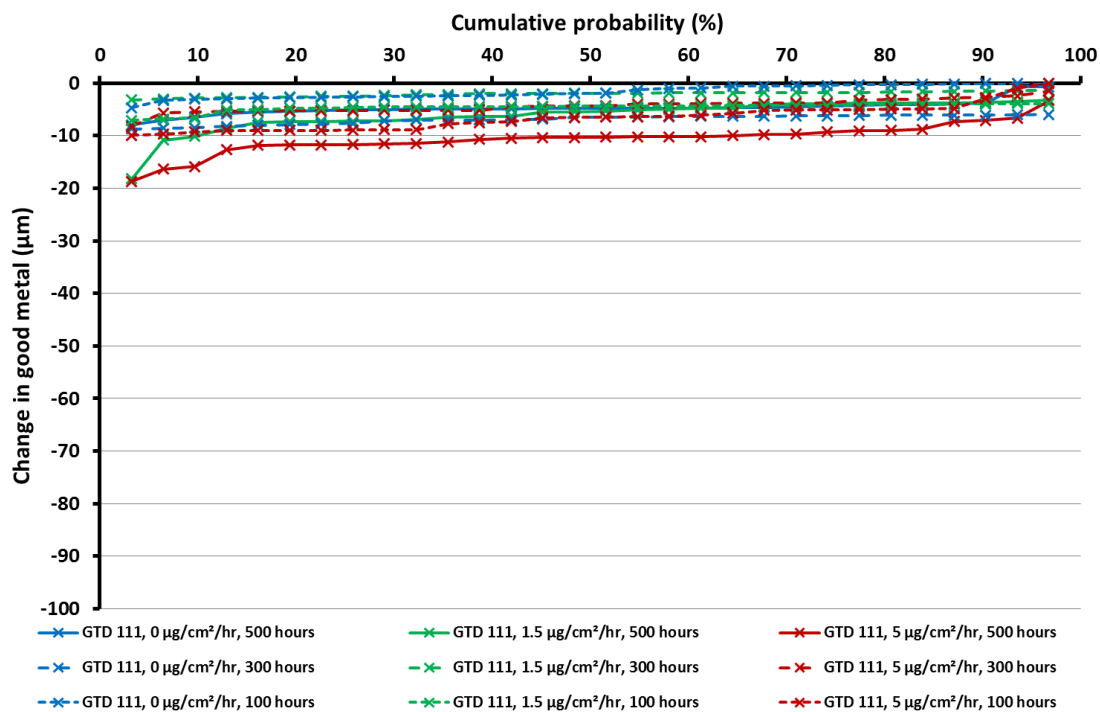


Figure B.13: Probability plot of good metal loss for GTD 111 exposed at 700 °C in test C with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

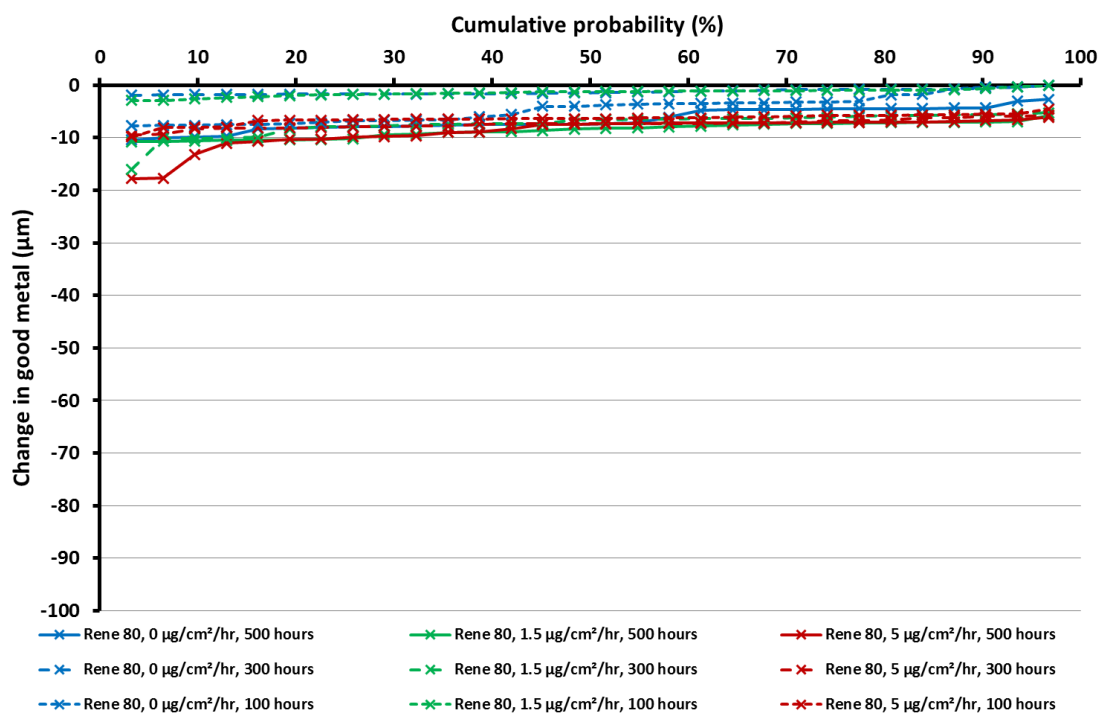


Figure B.14: Probability plot of good metal loss for Rene 80 exposed at  $700^\circ\text{C}$  in test C with a 80/20 (Na/K) $_2\text{SO}_4$  deposit.

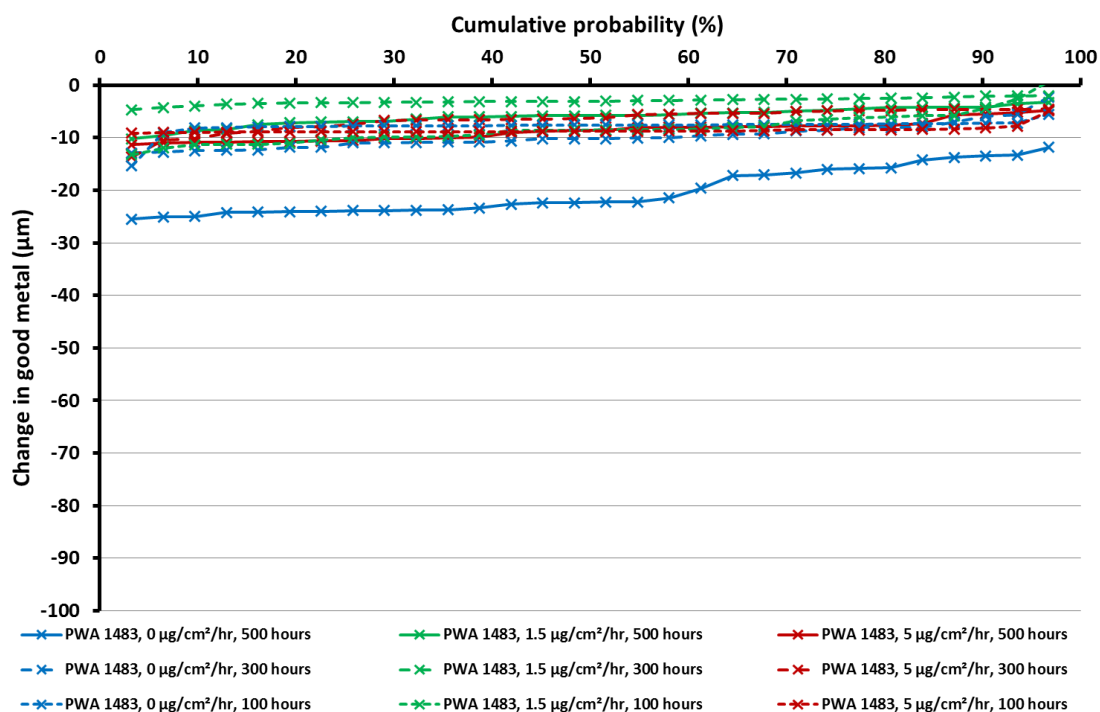


Figure B.15: Probability plot of good metal loss for PWA 1483 exposed at  $700^\circ\text{C}$  in test C with a 80/20 (Na/K) $_2\text{SO}_4$  deposit.

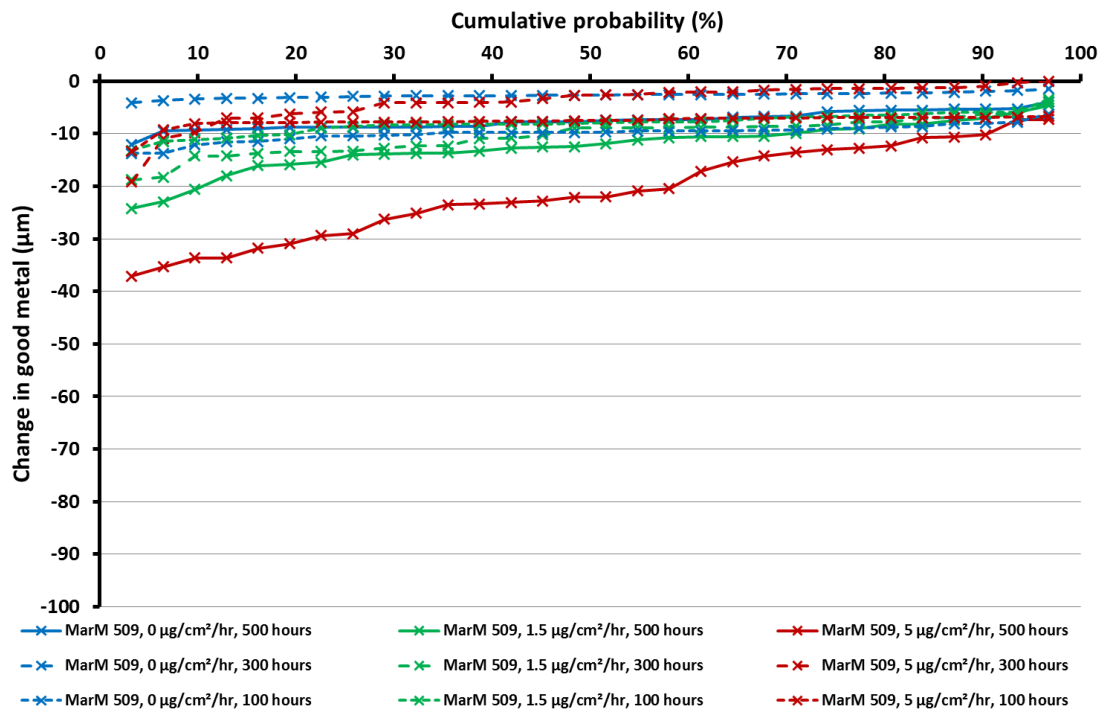


Figure B.16: Probability plot of good metal loss for MarM 509 exposed at 700 °C in test C with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

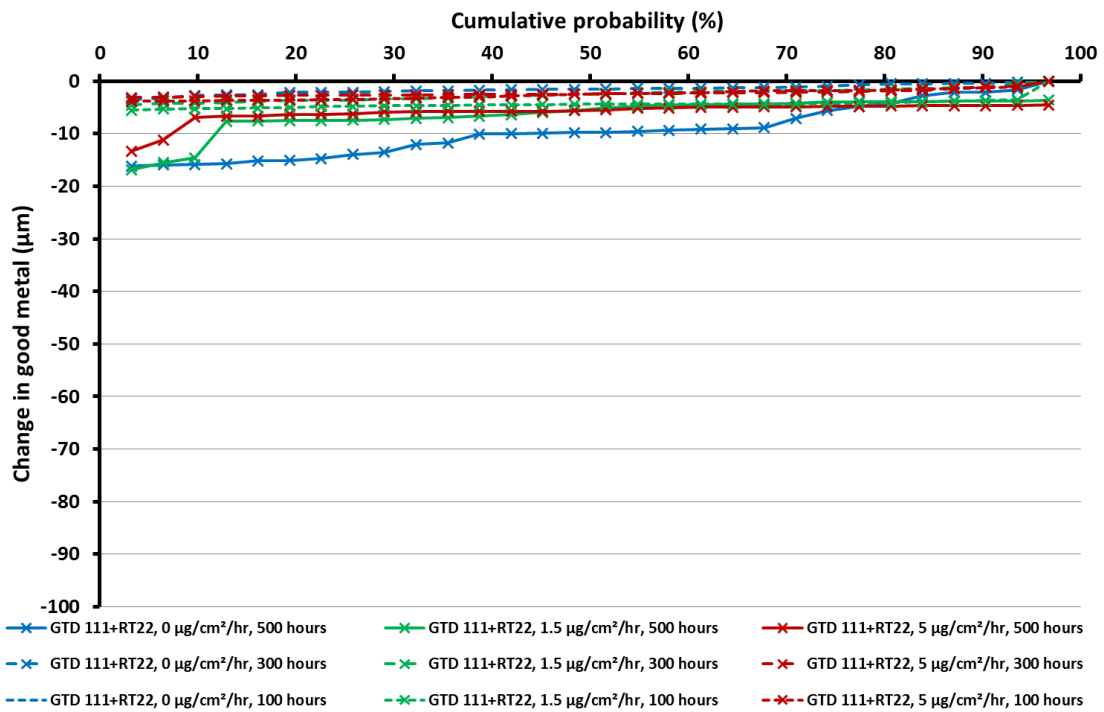


Figure B.17: Probability plot of good metal loss for RT22 coated GTD 111 exposed at 700 °C in test C with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

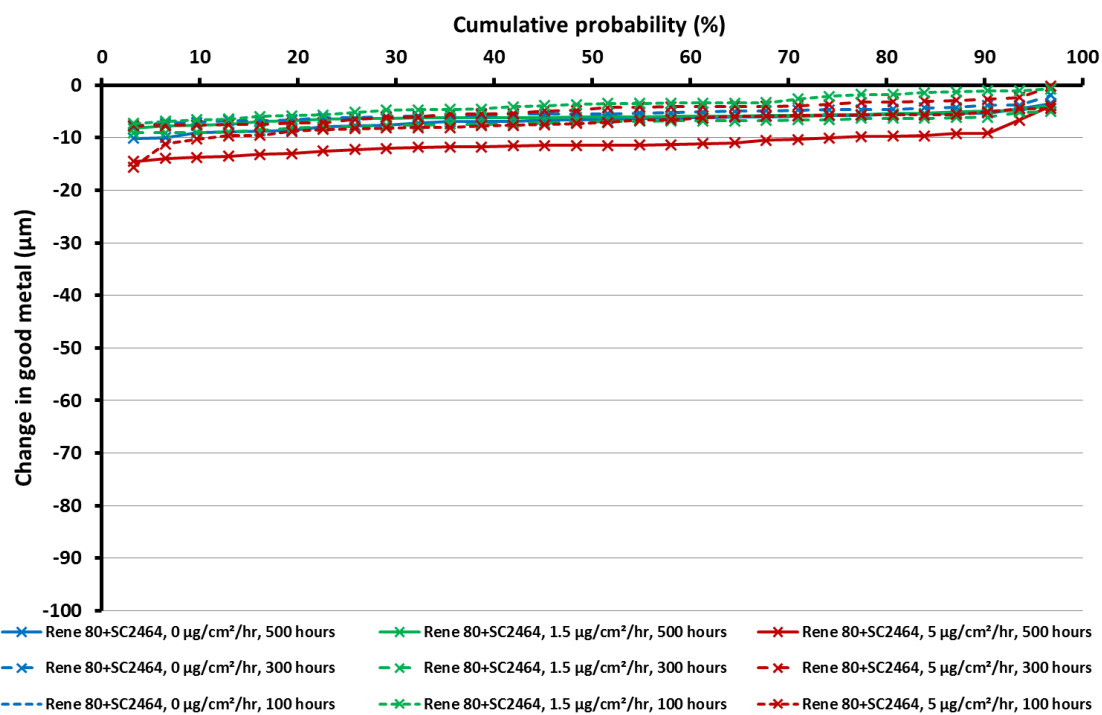


Figure B.18: Probability plot of good metal loss for SC2464 coated Rene 80 exposed at 700 °C in test C with a 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> deposit.

## Appendix C. Error analysis

This chapter lists the sources of error inherent in the methodology and, where possible, a statistical value is determined for the errors. Determined error values are combined with estimated values to give an overall error value.

### C.1 Initial sample metrology errors

Errors pertaining to the pre-exposure measurements of samples' dimensions translate directly to dimensional good metal loss values. The micrometer documentation gives the resolution as  $\pm 1 \mu\text{m}$  and the quantizing error as  $\pm 1 \mu\text{m}$ .

To assess the repeatability of measurements, a single sample was measured (at 8 points around its circumference) 10 times on five separate occasions by three different users. This equates to 400 measurements per user and 1200 measurements in total. The average standard deviation value of the 8 measurement locations are as follows:

- User A: average standard deviation =  $0.97 \mu\text{m}$   
maximum data range =  $5 \mu\text{m}$
- User B: average standard deviation =  $1.38 \mu\text{m}$   
maximum data range =  $9 \mu\text{m}$
- User C: average standard deviation =  $1.48 \mu\text{m}$   
maximum data range =  $8 \mu\text{m}$

$$\delta_{IM} = \sqrt{(\delta_{res})^2 + (\delta_{quant})^2 + (\delta_{user})^2} \quad \text{Equation C-1}$$

Where  $\delta_{IM}$  is the initial metrology error;  $\delta_{res}$  is resolution error;  $\delta_{quant}$  is quantizing error and  $\delta_{user}$  is the average user error.

$$\delta_{IM} = \sqrt{(1)^2 + (1)^2 + (1.28)^2}$$

$$\delta_{IM} = \pm 1.91 \mu m$$

## C.2 Post-test metrology errors

Errors generated post exposure relate to the correct positioning of remaining good metal coordinates after exposure. Such errors translate directly to good metal loss measurements.

If the sample cross section is not at 90° to the sample orientation then the shape of the cross section becomes elliptical. These errors in the cross-section could occur for several reasons; the sample may not sit fully parallel to the mounting jig locating pins; the cutting blade and vice of the precision saw may not be precisely at 90°; samples may sift slightly (and therefore change angle) within the resin during cutting; the grinding and polishing procedure may be uneven and shift the angle of the cross-section.

If the change in cross section angle is estimated to be up to 3°, and the diameter of the sample is approximated to 10 mm, then the increase in diameter can be calculated to be plus 1.4 µm. For one radius at the apex of the elliptical shape this is plus 0.7 µm. This error is always positive.

The movement of the x/y stage of the image analyser is subject to a degree of error. By replotting the sample co-ordinates and measuring the sample multiple times then taking the average difference between plots, a value for the stage error can be approximated. This was found to be ±1 µm.

The coordinates of remaining metal and remaining good metal are plotted by the user and as such are subject to user error. To determine this error, the coordinates of a single reference sample were plotted 10 times on the same set of images for a total of 300 measurements. The average standard deviation of the 30 measurement points was 0.49 µm with a maximum data range of 2.3 µm.

If the sample cross section is over polished, the metal adjacent to the resin can become rounded. As a consequence the sample coordinates that are to be plotted may be out of focus. Although this factor could cause an error of several microns, it is a relatively rare occurrence and is therefore not included in this analysis.

$$+ve \delta_{PM} = \sqrt{(\delta_{stage})^2 + (\delta_{plot})^2 + (\delta_{angle})^2} \quad \text{Equation C-2}$$

$$-ve \delta_{PM} = \sqrt{(\delta_{stage})^2 + (\delta_{plot})^2} \quad \text{Equation C-3}$$

Where  $\delta_{PM}$  is the post-test metrology error;  $\delta_{res}$  is resolution error;  $\delta_{quant}$  is quantizing error and  $\delta_{user}$  is the average user error.

$$+ve \delta_{PM} = \sqrt{(1)^2 + (0.49)^2 + (0.7)^2}$$

$$+ve \delta_{PM} = 1.3 \mu m$$

$$-ve \delta_{PM} = \sqrt{(1)^2 + (0.49)^2}$$

$$-ve \delta_{PM} = 1.2 \mu m$$

### C.3 Furnace temperature errors

Temperature has been identified as one factor that affects corrosion rates with type II hot corrosion thought to peak at approximately 700 °C. Furnace temperature profile measurements have been carried out using a K-type thermocouple, at 700 °C the associated measurement error is  $\pm 5.25$  °C (based on the manufactures guidance [122]). The error associated with the positioning of the thermocouple compared to the measurement error is likely negligible.

The sample carousel is approximately 12 cm in length with a temperature gradient from the middle to each extremity of 6.35 °C, this represents the maximum difference in exposure temperature between samples in a test. The difference between actual exposure temperature and the target temperature of 700 °C is equal to half of the temperature gradient across the carousel plus the thermocouple measurement error.

$$\delta_{temp} = \sqrt{\left(\frac{6.36\text{ }^{\circ}\text{C}}{2}\right)^2 + (5.25)^2\text{ }^{\circ}\text{C}} = \pm 6.14\text{ }^{\circ}\text{C} \quad \text{Equation C-4}$$

Where  $\delta_{temp}$  is the error in temperature:

Research by Haight et al. [95] quantified the degree of metal loss for the superalloy CMSX-4 at 25 °C intervals between 600 °C and 1000 °C after 200 hours of exposure. Around the type II hot corrosion peak,  $\pm 25\text{ }^{\circ}\text{C}$  appears to change the metal loss value by an average of 4  $\mu\text{m}$ . Using the same relationship with temperature,  $\pm 6.14\text{ }^{\circ}\text{C}$  produces a change in metal loss of  $\pm 1\text{ }\mu\text{m}$ .

The work by Haight et al. [95] followed the same deposit recoat procedure described in Chapter 3 however the deposit used differed (98% Na<sub>2</sub>SO<sub>4</sub> 2% NaCl with a flux of 5 $\mu\text{g}/\text{cm}^2/\text{h}$ ). The exposure time was 200 hours, however, CMSX-4 is known to have either a negligible incubation period in environments conducive to type II hot corrosion [99]. The metal loss derived by errors in exposure temperature may be imprecise but in the absence of better data to base the effect of temperature variations off, the derived figure of  $\pm 1\text{ }\mu\text{m}$  provides a rough estimate.

## C.4 Deposit application errors

The amount of deposit applied to the sample prior to exposures is known to affect corrosion rates (differences in flux are discussed in section 4.8). The degree to which deposit flux affects the corrosion rate is complex with other factors such as exposure atmosphere and sample composition affecting it.

The balance on which the samples were weighed during the deposit application process had a repeatability value of  $\pm 0.02$  mg and a linearity value of  $\pm 0.03$  mg. These errors can be combined with the following equation:

$$\delta_{balance} = \sqrt{n \left( (\delta_{repeatability})^2 + (\delta_{linearity})^2 \right)} \quad \text{Equation C-5}$$

$$\delta_{balance}(mg) = \sqrt{n((0.02 \text{ mg})^2 + (0.03 \text{ mg})^2)}$$

Where  $n$  is the number of cycles.

In terms of deposit flux the balance error can be calculated in the following manner:

**Equation C-6**

$$\delta_{balance}(\mu g/cm^2/h) = \left( \frac{\delta_{balance}(mg)}{area(cm^2) \times total \ exposure \ time(h)} \right) \times 1000$$

Other factors that may generate errors in deposition include the deposit composition, how the deposit is distributed around the circumference of the sample and if spallation removes some of the deposit between deposit application and sample exposure. The deposit used was 80% Na<sub>2</sub>SO<sub>4</sub> and 20% K<sub>2</sub>SO<sub>4</sub>, both constituents are sulphates and the difference in relative atomic mass between them is 18.5%. It is unlikely that small variations in the deposit composition based on preparation errors will have a significant effect on metal loss.

The distribution of deposit around the circumference is difficult to quantify. The side of the sample facing the deposit spray gun will receive more deposit than facings of the sample angled progressively away from the direct facing. To mitigate this effect, the samples were rotated through up to 90 degrees to apply the deposit on at least 4 facings. The deposit distribution factor is a more significant effect at lower flux levels since it becomes more difficult to distribute the deposit evenly. This factor is difficult to quantify and can be to some degree mitigated with good technique and therefore is not included in the error calculation.

Application of the salt deposit is subject to user error, aiming to achieve an application weight within 10% of the target flux. The user error for the application of deposit can therefore be written as:

$$\delta_{user} = \left( \frac{Target\ flux}{100} \right) \times 10 \quad \text{Equation C-7}$$

Combining the error in using the balance and the user error gives the following total error in deposit flux:

$$\delta_{flux} = \sqrt{(\delta_{balance})^2 + (\delta_{user})^2} \quad \text{Equation C-8}$$

Based on Section 4.8, for samples that have the majority of their surface entering propagation after 500 hours of exposure, the average increase in corrosion rate is 5  $\mu\text{m}/\mu\text{g}/\text{cm}^2/\text{h}$  (in test A). This value may be different for differing test atmospheres but can be used to estimate the effect of errors in deposit application.

For a 500 hour exposure with 100 hour cycles and deposit flux of 1.5  $\mu\text{g}/\text{cm}^2/\text{h}$  and sample area of 3.14  $\text{cm}^2$ , the flux error can be calculated:

$$\delta_{balance}(\mu g/cm^2/h) = \left( \frac{0.08 (mg)}{3.14 (cm^2) \times 500(h)} \right) \times 1000$$

$$\delta_{balance}(\mu g/cm^2/h) = 0.05$$

$$\delta_{user}(\mu g/cm^2/h) = \left( \frac{1.5}{100} \right) \times 10$$

$$\delta_{user}(\mu g/cm^2/h) = 0.15$$

$$\delta_{flux}(\mu g/cm^2/h) = \sqrt{(0.05)^2 + (0.15)^2}$$

$$\delta_{flux}(\mu g/cm^2/h) = \sqrt{(0.05)^2 + (0.15)^2}$$

$$\delta_{flux}(\mu g/cm^2/h) = 0.16$$

$$5 \mu m/\mu g/cm^2/h \times 0.16 \mu g/cm^2/h = 0.8 \mu m$$

## C.5 Other errors

There are a number of factors that are likely to affect the overall error of the methodology but are either small enough to be considered negligible or difficult to quantify with existing data.

### **C.5.1 Sample errors**

Nominal alloy compositions are shown in Table 3.2. The actual value of the alloys' element composition falls within a range an example of this is given here for PWA 1483 wt%: C 0.05–0.09; Cr 11.60–12.70; Co 8.50–9.50; Mo 1.65–2.15; W 3.50–4.10; Ti 3.90–4.25; Al 3.40–3.80; Ta 4.80–5.20, Ni balance [123]. Variations in key elements such as Cr will have an effect on the corrosion performance of the alloy. This effect is difficult to quantify due to limited information and the complexity of hot corrosion reactions. Furthermore, sample bars maybe provided from a single batch with the same composition value in the given range.

The roughness of a sample may affect the surface area in contact with adjacent phases. Furthermore, sample roughness may have effects on oxide scale growth and spallation.

### **C.5.2 Other exposure errors**

A number of sources of error incurred during test exposures can be identified. These are likely relatively small and can be disregarded in an overall error calculation but are listed here:

- Post cycle unloading temperature; cooling stresses may cause sample spallation, this effect would be greater if the unloading temperature is hotter. Unloading temperature was not recorded but the procedure dictated it to be below 200 °C.
- The time left in the furnace post exposure at low temperature in the test atmosphere
- Test gases were provided with a certification to be within 5% of their target composition. Additionally, were two gas inputs were used (tests A-C) errors associated with the mass flow controller become a factor. Errors in the test gas composition are both hard to quantify (due to a lack of

empirical data) and likely to have a negligible effect in terms of sample good metal loss.

- Test water vapour content is subject to multiple sources of error in the peristaltic pump calibration and throughput. There is insufficient data to quantify how errors in water vapour content may translate into good metal loss. Furthermore, Section 7.1 shows that the effect of water vapour is dependent on other factors such as test atmosphere.

## C.6 Combined error

If the quantified errors in this chapter are combined, the calculation of positive total error in terms of  $\mu m$  of good metal loss is as follows:

**Equation C-9**

$$\delta_{total}(+) = \sqrt{(\delta_{temp})^2 + (\delta_M)^2 + (\delta_{flux})^2 + (\delta_{stage})^2 + (\delta_{plot})^2 + (\delta_{angle})^2}$$

$$\delta_{total} = \sqrt{(0.98)^2 + (1.91)^2 + (0.79)^2 + (1)^2 + (0.49)^2 + (0.7)^2}$$

$$\delta_{total}(+) = 2.6 \mu m$$

**Equation C-10**

$$\delta_{total}(-) = \sqrt{(\delta_{temp})^2 + (\delta_M)^2 + (\delta_{flux})^2 + (\delta_{stage})^2 + (\delta_{plot})^2}$$

$$\delta_{total} = \sqrt{(0.98)^2 + (1.91)^2 + (0.79)^2 + (1)^2 + (0.49)^2}$$

$$\delta_{total}(-) = 2.5 \mu m$$

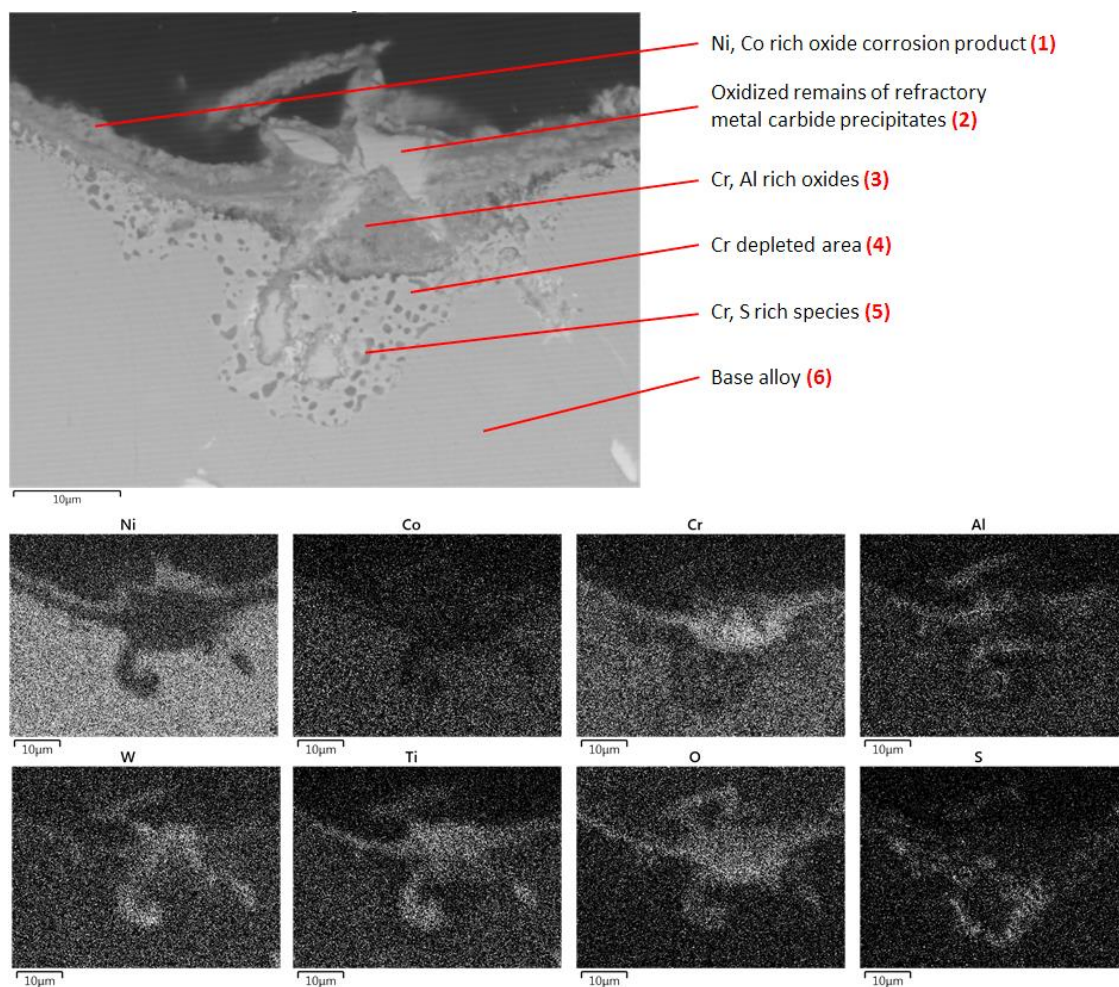
Total error is +2.6 and -2.5  $\mu m$ .

## Appendix D. Table atomic % conversion

This section provides compositional data, presented elsewhere in this thesis as weight %, in terms of atomic %. This includes the nominal alloy compositions and EDX data from exposed specimens.

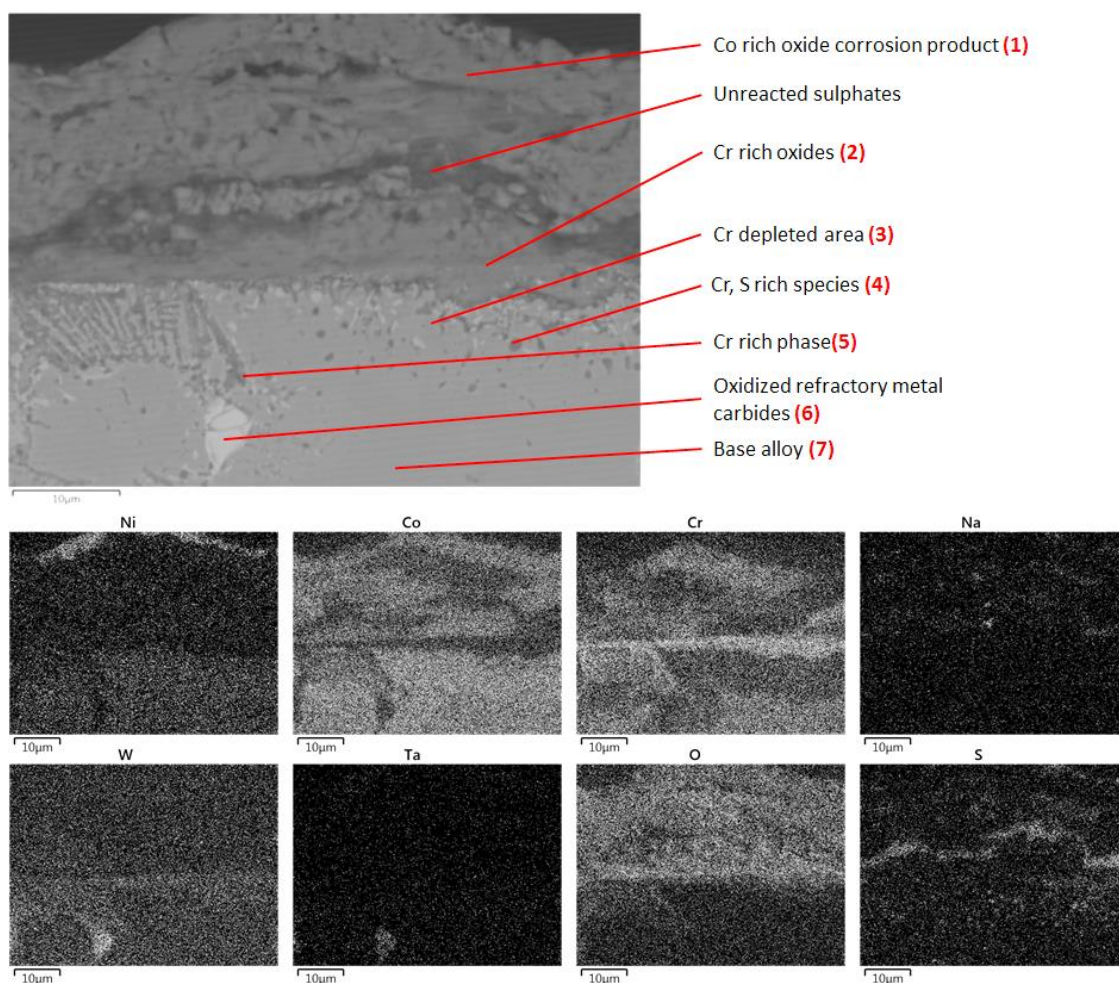
**Table D.1: Nominal alloy elemental compositions (atomic %).**

| Alloy    | Ni   | Co   | Cr   | Ti  | W   | Al  | Ta  | Mo  | Fe  | C   | B   | Zr  |
|----------|------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| GTD 111  | 59.4 | 9.3  | 14.9 | 5.7 | 1.2 | 7.0 | 0.9 | 0.9 | 0.2 | 0.4 | 0.1 | ... |
| Rene 80  | 58.6 | 9.2  | 15.4 | 6.0 | 1.2 | 6.3 | ... | 2.4 | ... | 0.8 | 0.1 | ... |
| PWA 1483 | 60.2 | 8.9  | 13.7 | 5.0 | 1.2 | 7.8 | 1.6 | 1.2 | ... | 0.3 | ... | ... |
| MarM 509 | 10.2 | 55.7 | 27.1 | 0.3 | 2.3 | ... | 1.2 | ... | ... | 3.0 | ... | 0.3 |



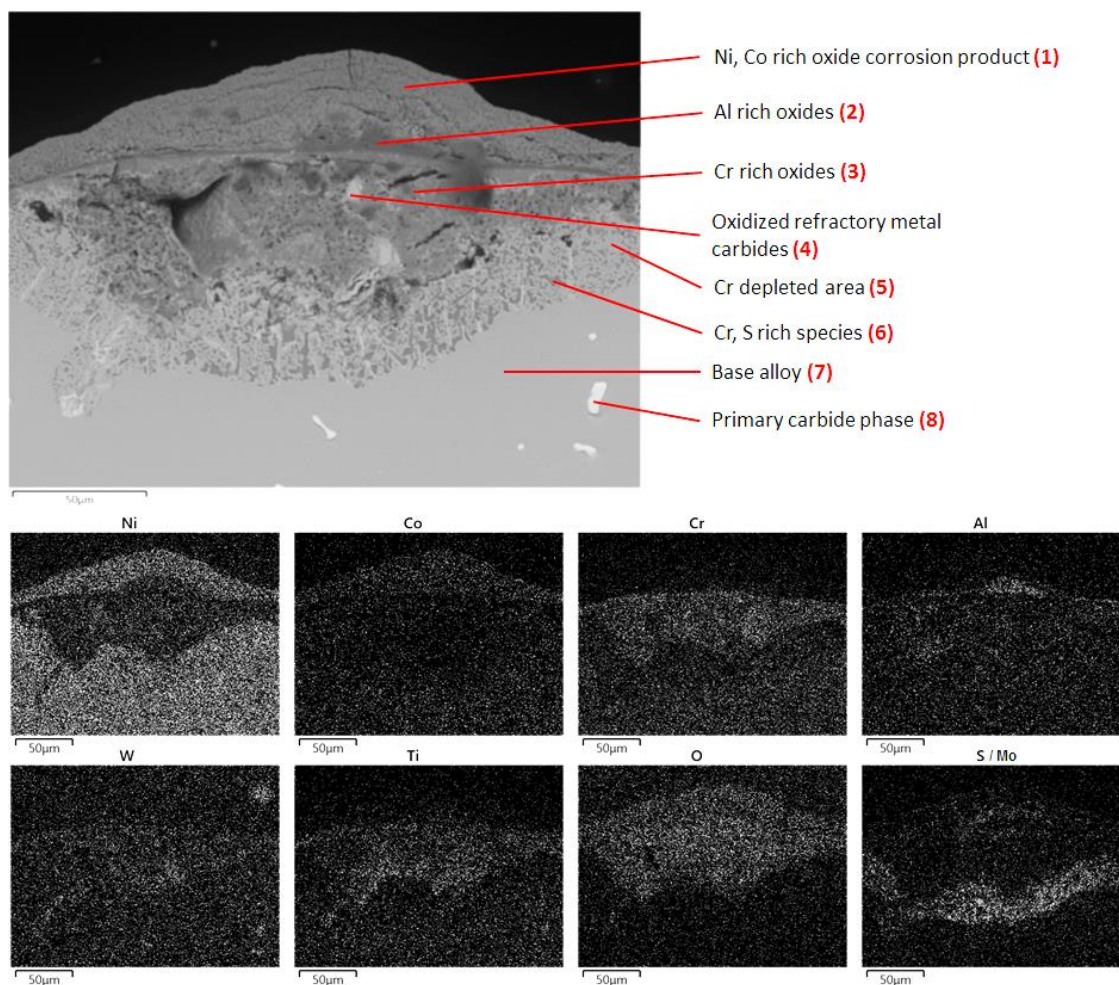
|     | Ni   | Co  | Cr   | Al  | Ti  | W   | Ta  | Mo  | S    | O    | Na  |
|-----|------|-----|------|-----|-----|-----|-----|-----|------|------|-----|
| (1) | 31.0 | 4.5 | 5.5  | 2.5 | 2.2 | 1.9 | 2.2 | 4.8 | 1.0  | 44.5 |     |
| (2) | 18.6 | 2.7 | 8.6  | 2.8 | 9.4 | 1.0 | 5.1 | 1.2 | 0.1  | 50.5 |     |
| (3) | 15.1 | 2.8 | 16.8 | 2.7 | 5.0 | 1.5 | 2.4 | 0.6 | 0.7  | 50.1 | 2.2 |
| (4) | 52.3 | 7.2 | 6.3  | 4.5 | 2.4 | 0.8 | 0.7 | 0.7 | 1.9  | 20.2 | 2.9 |
| (5) | 37.4 | 6.6 | 10.6 | 3.0 | 4.1 | 1.0 | 1.0 | 1.2 | 13.2 | 19.8 | 2.1 |
| (6) | 48.6 | 6.4 | 10.3 | 6.7 | 5.0 | 2.1 | 1.2 | 0.5 |      | 19.3 |     |

Figure D.1: Backscattered electron image with EDX point analyses (atomic %) and elemental maps of corrosion features on PWA 1483 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.



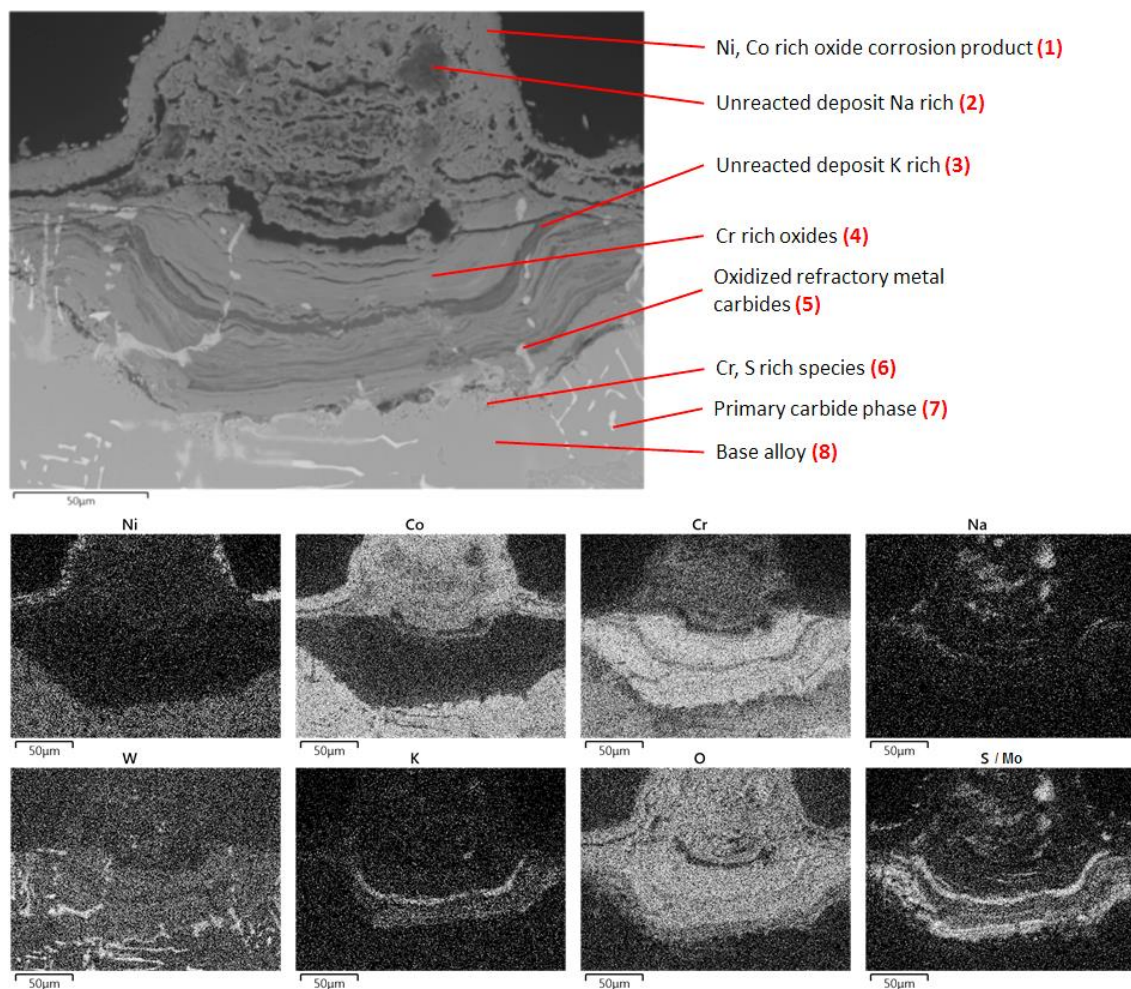
|     | Ni   | Co   | Cr   | W   | Ta  | S   | O    | Na  |
|-----|------|------|------|-----|-----|-----|------|-----|
| (1) | 23.5 | 23.3 | 5.3  | 1.2 | 2.2 | 0.0 | 41.8 | 2.7 |
| (2) | 15.4 | 10.3 | 21.4 | 1.2 | 1.6 | 4.4 | 43.2 | 2.4 |
| (3) | 49.6 | 25.0 | 7.7  | 1.8 | 2.0 | 0.6 | 13.3 |     |
| (4) | 39.6 | 23.8 | 11.3 | 1.9 | 1.7 | 6.3 | 13.3 | 2.2 |
| (5) | 36.0 | 19.6 | 13.3 | 2.4 | 1.7 | 2.1 | 24.9 |     |
| (6) | 26.6 | 15.1 | 9.6  | 2.0 | 8.1 | 1.5 | 37.0 |     |
| (7) | 56.2 | 27.0 | 13.8 | 1.9 | 0.4 | 0.7 |      |     |

Figure D.2: Backscattered electron image with EDX point analyses (atomic %) and elemental maps of corrosion features on MarM 509 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub> and 0% H<sub>2</sub>O. The deposit flux was 1.5 µg/cm<sup>2</sup>/h of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub>.



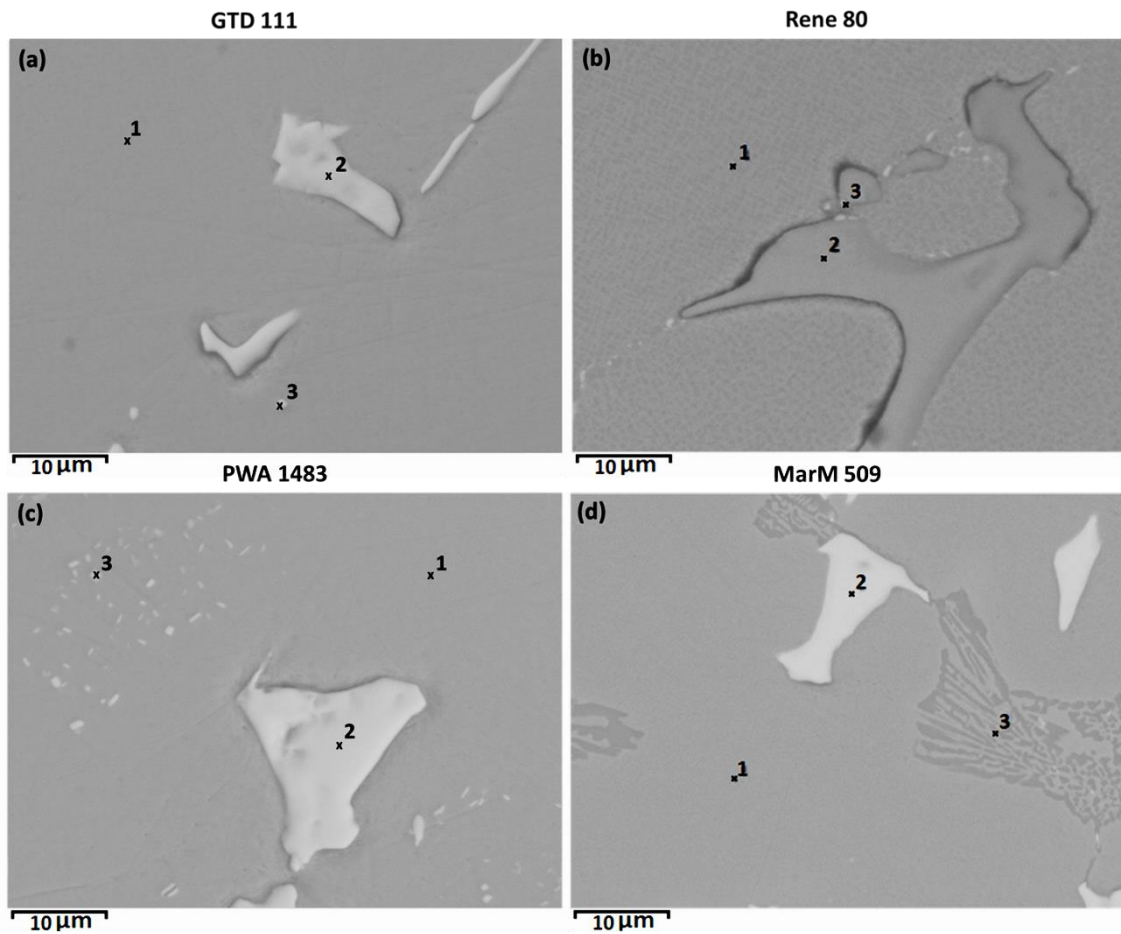
|     | Ni   | Co  | Cr   | Al   | Ti   | W   | Ta   | S/Mo | O    | Na   |
|-----|------|-----|------|------|------|-----|------|------|------|------|
| (1) | 36.0 | 7.4 | 1.7  | 2.0  | 0.9  | 0.0 | 0.0  | 1.2  | 50.9 | 0.0  |
| (2) | 11.3 | 5.6 | 5.3  | 17.1 | 1.9  | 0.0 | 0.0  | 1.6  | 54.9 | 2.3  |
| (3) | 11.1 | 2.2 | 8.1  | 2.5  | 2.8  | 0.5 | 0.5  | 5.4  | 56.4 | 10.6 |
| (4) | 12.0 | 2.0 | 6.1  | 2.1  | 8.8  | 0.0 | 6.4  | 1.7  | 58.7 | 2.3  |
| (5) | 62.3 | 6.2 | 4.5  | 4.7  | 1.7  | 1.1 | 0.0  | 3.5  | 15.9 | 0.0  |
| (6) | 23.4 | 2.7 | 13.6 | 9.8  | 2.2  | 0.0 | 0.0  | 34.1 | 14.2 | 0.0  |
| (7) | 54.7 | 7.6 | 11.3 | 8.8  | 5.0  | 0.8 | 0.0  | 1.3  | 10.5 | 0.0  |
| (8) | 29.6 | 4.1 | 7.3  | 3.0  | 19.2 | 2.4 | 15.3 | 5.5  | 13.7 | 0.0  |

Figure D.3: BSE image with point analysis (atomic %) and EDX element map of a corrosion feature on PWA 1483 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h each of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo.



|     | Ni  | Co   | Cr   | Ti  | W   | Ta   | S/Mo | O    | Na   | K   |
|-----|-----|------|------|-----|-----|------|------|------|------|-----|
| (1) | 3.6 | 35.5 | 3.2  | 0.0 | 0.3 | 0.3  | 0.8  | 52.7 | 3.7  | 0.0 |
| (2) | 2.1 | 11.5 | 4.0  | 0.0 | 0.0 | 0.1  | 13.5 | 52.4 | 14.8 | 1.5 |
| (3) | 1.1 | 6.4  | 13.7 | 0.0 | 0.7 | 0.3  | 12.8 | 58.5 | 1.5  | 5.0 |
| (4) | 1.3 | 7.5  | 28.6 | 0.3 | 2.4 | 0.3  | 1.7  | 55.4 | 2.2  | 0.4 |
| (5) | 4.7 | 28.0 | 18.1 | 4.3 | 2.4 | 12.6 | 1.8  | 26.2 | 1.9  | 0.0 |
| (6) | 5.9 | 31.1 | 23.6 | 0.0 | 1.3 | 0.6  | 19.6 | 16.1 | 1.7  | 0.0 |
| (7) | 5.5 | 27.4 | 17.7 | 4.2 | 2.5 | 13.9 | 1.5  | 25.5 | 1.8  | 0.0 |
| (8) | 9.5 | 48.4 | 26.0 | 0.4 | 2.4 | 0.5  | 0.5  | 10.1 | 2.2  | 0.0 |

Figure D.4: BSE image with point analysis (atomic %) and EDX element map of a corrosion feature on MarM 509 after 500 hours of exposure at 700 °C in an air atmosphere with 300 ppm SO<sub>2</sub>. The deposit flux was 1.5 µg/cm<sup>2</sup>/h each of 80/20 (Na/K)<sub>2</sub>SO<sub>4</sub> and Mo.



| (a) GTD 111 |     |      |      |      |      |     |     |     | (b) Rene 80 |     |      |      |      |      |     |     |
|-------------|-----|------|------|------|------|-----|-----|-----|-------------|-----|------|------|------|------|-----|-----|
|             | Co  | Ni   | Cr   | Ta   | Ti   | W   | Mo  | Al  |             | Co  | Ni   | Cr   | Mo   | Ti   | W   | Al  |
| Point 1     | 9.9 | 60.1 | 15.8 | 1.2  | 4.5  | 1.8 | 0.8 | 5.9 | Point 1     | 9.0 | 58.7 | 15.1 | 2.5  | 7.8  | 1.6 | 5.2 |
| Point 2     | 5.9 | 41.0 | 12.4 | 10.5 | 22.7 | 3.8 | 0.5 | 3.2 | Point 2     | 5.3 | 33.0 | 9.8  | 6.8  | 36.5 | 6.1 | 2.4 |
| Point 3     | 7.6 | 51.0 | 12.5 | 6.1  | 12.8 | 3.1 | 1.9 | 5.0 | Point 3     | 7.1 | 44.0 | 17.9 | 11.8 | 11.5 | 4.3 | 3.4 |

| (c) PWA 1483 |     |      |      |      |      |     |     |     | (d) MarM 509 |      |      |      |      |     |     |     |
|--------------|-----|------|------|------|------|-----|-----|-----|--------------|------|------|------|------|-----|-----|-----|
|              | Co  | Ni   | Cr   | Ta   | Ti   | W   | Mo  | Al  |              | Co   | Ni   | Cr   | Ta   | Ti  | W   | Zr  |
| Point 1      | 8.6 | 60.7 | 12.3 | 1.8  | 6.0  | 1.4 | 1.0 | 8.1 | Point 1      | 55.5 | 10.5 | 28.8 | 1.6  | 0.3 | 3.1 | 0.3 |
| Point 2      | 6.0 | 40.6 | 10.0 | 15.6 | 20.2 | 2.4 | 1.5 | 3.7 | Point 2      | 39.9 | 7.8  | 22.5 | 17.9 | 4.2 | 3.6 | 4.0 |
| Point 3      | 8.6 | 52.6 | 14.6 | 5.6  | 9.4  | 1.7 | 1.6 | 5.7 | Point 3      | 44.2 | 8.3  | 41.8 | 1.8  | 0.3 | 3.4 | 0.3 |

**Figure D.5: BSE images and elemental compositions (atomic %) of selected points showing the larger carbide phases present in (a) GTD 111, (b) Rene 80, (c) PWA 1483 and (d) MarM 509.**