



Comparison of Performance of NiCr_2O_4 and Cr_2O_3 Formed on the Ni-Based Superalloy RR1000 Under Corrosive Conditions

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Abstract

Samples of the Ni-based superalloy, RR1000, were exposed to 98% Na_2SO_4 /2% NaCl salts at 700 °C with a flux of $1.5 \mu\text{g cm}^{-2} \text{h}^{-1}$ in flowing air+ 300 ppm SO_2 for a total of 250 h. Three pre-exposure conditions were studied: a bare reference alloy; fast heating to the test temperature followed by a 100 h hold; heating at a rate of 5 °C min^{-1} to the test temperature following by a 100 h hold. The surface oxide formed under the latter two conditions were Cr_2O_3 or NiCr_2O_4 , respectively. The results show corrosion pit formation on the surface of the base, reference sample, and no pits present on the sample with the preformed Cr_2O_3 . Some protection was found for the sample heated at 5 °C min^{-1} with a delay in the progression to accelerated corrosion attack. Additional testing under moisture containing air was also conducted. This showed no obvious difference in surface oxide morphology under the two tested heating rates for the short-term exposures examined but a difference was noted to be dependent on the moisture content of the air.

Keywords NiCr_2O_4 spinel · Cr_2O_3 · Ni-based superalloy · Corrosion · Moisture

Introduction

Ni-based superalloys are used in the manufacture of critical components in the hot sections of gas turbine engines in land-based and aero applications. Optimisation of the composition and microstructure of the alloy enables operation under high stress conditions at elevated temperatures. An additional consideration is the degradation of the alloys under the oxidising and corrosion environments encountered. Under oxidising conditions, the ability of an alloy to form a protective oxide arises from the bulk composition, which must maintain mechanical integrity despite elemental depletion due to the selective oxidation process [1]. Corrosive environments elicit

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Table 1 Composition of RR1000, wt%, taken using EDS from area scans during this investigation, comparing favourably with the nominal max and min values for this alloy, taken from ref [13]

wt%	Ni	Co	Cr	Mo	Ti	Ta	Al	Hf	Zr	C
Min	bal	19.0	14.35	5.25	3.45	1.35	3.15	0.5	0.5	0.033
Max	bal	14.0	15.15	4.25	4.15	2.15	2.85	1.0	0.7	0.012
EDS	51.4	18.7	15.0	4.9	3.6	2.8	3.1	0.1	0.06	

different behaviour depending on the temperature and the chemical compositions of the salts and alloy [2, 3]. Moisture in oxidising and corrosive conditions tends to accelerate the degradation processes [4–6]. These degradation processes contribute to determining the lifetimes of the components and thus understanding the governing mechanisms is essential.

The alloy explored in this study, RR1000, obtains optimum environmental protection under operating conditions by the formation of a protective Cr_2O_3 surface layer. Many studies have been performed to evaluate its performance under oxidising conditions, with and without applied stress, and covering a range of surface conditions; a few examples are included in refs [7] and [8]. The oxidation behaviour of some alloys can be affected by the initial rate of heating up to the test temperature [9, 10]. The alloy of interest in this work has previously demonstrated that a range of oxide chemistries form dependent on the heating rate [9]. It has been demonstrated that a continuous and protective NiCr_2O_4 spinel formed on the surface of the alloy RR1000 following a controlled heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$. The effect was not found to be affected by gas pressure or surface preparations, but did have an upper temperature limit [11, 12].

In this paper the results of continuing investigations into the benefit or otherwise of the NiCr_2O_4 formed on the same alloy under corrosion conditions and also moist air, at 700°C , are shown. The findings are compared to the behaviour following a fast heating rate, i.e. $> 100^\circ\text{C}\cdot\text{min}^{-1}$, where the more usual Cr_2O_3 formed.

Experiment Procedures

Materials and Initial Sample Preparation

The alloy used in this study was the polycrystalline nickel-base superalloy RR1000, the composition is shown in Table 1, ref [13]. The composition was determined using energy dispersive spectroscopy, EDS, which agrees well with nominal values, Table 1. Samples of approximate dimensions – $15\text{ mm}\times 10\text{ mm}\times 2\text{ mm}$ were sequentially ground and polished on all surfaces to a $6\text{ }\mu\text{m}$ diamond finish. This removed residual stresses induced by the sectioning process and produced samples with a uniform surface finish. The edges and corners were chamfered and polished to the same level; reducing the accumulation of stress associated with oxide growth

at these sites. The samples were measured, cleaned in an ultrasonic bath in soapy water for 5 min, followed by 5 min in acetone and 5 min in ethanol.

Batches of samples were placed in alumina boats and heated to a test temperature of 700 °C in a tube furnace at one of two heating rates; either a rate of 5 °C min⁻¹ up to the test temperature of 700 °C, or the samples were placed into a hot furnace, > 100 °C min⁻¹. The temperature in the furnace chamber was monitored using independent, calibrated thermocouples. Once 700 °C was reached, the samples were extracted, cooled to room temperature and stored ready for the next stage in the testing processes.

Corrosion Testing

Two samples, one following a heating rate of 5 °C min⁻¹ and one following the fast heating rate, were placed into an alumina boat and inserted into a furnace set to 700 °C for a further 100 h isothermal hold in laboratory air. This was done to develop a surface oxide of either NiCr₂O₄, in the case of the sample subjected to a heating rate of 5 °C min⁻¹, or the more usually formed Cr₂O₃, following the fast heating rate. At the end of the 100 h the samples were removed, cooled to room temperature, and stored.

Corrosion tests were performed on three samples of the alloy: one sample of the bare alloy with no preformed oxide, used as a reference sample, one following the 5 °C min⁻¹ heating rate with a 100 h isothermal hold, and one following the fast heating rate with a 100 h isothermal hold. These samples were salted with 98% Na₂SO₄/2% NaCl at a flux of 1.5 µg cm⁻² h⁻¹ on one side and exposed to flowing air+300 ppm SO₂ at 700 °C for a total of 250 h. The samples were removed from the furnace at periods of 50 h for weighing and resalting. A summary of the testing protocol for these samples is shown in Table 2.

Oxidation under Dry and Moist Air

Polished samples of the alloy were placed into a rig consisting of two furnaces in series. At the junction between the two furnaces a conical flask containing deionized water was located. Adjacent to this flask a hydrometer was placed in-line and the moisture levels of the gas measured throughout the test run. Once sealed, and the air flow and the moisture content of the gas stabilised, the furnaces were switched on and heated at a rate of > 20 °C min⁻¹ to the test temperature of 700 °C and held for 6 h. The furnaces were switched off and the samples were removed and examined. The same samples were returned to the furnace for a further 24 h exposure.

To assess the effect of the heating rate, samples were exposed to either a heating rate of 5 °C min⁻¹ to the test temperature of 700 °C or were placed directly into hot furnaces. This was performed in laboratory air using the same level of control of the heating stage as used previously, to maintain consistency with the earlier work. These samples were transferred to the test rig with one sample following each heating rate placed into each furnace. The bottled air was run through the rig and, once flow rate and moisture levels were stable, the furnaces were switched on.

Table 2 Summary of corrosion testing conditions

Sample	Heating rate	Pre-exposure (h)	Salts	Environment	Exposure time
Reference	NA	0	98% Na ₂ SO ₄ /2% NaCl at a flux of 1.5 µg·cm ⁻¹ h ⁻¹	Flowing air + 300 ppm SO ₂	250 h in intervals of 50 h
5	5 °C·min ⁻¹	100			
fast	> 100 °C·min ⁻¹	100			

The moisture level, measured throughout, was maintained at a relative humidity of between 45 to 55%. The moisture content of the bottled air was recorded at 0.5%. The samples were removed after 5 h exposure and examined under SEM. These were returned to the furnaces for a further 24 h exposure under the same conditions used previously. A summary of the testing protocol for these samples is shown in Table 3.

Examination of Samples

Examination of the surfaces of the samples was performed using Scanning Electron Microscopy, SEM. Cross-sections through the samples exposed to the corrosive conditions were prepared by mounting the samples in conducting Bakelite. The samples were ground through by 3 mm to reveal the cross-section followed by grinding on successively finer SiC papers to 1200 grit. The sections were polished using 6 μm and 1 μm diamond with a finish on a silica sol. SEM and BSE images were collected and compositional information was measured using EDS.

Results

Effect of Exposure Under Corrosion Conditions

The mass change, normalised to surface area, for each sample tested and recorded at 50 h intervals, are shown in Fig. 1. This shows, for the reference sample, with no preformed surface oxide, a steady increase in mass up to 150 h. After this incubation period the mass increased rapidly indicating accelerated corrosion. The two samples with a preformed surface oxide followed the same mass change trend for the duration over the test period, i.e., no acceleration in mass change was observed indicating that the samples were still in the incubation stage. The sample that had the fast initial heating rate showed the lowest mass gain.

Micrographs of sections through the three samples are shown in Fig. 2. Pit formation across the surface of the reference sample was clearly present, Fig. 2a and b. This is characteristic of Type II corrosion behaviour. Note in Fig. 2a to the left-hand

Table 3 Summary of oxidation testing conditions

Test conditions	Heating rate	Test temperature (°C)	Relative humidity (%)	Total exposure time (h)
Reference	NA	700	0.5	36
Dry air	5 °C·min ⁻¹	700	0.5	29
Dry air	> 100 °C·min ⁻¹	700	0.5	29
Reference	NA	700	45–55	36
Moist air	5 °C·min ⁻¹	700	45–55	29
Moist air	> 100 °C·min ⁻¹	700	45–55	29

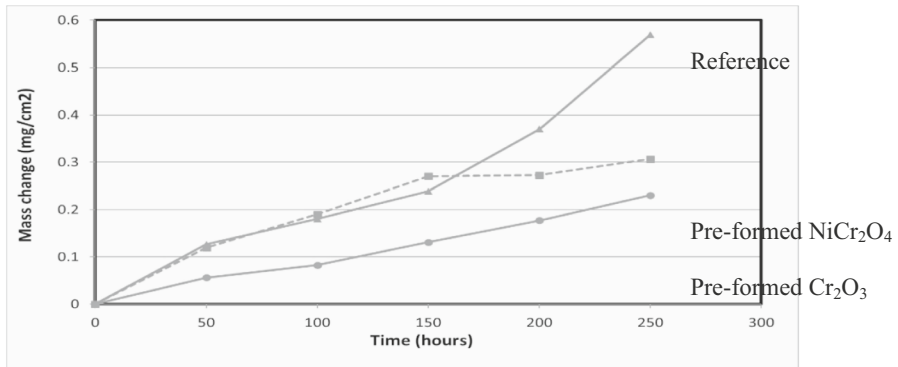


Fig. 1 Plot of mass change, normalised to surface area, against time in hours for samples tested under corrosion conditions at 700 °C for: the reference sample with no preformed surface oxide, samples following heating rate to pre-form either NiCr₂O₄ or Cr₂O₃. Accelerated mass gain was noted in the reference sample after 150 h exposure, this was not seen in either of the samples with a preformed surface oxide

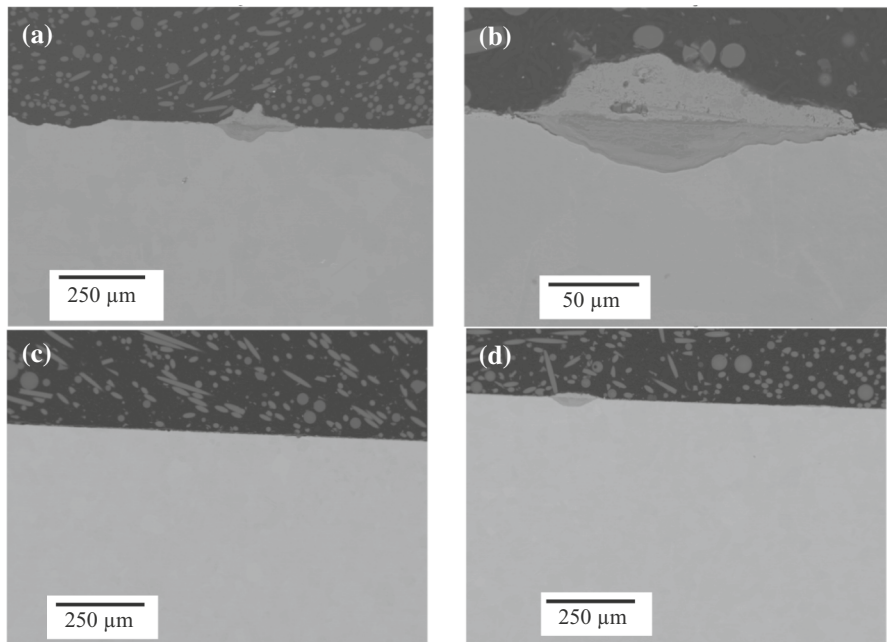


Fig. 2 BSE images of sections through the samples exposures under corrosion conditions for a total of 250 h at 700 °C for **(a and b)** the reference sample with no preformed surface oxide and showing pit formation, **c** the sample following fast heating rate with additional 100 h isothermal exposure showing no pit formation and **d** sample following a heating rate of 5 °Cmin⁻¹ and an additional 100 h exposure showing pit formation

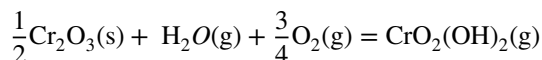
side a region, where spallation of the corrosion products has occurred. The sample that had the fast heating rate plus a 700 °C isothermal hold for 100 h, showed no pit formation across the surface, Fig. 2c. This demonstrated that the formation of a Cr₂O₃ layer at the surface of the alloy before the application of the salt solution provided protection, preventing the development of the corrosion pits. This is corroborated by a lower mass gain recorded for this sample, Fig. 1. Pit formation was observed in the sample heated at 5 °C·min⁻¹ plus a 100 h isothermal hold at 700 °C. This agrees with the mass gain data, possessing a similar response to the reference sample. However, whereas the reference sample showed accelerated attack from 150 h onwards, the sample with the preformed oxide following the 5 °C·min⁻¹ heating rate did provide some continued protection. Fewer pits observed in the cross-section of the sample, Fig. 2d compared to the reference sample, Fig. 2a.

Compositional analysis of a corrosion pit formed on the reference sample is shown in Fig. 3. EDS maps of the region show compositionally varying layers with Co and Ni oxides at the outer surface, an internal layer of Cr-rich oxides and sulphur penetration with the formation of Al and Cr phases. The alloy also contains Mo which is also shown in Fig. 3 for completeness. Clashes between S and Mo due to the similarity in the energy levels for these two elements makes distinguishing these elements difficult using EDS maps. However, by studying the K peaks for Mo it was possible to state that the signal from the base of the pit was predominantly due to S. The presence of Na from the salt can also be seen at the outer layers of the corrosion products and also penetrating into the pit. Examination of the pits on the pre-oxidised sample following a heating rate of 5 °C·min⁻¹ showed similar layering and compositional variations.

Effect of Moisture in Air

Reference samples, with no preformed oxide, were exposed for a total of 36 h in either dry or moisture laden bottled air. The heating rate to the test temperature of 700 °C was > 20 °C·min⁻¹. The level of control of the moisture content and flow rate of the bottled air in these initial tests were not as consistent as later runs. SEM images of the surfaces of these samples showed differences in oxide morphology under the two conditions, Fig. 4. Under dry air, Fig. 4a, a complete covering of oxide was evident over the surface of the sample. Under moisture laden air islands of oxides were shown, Fig. 4b. The distribution and shape of these islands strongly suggests a link to the location of emergent grain boundaries. The majority of the surface appeared smooth.

Volatilization of Cr₂O₃ occurs via the reaction:-



The observation of the morphology and location of the islands of oxide, i.e., at emergent grain boundary regions, is consistent with the rate of Cr₂O₃ growth at these sites being greater than the rate of volatilisation. The rate of volatilisation over the rest of the surface appears to match that of the growth of Cr₂O₃; and thus

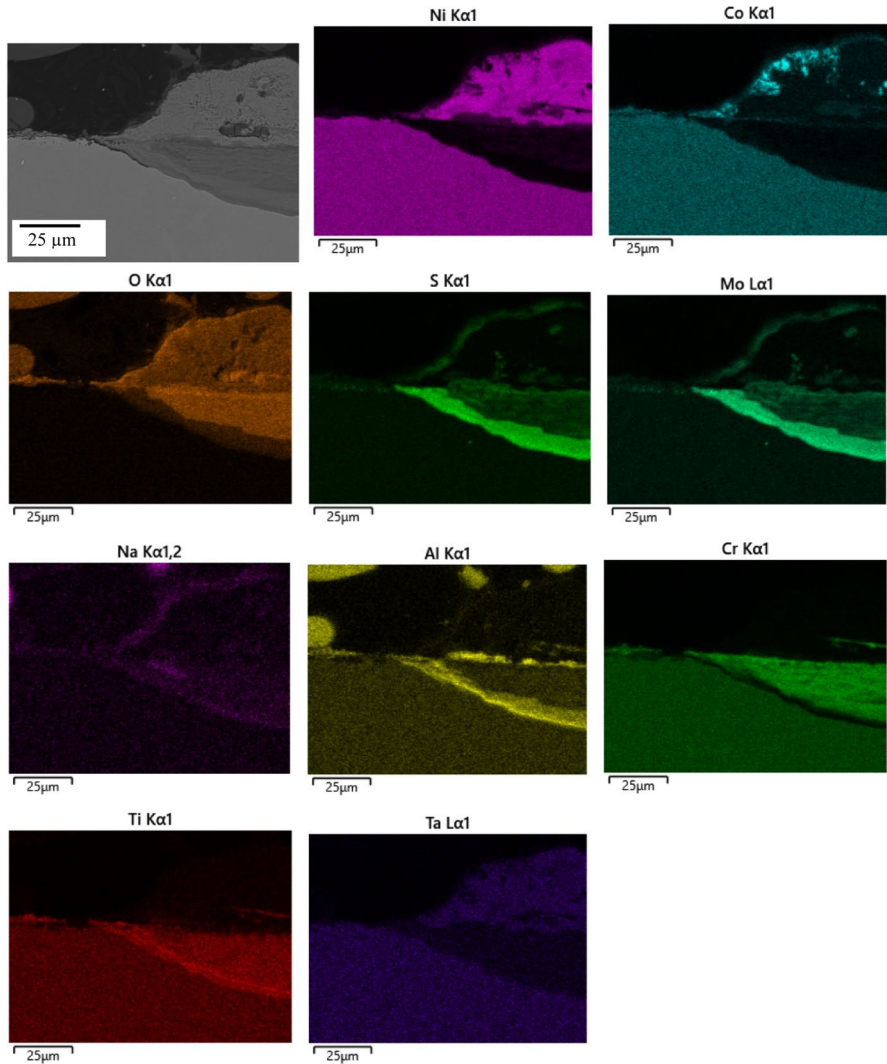


Fig. 3 BSE image of a section through the reference sample with EDS maps showing details of the composition of the corrosion pit. Compositionally layering was observed as expected in this type of corrosion with oxides of Al, Cr and Ti formed adjacent to the alloy surface. The S and Mo maps show the difficulty in differentiating between these elements using EDS analysis

the presence of a surface oxide is not clear on these regions. The overall effect on the alloy will be to increase the rate of depletion of Cr from the alloy, accelerating the depletion process.

The results of exposure of samples of the alloy following the two heating rates assess under dry and moisture containing air are given in Fig. 5. Figures 5a and b show the surfaces after exposure to dry air and Figs. 5c and d to moisture laden

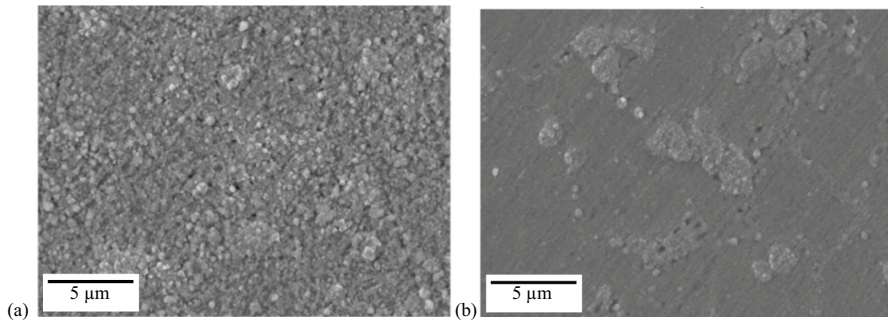


Fig. 4 SEM micrographs from a planar view of surface of alloy after thermal exposure at 700 °C for a total of 36 h under **a** dry air producing a complete coverage of oxide and **b** moisture laden air revealing islands of oxides with the polishing marks on the underlying sample still visible

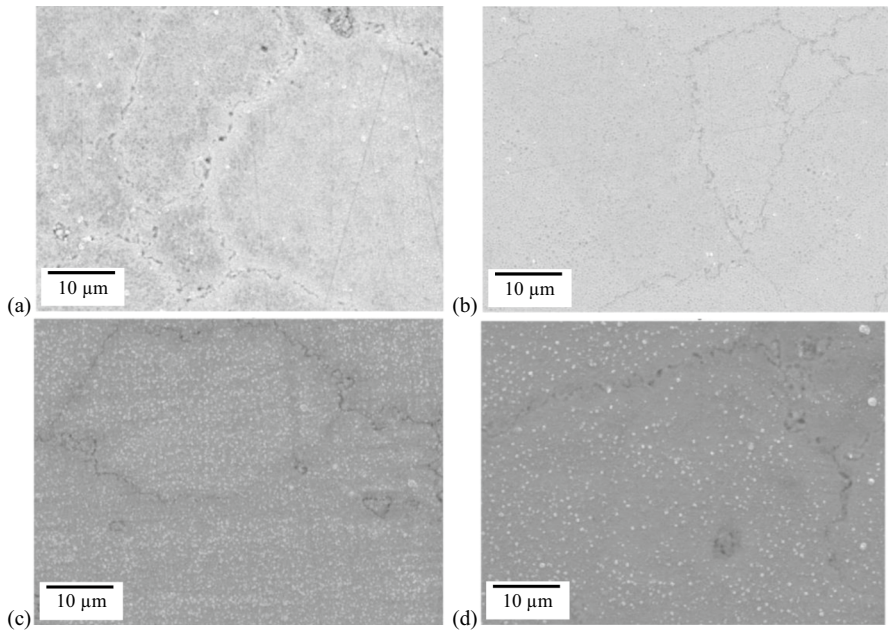


Fig. 5 SEM images of the planar surface of the alloy following exposure for 29 h at 700 °C under **(a, b)** dry air and **(c, d)** moisture containing air. **a** and **c** show the sample exposed to a fast heating rate to the test temperature, **b** and **d** show the samples exposures to a heating rate of 5 °C min⁻¹. Under dry air a more uniform coverage of oxide was achieved. The presence of moisture produced more light contrast crystallites on the surface of both samples. No significant differences were observed based on heating rate over these short durations

air. Figures 5a and c are taken from samples following a fast heating rate, and (b and d) 5 °C·min⁻¹ heating rate.

Under dry conditions a continuous uniform coverage of oxide had formed with some dark contrast definition of the grain boundaries. In the presence of moisture, light

contrast crystallites were present on the surface of the alloy. Also, the dark contrast grain boundaries appeared more pronounced. Light contrast precipitates visible on the surface of the alloy exposed under dry air were identified as Ti and Ta rich and were found distributed throughout the alloy. The Ti, Ta rich precipitates were present at the surface of the samples exposed under moisture laden air but the majority of the light contrast features present on these samples were Cr-rich and were thus either Cr_2O_3 or NiCr_2O_4 . The Cr-rich crystallites were not present on either of samples exposed under dry air and this indicates that the formation was linked to the moisture content of the air. Further work, at higher resolution, is needed to explain the formation of these crystallites and to determine, whether the composition of the crystallites is the same for each heating rate. Additional work in determining the chemical reactions between H_2O in the air and the oxides formed on the surface of the alloy over the heating stage are also needed to fully reveal the influence of heating rate on the oxidation mechanisms for this alloy.

Discussion

It has been established that the alloy RR1000 exhibits a heating rate sensitivity which is reflected in the chemistry of the surface oxide formed [9, 11]. It has been shown that following an initial heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, to temperatures up and including $725\text{ }^\circ\text{C}$, a NiCr_2O_4 spinel formed on the surface of the alloy. At faster heating rates Cr_2O_3 formed [7, 8]. Under purely oxidising conditions in laboratory air the kinetics of growth following a heating rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ were slower than of Cr_2O_3 formation on this alloy [12]. Examination of the mass change under corrosion conditions of the alloy RR1000, found in this study, showed a reversal in mass change kinetics with slower kinetics following the fast heating rate. There are implications of this finding to components which experience a range of heating rates during heat treatments and under operating conditions.

Examination of the cross-sections through the samples showed that the same pitting behaviour observed on the reference sample was found on the sample with the preformed NiCr_2O_4 . However, whereas the reference sample transfers from the incubation stage to accelerated kinetics at approximately 150 h exposure, the presence of a NiCr_2O_4 scale inhibited this transition and continued to provide some level of protection under the prevailing corrosion conditions. No corrosion pits were revealed for the sample pre-heat treated to form Cr_2O_3 demonstrating the superior protection this oxide offers under corrosion conditions chosen in this study. One factor to consider is the thickness of the preformed surface oxide. Slower oxidation kinetics have been demonstrated by the NiCr_2O_4 spinel compared to the more usual Cr_2O_3 formed on this alloy and this the thickness of the surface oxide would reflect this. The thickness of the surface oxide may be a factor and is the subject of a continuing investigation.

A short-term study of the effect of the level of moisture in the test air on the morphology of the surface oxides formed has been conducted. Exposure of the bare reference alloy to moisture laden air showed a marked effect on the morphology. Short-term exposure of samples heated at the different rates used here suggests that the effect of increased moisture levels in the test gas is independent of the initial heating rate. Further testing is planned with a full assessment of the potential chemical reactions with all the oxides formed over the heating stage.

Conclusion

The continuing investigation into the influence of the heating rate of the first thermal transient on the oxidation and corrosion behaviour of the nickel-based superalloy RR1000 have been presented. These preliminary results show that the presence of a preformed Cr_2O_3 layer on the surface of the alloy enhanced the corrosion resistance of the alloy, preventing the formation of pits over the test time of 250 h. The surface oxide, formed after heating at a rate of $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, proved less protective with pit formation occurring. Intriguingly, this alloy condition provided a longer incubation time compared to the reference sample, with no preformed surface oxide. The surface oxide formed at both heating rates demonstrated similar behaviour under the presence of moisture laden air. Further testing is continuing into this fascinating effect.

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Author Contribution S.G. and M.P.T. devised the experimental approach. C.J. and M.C.H. provided the alloys and funding. S.G. performed the corrosion testing with examination and analysis. M.M. performed the moisture testing and initial examination of samples under the supervision of M.P.T. and D.M.C. M.P.T. examined all samples and produced the initial draft of the paper. All authors reviewed the manuscript.

Data Availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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