EFFECTS OF SEA SALT ON THE OXIDATION OF CMSX-4® AT 1100 °C

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Abstract

Recently, a new High Temperature Environmental Testing (HTET) methodology has been described which combines cyclic oxidation with the addition of synthetic sea salt. The current investigation aims to further understand the effects of synthetic sea salt deposition on the oxidation behavior of a second-generation nickel-base single-crystal superalloy CMSX-4®. A series of isothermal and cyclic oxidation tests at 1100 °C were carried out on bare and salt-deposited samples. The effects of different salts and altered salt application regimes on cyclic oxidation at 1100 °C were also evaluated. Further experiments were carried out using thermo-gravimetric analysis (TGA) to study the cyclic oxidation process in greater detail for both the bare and sea salt-deposited samples. During both isothermal and cyclic oxidation, synthetic sea salt deposition generally resulted in enhanced oxidation attack compared to the bare sample. Prior oxidation to produce a stable coherent protective alumina coating loses its protective capability as soon as salt is added. Conversely, after being subjected to cyclic oxidation with salt deposition, poorer oxidation resistance was noted in subsequent cyclic oxidation without salt deposition. Cyclic oxidation investigated with TGA shows that with salt deposition, significant oxidation attack occurs within the first few cycles, after which a steady-state oxide regeneration and spallation regime was progressively attained. The effects of salt on high temperature oxidation, even at the low dosages used in the current study, are clearly critical and have lasting effects on the oxidation resistance performance on the test samples as well as components made of similar alloys; these are discussed in light of the results obtained.

Introduction

Oxidation and corrosion resistance of nickel-base superalloys are increasingly becoming the life-limiting property for modern turbine blades [1, 2]. Burner rig tests were traditionally used to evaluate the corrosion resistance of nickel-based superalloys. However, it is difficult to control the test conditions, as such the repeatability of tests is questionable and there may be inconsistencies in the data generated [3-5]. Cyclic oxidation tests are also used to study the oxidation behavior of nickel-base superalloys. However, bare cyclic oxidation in air often takes a significant amount of time to reach the same degree of degradation. In addition, bare cyclic oxidation in air very often does not reproduce the degraded microstructure of the turbine blade components removed from aero-engines after service [6-8].

Recently, a new High Temperature Environmental Testing (HTET) methodology has been introduced which combines cyclic

oxidation with the addition of synthetic sea salt to reproduce the damage to turbine blades seen in service temperatures in excess of 1000 °C [9, 10]. The synthetic sea salt consists nominally of 86% NaCl and small quantities of several other salts. The small amount of salt deposited, of the order of 40-140 µg/cm², was found to accelerate both oxide formation and spallation. This new method allows the oxidation properties of materials in the service environment to be characterized rapidly, typically within weeks; in addition, small differences in the oxidation resistance of various alloys may be distinguished. Of greater significance is that this new method was able to reproduce oxide morphologies that closely resemble the in-service degradation of aero-engines turbine blades. This highlights the relevance of the HTET methodology as a testing method, and allows the degradation mechanism of turbine components at temperatures well above those characteristic of Type I hot-corrosion to be studied.

Despite the advantages associated with the HTET methodology, an in-depth understanding of the effects of salt on oxidation attack in nickel-base superalloys at temperatures above 1000 °C is still lacking. In this paper, the HTET methodology, in addition to various other experiments were carried out to investigate the mechanisms by which salt additions affect the degradation of nickel-base superalloy CMSX-4 at 1100 °C.

Experimental

Material

The nominal composition of CMSX-4 used in the current study is shown in Table I. The test material was supplied as single-crystal test bars approximately 13.5 mm diameter and 150 mm length in fully heat-treated condition.

Table I: Nominal Composition (wt. %) of
Ni-base Superalloy CMSX-4, Balance Ni [11]

Al	Ti	Cr	Co	Mo	Hf	Ta	W	Re
5.6	1.0	6.5	9.6	0.6	0.1	6.5	6.4	3.0

Salt Deposition

The composition of the synthetic sea salt used in the present study as well as the melting and boiling points of its constituents are shown in Table II. Most tests involving salt utilized the synthetic sea salt recipe. Limited tests were carried out with NaCl only and MgSO₄ only to separate the individual effects of these salts on the oxidation behavior of the test samples.

In tests requiring salt, the salt was deposited on the surfaces of the samples via semi-automated spraying of the dilute salt solution. Full details of the salt spray procedure have been described elsewhere [9, 10]. Briefly, during the salt spray, samples were heated on a hot plate prior to the start and throughout the spraying

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process. The spraying process deposits a fine mist of the dilute salt solution on the sample surface; the water in the solution evaporates rapidly, leaving a fine salt coating on the sample surface. Each spraying pass deposits a relatively constant amount of salt on the sample surface. The amount of salt required varies for each test; the amount of salt deposited was varied by altering the number of spraying passes.

Table II. Composition of Synthetic Sea Salt.

Salt	Melting Point (°C)	Boiling Point (°C)	Concentration in Synthetic Sea Salt (g/L)
NaCl	801	1465	26.50
MgCl ₂	714	1412	2.40
MgSO ₄	1124	>1500	3.30
KCl	770	1500	0.73
NaHCO ₃	50	851	0.20
NaBr	755	1393	0.28
CaCl ₂	782	1935	1.10

Thermogravimetric Analysis (TGA)

A vertical tube furnace capable of 1500 °C was utilized for the TGA experiments. The hot zone size of the furnace is approximately 100 mm, and the temperature is controlled to within ± 3 °C. TGA samples were hung on a thin platinum wire attached to an electrical microbalance. The mass of the sample was measured and recorded using a data acquisition computer every 60 seconds; in addition, the data recording may also be triggered when significant mass change greater than 0.1 mg was detected. Thin disks of approximately 0.40 mm were cut from the 13.5 mm diameter test bars. These samples were ground with SiC paper to 2500-grit finish and subsequently ultrasonically cleaned in methanol and blow dried. The TGA experiments were carried out on bare samples without salt deposition as well as on samples which have been deposited with 40 $\mu\text{g}/\text{cm}^2$ and 140 $\mu\text{g}/\text{cm}^2$ on both faces of the thin disc samples.

Additional TGA experiments with salt were also carried out on pre-oxidized samples to evaluate the concomitant effects of the synthetic sea salt. It is well acknowledged that pre-oxidation in air facilitates the formation of a continuous, compact Al₂O₃ layer, which controls the rate of further oxidation of the alloy substrate [12, 13]. In these TGA experiments, the sample was oxidized in air at 1100 °C for 40 hours, after which the sample was removed from the TGA furnace and allowed to cool. Synthetic sea salt at 40 $\mu\text{g}/\text{cm}^2$ was applied and the sample was subsequently subjected to further isothermal oxidation at 1100 °C for 60 hours.

Cyclic Oxidation Tests

Cyclic oxidation tests were carried out in a vertical tube furnace of diameter 120 mm equipped with an automated sample loading mechanism, which allows up to sixteen samples to be tested simultaneously. The sample loading mechanism is controlled by computer, and the 'hot-time' and 'cool-time' of the cyclic oxidation tests could be specified in the computer software as required. Each cycle consists of 1 hour 'hot-time' at 1100 °C and 10 minutes 'cool-time' at room temperature. When loaded into the furnace, the samples attained 1100 °C almost instantaneously due to the large heat capacities of the furnaces; on unloading, the samples cooled to room temperature within 3-4 minutes in laboratory air.

Disc samples for cyclic oxidation tests were cut from the supplied test bars to thicknesses between 1.2 mm and 1.5 mm. The edges of the samples were rounded in order to reduce the occurrence of sharp-edge spallation. The disc samples were then 'barrelled' (also known as barrel finishing) in a stone grit media to produce a smooth surface. The diameter and thickness of each sample were carefully measured with a digital caliper prior to the start of the test. Samples were weighed prior to the start of the tests and after every 20 cycles using a microbalance with a resolution of 0.01 mg. Cyclic oxidation testing was terminated for a given sample when the mass loss has reached approximately 200 mg/cm².

Where required, samples were sprayed with salt solution prior to the start of the cyclic oxidation test and after every 20 cycles. The amount of synthetic sea salt applied was 40 $\mu\text{g}/\text{cm}^2$ and 140 $\mu\text{g}/\text{cm}^2$. Bare samples without salt deposition were also subjected to the cyclic oxidation test for comparison. In addition, samples deposited with NaCl only and MgSO₄ only were also tested in this series of test to study the individual effects of these two salt species. The amount of salt applied for the NaCl only sample and MgSO₄ only sample were 61.4 $\mu\text{g}/\text{cm}^2$ and 7.6 $\mu\text{g}/\text{cm}^2$ respectively. These amounts represent twice the molar concentrations (per unit area) of these individual salts compared to those deposited in the case of 40 $\mu\text{g}/\text{cm}^2$ synthetic sea salt.

Further cyclic oxidation testing was also carried out with altered salt spray regimes to evaluate the concomitant effects of the synthetic sea salt. Cyclic oxidation tests were carried out on pre-oxidized samples to assess the protection of an existing Al₂O₃ protective layer against further elevated temperature cyclic oxidation attack in the presence of salt.

In addition, cyclic oxidation test was also carried out where the samples were subjected to the usual salt deposition every 20 cycles for the first 80 cycles, after which salt was no longer applied but the samples continued to be subjected to the cyclic oxidation test. This was to assess the legacy effects of the salt, if any, on the subsequent oxidation behavior of the samples.

TGA Cyclic Oxidation Experiments

In order to study the detailed mechanisms associated with the salt-accelerated cyclic oxidation attack, TGA cyclic oxidation experiments were carried out to continuously monitor the mass change during the cyclic oxidation process, to elucidate the effects of salt. The tests utilized the same TGA equipment described earlier. The electrical microbalance of the TGA is mounted on a fixed frame while the vertical tube furnace is attached to a vertical linear sliding mechanism, allowing the samples to be introduced into and removed from the furnace solely by the movement of the furnace alone without unsettling the stabilized sample and microbalance. The sample was subjected to the temperature profile and salt spray regime of the cyclic oxidation test. The temperature profile was achieved via manually sliding the furnace to introduce the sample to the temperature of 1100 °C and vice versa during the cooling period. The amount of synthetic sea salt deposited was 40 $\mu\text{g}/\text{cm}^2$, prior to the start of the test and after 20 cycles. Bare sample without salt deposition was also tested for comparison.

Oxide Analyses

After isothermal and cyclic oxidation testing, selected samples were analyzed with a Philips PW1050 advanced powder diffractometer at the surface to identify the oxide phases present. Lattice reflections were recorded using a monochromatic Cu-K α long fine focus (LFF) source (40 kV, 40 mA), coupled with a divergence slit of 0.5°, a receiving slit of 0.2 mm and an anti-scatter slit of 0.5°. Data was collected using Philips X'Pert Data Collection and analyzed by Philips X'Pert HighScore Plus utilizing the JCPDS ICDD PDF-2 2001 database.

Samples for oxide examination were sectioned with a precision saw utilizing a SiC blade, with a dry-cut method (without cutting fluid) and a low feed speed in order to preserve the oxide layers on the sample surfaces. Sectioned samples were then mounted in Bakelite, and subsequently ground and polished to 0.25 μ m diamond finish. The microstructures of the oxides and alloy substrate were examined in a JEOL 5800LV scanning electron microscope (SEM) equipped with an Oxford Instruments energy dispersive X-ray (EDX) detector.

Selected samples were also further analyzed using a Cameca SX100 electron probe micro-analyzer (EPMA) equipped with wavelength dispersive (WD) X-ray detector. The EPMA equipment is equipped with five WD spectrometers, and operates via Cameca Windows-based PeakSight software (Version 4.2). The beam conditions were 15 kV, 100 nA and was fully focused. Selected representative areas were mapped at 1 μ m resolution with a dwell time of 40 ms at each location. The following X-ray lines were used (the choice of lines is constrained by the need to avoid significantly overlapping lines): K α 1 – O, Al, Ti, Cr, Co, Ni; L α 1 – Mo, W; M α 1 – Hf, Ta; and M β 1 – Re. All calibration standards were pure (99.999%) metals except for Al, for which pure synthetic corundum (Al₂O₃) was used. The analyzing crystals used were PC0 (O), LIF (Co, Ni), LLIF (Cr, W), LPET (Ti, Mo, Re) and LTAP (Al, Hf, Ta).

Results

Isothermal oxidation at 1100 °C

Isothermal kinetic curves of CMSX-4 without salt as well as with 40 μ g/cm² and 140 μ g/cm² sea salt deposition obtained via TGA measurements are shown in Fig. 1. All samples showed rapid initial mass gains which were correlated to the amount of salt deposited, with higher mass gain noted for higher amount of salt deposited. Salt deposition at 40 μ g/cm² leads to small increase in mass gain (at a given point in time) compared to that of the bare sample. Further salt deposition at 140 μ g/cm² leads to a large and significant increase in mass gain, and mass gain rate compared to that of the 40 μ g/cm² salt sample. In all cases, the rapid initial mass gains progressively slowed down. Oxidation of the bare sample slowed down very quickly within the first hour, while the samples with 40 and 140 μ g/cm² salt after approximately 10-20 hours and 60 hours, respectively. Beyond these, each sample kept relatively similar mass gain rates for the remainder of the tests. The mass gain curves generally followed a parabolic growth behavior, indicating the formation of continuous protective oxide layers. This was confirmed by the square of mass change against time plots (not shown). Parabolic growth constant, k ($\times 10^{-12}$ g² cm⁻⁴ s⁻¹) calculated for the final 20 hours of oxidation are shown in Fig. 1.

Fig. 1 Isothermal oxidation at 1100 °C of CMSX-4 samples without salt and with 40 μ g/cm² and 140 μ g/cm² sea salt deposition. k values are in 10^{-12} g² cm⁻⁴ s⁻¹.

Cyclic oxidation at 1100 °C

The results of cyclic oxidation tests at 1100 °C with different types and amounts of salt are shown in Fig. 2. The bare sample showed negligible mass loss for up to 500 cycles, i.e. an “incubation period”, followed by a low and relatively constant rate of mass loss up to 1000 cycles. With salt deposition, the incubation period was significantly reduced, to within 20-40 cycles. Salt deposition also leads to significantly greater rates of mass loss compared to the bare sample, the mass loss rates increase with the amount of salt deposited.

Fig. 2 Kinetic curves for the cyclic oxidation of CMSX-4 without salt, with 40 μ g/cm² and 140 μ g/cm² sea salt as well as with NaCl only and MgSO₄ only salts at 1100 °C.

Results of cyclic oxidation with NaCl only and MgSO₄ only salts are also shown in Fig. 2. The MgSO₄ only sample showed a minor increase in mass loss compared to the bare sample. In the case of NaCl only salt, progressively greater mass loss was noted compared with the bare sample and the sample with MgSO₄ only, however, at a given cycle, the mass loss of the NaCl only sample was less than that of the sample with 40 μ g/cm² synthetic sea salt. The mass loss characteristics of the NaCl only sample were relatively similar compared to those of the 40 μ g/cm² sea salt sample, but appear delayed by approximately 100 cycles.

An interesting point to note in Fig. 2 is that the 40 μ g/cm² salt sample appears to show very high mass loss rates between 200-300 cycles, which resembles the relatively constant mass loss

rates observed for the $140 \mu\text{g}/\text{cm}^2$ sample. This accelerated mass loss was also observed for the NaCl only sample, albeit delayed and occurring slightly later compared to the $40 \mu\text{g}/\text{cm}^2$ sea salt sample.

Altered Salt Spray Oxidation Behavior at 1100°C

Fig. 3 shows the TGA results associated with a pre-oxidized sample. The bare sample was oxidized in air for 40 hours, the mass gain behavior of which was similar to that shown for the bare sample in Fig. 1. Slow, parabolic mass gain was attained after approximately 2 hours, indicating good protection against further significant oxidation of the alloy substrate. After application of $40 \mu\text{g}/\text{cm}^2$ sea salt and subjected to further isothermal oxidation, a large mass gain was noted, which gradually slowed down within the subsequent 10 hours. Beyond this point, there was no distinct mass change for the remainder of the test up to 100 hours. At the termination of the test when the sample was removed from the elevated temperature and left to cool (by removal of the furnace while keeping the sample hung from the TGA microbalance), a large mass loss was noted. The buoyancy effect on this mass loss has been compensated for by comparison with a pure alumina disc, therefore the mass loss on cooling shown in Fig. 3 was due to the spallation of oxide from the sample surface.

Fig. 3 TGA kinetic curve for CMSX-4 sample oxidized in air at 1100°C for 40 hours, then deposited with $40 \mu\text{g}/\text{cm}^2$ sea salt and further exposed at 1100°C for 60 hours.

The kinetics of the cyclic oxidation with altered salt deposition regimes are shown in Fig. 4. One sample, denoted 0+40salt, was cyclically tested without salt for the first 80 cycles, and then subjected to $40 \mu\text{g}/\text{cm}^2$ sea salt deposition every 20 cycles for the remainder of the test. Another sample, denoted 40salt+0, was subjected to $40 \mu\text{g}/\text{cm}^2$ sea salt deposition every 20 cycles for the first 80 cycles, after which salt was no longer applied for the remainder of the test. The 0+40salt sample showed similar mass loss behavior to the bare sample for the first 80 cycles, after which on application of sea salt, the mass loss behavior changes to mimic that of the $40 \mu\text{g}/\text{cm}^2$ salt. The mass change behavior of the 0+40salt was delayed for 80 cycles compared to that of the $40 \mu\text{g}/\text{cm}^2$ salt.

On the other hand, the mass loss behavior of the 40salt+0 sample follows that of the $40 \mu\text{g}/\text{cm}^2$ salt sample for the first 80 cycles as expected. However, when salt was no longer applied beyond 80 cycles, the mass loss rates reduced, but remained significantly higher than those of the bare sample.

Fig. 4 Kinetics of salt-accelerated cyclic oxidation of CMSX-4 with different salt spray regime at 1100°C .

TGA Cyclic Oxidation Experiments

Results of the TGA cyclic oxidation experiments carried out on the bare sample and the $40 \mu\text{g}/\text{cm}^2$ salt sample are shown in Fig. 5. These results correspond to those of the first 40 cycles shown in Fig. 2. There are two important aspects to be noted in each cycle i) the mass change within the 1-hour 'hot-time', and ii) the mass change during cooling after the 'hot-time' (shown by the difference in mass at the end of a particular 'hot-time' and at the start of the following 'hot-time').

In the first hour, the mass gains for both the bare sample and salt-deposited sample were low, of the same order as that observed during corresponding isothermal TGA tests shown in Fig. 1. The bare sample show marginal mass gain during subsequent 'hot-time' with further temperature cycling, however there was no detectable mass loss during all the cooling stages after the 'hot-time'. Note that due to the buoyancy effects at 1100°C , the sample mass recorded by the TGA equipment for the bare sample was lower in the 'cool-time' but returns to the levels of the 'hot-time' on re-heating. The TGA cyclic oxidation curve of the bare sample essentially traces the isothermal TGA curve of the bare sample in Fig. 1, bar the interruptions of the various 'cool-time'.

For the salt-deposited sample, significant mass change was not detected during cooling after the first 'hot-time'. However, significant mass gain was noted during the 'hot-time' in the second cycle, and, to a lesser extent, in the third cycle. In the fourth cycle and beyond, negligible mass gains were detected within the 'hot-time', i.e. the sample has attained fully protective oxide layer in the fourth 'hot-time' and beyond. During cooling at the end of the second and third cycles, marginal mass losses were observed, after accounting for buoyancy effects. The mass loss during cooling appears to stabilize for the subsequent 2-3 cycles, after which increasing mass losses were noted during cooling at the end of the fifth to the eighth cycle. At the eighth cycle and beyond, the mass loss associated with cooling remained relatively constant.

When fresh salt was re-applied to the sample after 20 cycles, there was little mass change in the first subsequent 'hot-time'. On cooling after this 'hot-time', there was a marked mass loss followed by a notable mass gain within the following 'hot-time', echoing the initial behavior observed in the second cycle. Beyond this, the mass gain during each 'hot-time', and mass loss associated with each cooling stage were relatively unchanged for subsequent thermal cycles.

Fig. 5 Kinetics of cyclic TGA oxidation of CMSX-4 at 1100 °C without salt and with 40 µg/cm² salt.

Oxide Analysis

Results of oxide identification carried out using X-ray diffraction on CMSX-4 samples which had been subjected to isothermal and cyclic oxidation at 1100 °C are shown in Fig. 6. In all four samples, the peaks identified were relatively similar; peaks of NiO, CoAl₂O₄, Ni₃Al substrate, Al₂O₃, CrTaO₄ and CoO were observed. The two samples subjected to isothermal oxidation showed higher peaks of Al₂O₃ than the corresponding samples subjected to cyclic oxidation, indicating that higher quantities of Al₂O₃ oxide were retained during isothermal oxidation. The two bare samples also showed higher peaks for CoAl₂O₄. The salt deposited sample subjected to cyclic oxidation showed much higher peaks for NiO compared to other samples.

Fig. 6 X-ray diffraction peaks associated with CMSX-4 samples (in bare condition as well as with salt deposition) after 100-hour isothermal oxidation and 500 cycles of cyclic oxidation at 1100 °C.

Cross-sections of the oxide microstructures are shown in Figs. 7-10. Note that these cross-sections were obtained from samples oxidized at elevated temperature, and therefore were subject to possible oxide spallation on cooling from the test temperature. Nevertheless, care was taken to ensure representative areas, of the

worst attacked areas as well as the spalled areas were captured, where possible.

The cross-section of the oxide microstructures for the bare condition and with 40 µg/cm² salt deposition after being subjected to 2 minutes and 1 hour exposure at 1100 °C are shown in Fig. 7. The bare sample which had been exposed for 2 minutes exhibited a thin continuous layer of external oxide, which was subsequently covered with a continuous Al₂O₃ scale after 1 hour exposure. The sample with 40 µg/cm² salt deposition showed curved interfaces between the oxide layer and alloy substrate after 2 minutes exposure; some cracks in the oxide were observed, and the Al-depletion layer was approximated to be 10 µm. After 1 hour exposure, the salt deposition resulted in a greater extent of oxide spallation and a discontinuous oxide layer; in addition, a large number of internal oxides were observed.

The cross-sections of the oxide microstructures in Fig. 8 are of samples in the bare condition and with 40 µg/cm² salt deposition which have been subjected to 40, 200 and 500 cycles of cyclic oxidation. After 40 cycles, the bare sample showed a continuous oxide layer with some trace of internal oxides. The corresponding sample with salt deposition showed significant pitting and a number of TiN particles were also observed in the substrate near the oxide interface; EDX results and XRD analysis revealed that the grey outermost layer was NiO, the middle layer consist Cr₂O₃ very often together with W and / or Ta oxides, and the dark innermost layer adjacent to the substrate was protective Al₂O₃.

After 200 cycles, the bare sample had very similar oxide layers to that seen after 40 cycles, in which the Al₂O₃ was continuous and compact, and hence protective. In contrast, corresponding sample with salt deposition showed a layered oxide structure, with numerous TiN particles and some Al-rich needles. The inner Al₂O₃ layer was neither continuous nor compact, and as such was less protective to the substrate. After 500 cycles, the oxide layer in the bare sample was still relatively unchanged compared to earlier

Fig. 7 Cross-section of the oxide microstructures for the bare condition and with 40 $\mu\text{g}/\text{cm}^2$ salt deposition after 2 minutes and 1 hour exposure at 1100 °C.

Fig. 8 Cross-sections of the oxide microstructures for the bare condition and with 40 $\mu\text{g}/\text{cm}^2$ salt deposition after 40, 200 and 500 cycles of cyclic oxidation at 1100 °C.

Fig. 9 Elemental distribution in oxide microstructures for bare sample and $40 \mu\text{g}/\text{cm}^2$ salt sample which have been subjected to 200 cycles of cyclic oxidation at 1100°C . The size of each map is $200 \mu\text{m} \times 100 \mu\text{m}$.

stages, although the layer was noted to become slightly curved. However, corresponding sample with salt deposition showed numerous internal oxides, discontinuous Al_2O_3 oxide, and some pitting attack.

The elemental distributions in the oxide microstructures obtained via EPMA are shown in Fig. 9 for the bare sample and $40 \mu\text{g}/\text{cm}^2$ salt sample which had been subjected to 200 cycles of cyclic oxidation at 1100°C . The mapped area in each case was $200 \mu\text{m} \times 100 \mu\text{m}$. The bare sample showed a continuous thin layer rich in O and Al; the elements W, Mo, Re and Hf were not significantly enriched on either side of the oxide or substrate interface. The salt deposited sample showed much thicker oxide layers, rich in Ni, Co, Al, Cr, W and Ta. The alumina layer is the innermost layer below all the other oxides; however, this Al_2O_3 layer was serpentine and non-compact. Numerous internal precipitates rich in Al and Ti were also observed in the salt deposited sample. After 200 cycles, the Al-depletion layers were estimated to be

approximately $20 \mu\text{m}$ and $60 \mu\text{m}$ respectively, for the bare sample and the $40 \mu\text{g}/\text{cm}^2$ salt sample. These were typical values which were verified against other optical and SEM examinations of various regions of oxide layers.

Examination of the oxide microstructures to reveal the effects of salt on pre-oxidized samples was also carried out as shown in Fig. 10. After 40 hours isothermal oxidation in air at 1100°C , a continuous and protective Al_2O_3 layer was formed. However, after sea salt deposition and 2 minutes exposure at 1100°C , more oxides were formed and a thicker oxide layer was noted. With further exposure after 1 hour, on cooling, most of the oxides were spalled off; the oxide layer became curved due to pitting and some internal oxides were formed. After 5 cycles of oxidation (with prior 40 hour pre-oxidation), even greater quantities of oxides were formed at the sample surface and a thin, continuous Al_2O_3 was observed adjacent to the substrate.

Fig. 10 Cross-sections of oxide microstructures of CMSX-4 after 40 hours pre-oxidation at 1100 °C, as well as after 40 µg/cm² sea salt deposition and further exposures at 1100 °C for 2 minutes, 1 hour and after 5 cycles of cyclic oxidation.

Discussion

In the current study, the application of synthetic sea salt, over a range of dosages and at 1100 °C, has been shown to significantly enhance the oxidation attack in CMSX-4. The effects of salt above 1000 °C have been neglected for decades, perhaps due to the fact that the salt evaporates very quickly at these elevated temperatures and was not believed to have any significant effect. Indeed, at the sea salt dosages applied in the current study (40-140 µg/cm²), the bulk of the salt is expected to evaporate within seconds of the samples entering the furnace at 1100 °C [9]. Sea salt, applied at 40 µg/cm², is damaging for both isothermal and cyclic oxidation. This is demonstrated at the start of isothermal oxidation in Fig. 1, and is due to the accelerated formation of non-protective oxide species in the presence of salt, prior to the formation of any Al₂O₃ species. After 2 minutes exposure at 1100 °C, the 40 µg/cm² salt sample showed a thicker but much more disordered NiO, CoO or Cr₂O₃ oxide compared to the bare sample (Fig. 7). The presence of salt also results in the formation of internal alumina and it takes longer to establish slower Al₂O₃-protected oxidation, but after about 20 hours the curves for the bare sample and the 40 µg/cm² salt sample were essentially parallel. The types of oxides formed do not appear to be altered with salt deposition, even though the proportions of the different oxides formed may be slightly altered (Fig. 6). Thus the salt appears to primarily accelerate the oxide nucleation and formation processes for all oxide species, and does not appear to favor nor inhibit the nucleation and growth of any particular oxide species.

During subsequent thermal cycling, Fig. 5 shows the persistent effect of the salt. The first hour closely followed the isothermal curve (Fig. 1), but during the second cycle there was a rapid and unexpected rise in the mass gain suggesting that the first cooling cycle had cracked the oxide, but without mass loss, allowing access to the bare metal and accelerated oxidation. The mass gain in the second 'hot-time' is very similar in shape and magnitude to that observed when the isothermally exposed bare sample was sprayed with salt after 40 cycles, Fig. 3. The next few cycles did not result in any sudden change in behavior, the overall weight

gain mirroring that in the isothermal case in Fig. 3, but the rate at which the stable weight was achieved is faster with the thermal cycling (5 hours cyclic rather than 10 hours isothermal). However, further oxide spallation was observed on cooling from the 5th cycle onwards in Fig. 5, but without significant weight gain during the subsequent hot cycle. Thereafter a steady mass loss is experienced on cooling at every cycle until the salt is reapplied after the 20th cycle. The behavior in the 21st and 22nd cycles is similar to that in the 1st and 2nd cycles: retaining a steady weight in the 1st but spalling significantly on cooling and showing an accelerated mass gain during the 22nd cycle. Thereafter a similar pattern of a small loss on cooling and minimal gain during the 'hot-time' is rapidly regained. The effect on the second application of the salt is not as extreme as the first or indeed that on the isothermal sample after 40 hours, indicating that some salt had been retained in some form from the first application.

The fully protective nature of the alumina, despite being thick and non-compact, is seen in all the 'hot-time' for the 4th cycle and beyond. The very small weight changes observed in these 'hot-time' show that the spallation occurs without damaging the protective alumina layer, probably by the spallation of the outer layers of friable spinels and other transient oxides. This implies that the salt is retained in some form, near the oxide-substrate interface, in order for its effect to be continuously observed. If salt was retained at the top oxide layers, this would have been lost and the effect of the salt diminished. The thicker transient oxides produced in the presence of salt is brittle and more prone to fracture when subjected to temperature cycling. The higher force generated by the mismatch of thermal expansion coefficients acting on the thicker oxide, as well as higher number of voids and cracks in the oxide layer results in spallation on cooling. On fresh application of salt, the protective alumina is damaged, resulting in further formation of transient oxides and the significant mass gain in the 22nd cycle. Therefore, the cycle of further formation of transient oxides, gradual regeneration of the protective alumina layer and spallation of the transient oxides on temperature cycling recurs on repeated application of salt. This is the key detrimental effect of salt at these elevated temperatures and the fundamental issue to be addressed.

The 40 µg/cm² dosage level of sea salt used in this study would give a 185 nm layer if spread evenly over the surface. Examination of the salt spray after application but before exposure indicated that the salt is present on the surface as isolated crystals following the evaporation of water in the salt solution. The crystals melt on entering the hot zone as the samples reach 1100 °C very rapidly. During the short heating period the salt reacts with the metal surface, particularly as the sample goes through the critical temperatures of 700-950 °C associated with hot corrosion processes. At the same time, the outer layers of the deposited salt evaporate. Our previous work [9] shows this time is of the order of 5 seconds. With a higher salt deposition of 140 µg/cm², a greater amount of salt would be retained and hence show more severe oxidation attack during both isothermal and cyclic oxidation, Figs. 1 and 2. The higher salt retained forms a thicker oxide layer, which causes a greater mass loss as it spalls during each thermal cycle (Fig. 2).

The abrupt change in the mass loss rate at about 240 hours observed in the 40 $\mu\text{g}/\text{cm}^2$ and the NaCl sample is thought to be due to the dynamic effects of aluminum depletion in the substrate and oxide loss at the surface. This accelerated gradient lasts for about 100 hours and tracks the higher mass loss from the 140 $\mu\text{g}/\text{cm}^2$ sample. It is observed for both the 40 $\mu\text{g}/\text{cm}^2$ sea salt sample, the pre-oxidized 0+40 salt sample and also for the NaCl only sample (Figs. 2 and 4). Fig. 9 shows that after 200 cycles there was considerable depletion of Al below the oxide layer, and that this would continue until the level reaches a critical point. At this level of Al-depletion, the alumina layer is unable to repair itself leading to even more rapid oxidation, spallation and mass loss. For the 40 $\mu\text{g}/\text{cm}^2$ sample this removes the depleted zone over the next 100 cycles until the mass loss rate returns to earlier levels. For the greater salt level of 140 $\mu\text{g}/\text{cm}^2$, the dynamic equilibrium is never restored and the steeper gradient continues throughout.

The comparison of the different salts shown in Fig. 2 is also of interest. Despite having twice as high Cl^- concentrations per unit area as the 40 $\mu\text{g}/\text{cm}^2$ synthetic sea salt, the initial mass loss of the NaCl only sample was low and the rapid loss similar to the synthetic sea salt, was delayed by ~ 100 cycles. The prolonged incubation period indicates that NaCl on its own was less effective at oxide nucleation and formation processes, but was equally potent in causing spallation and mass loss in the later stages of cyclic oxidation. Similarly, the MgSO_4 only sample, in this case containing double the SO_4^{2-} concentration per unit area compared to that of the 40 $\mu\text{g}/\text{cm}^2$ sea salt, but only 6% of the cathodic ion concentration of the 40 $\mu\text{g}/\text{cm}^2$ sea salt, also showed negligible mass loss only marginally higher than the bare sample. This shows the potent and synergistic effect of MgSO_4 , when combined with salts containing Cl^- , in enhancing the oxide nucleation and formation processes.

Pre-oxidation to produce a stable coherent protective Al_2O_3 did not show any benefit during either isothermal or cyclic oxidation. The cyclic sample where the salt was added after the 80th cycle Fig. 4, tracked the sample with salt added from the start but with an 80 cycle delay. For the isothermal case, the salt deposition after 40 hours results in the immediate disruption of the existing protective Al_2O_3 layer to cause rapid oxidation in the substrate (Fig. 10) and the large mass gain after 40 hours (Fig. 3). The protective Al_2O_3 layer formed after 40 hour pre-oxidation is extremely robust and does not crack or spall on cooling, evidenced by the negligible mass gain of the bare sample for up to 500 cycles (Fig. 2). Salt retained on the oxide surface is rapidly transported to the oxide-substrate interface, most likely along grain boundaries in the alumina layer, resulting in rapid oxide formation in the substrate and the substantial mass gain, similar to the conditions at the start of the 2nd cycle in Fig. 5. Note also the mass gains seen in Fig. 3 on fresh application of salt after 40 hours, and that of the 2nd cycle of Fig. 5 were of a very similar order.

The reverse sample, 40+0salt in Fig. 4, was subjected to cyclic oxidation with salt deposition for 80 cycles but subsequently salt deposition was halted. It does not regain the mass loss rates of the bare sample. It is arguable that the higher mass loss observed after halting of salt deposition was due to the depletion of Al pool as well as the internal oxides. However, one would expect the Al-depleted zone to have eventually recovered to result in the formation of a compact protective Al_2O_3 . Therefore, the persistent higher mass loss rate suggests that the retention of salt, and its effect on oxidation are still at play.

The test temperature in the current study is much higher than those where hot corrosion occurs in nickel-base superalloys in the presence of salt. At lower temperatures between 700-950 $^\circ\text{C}$, Type-I hot corrosion is triggered as Na_2SO_4 salt deposits become molten. The alloying elements would accelerate the hot corrosion process by altering the oxide ion activity of Na_2SO_4 . Many studies exploring the mechanisms of hot corrosion [14-16] argue that the acidic melts are deficient in oxide ions, and cause self-sustaining catastrophic oxidation. A negative solubility gradient of the protective oxide can be used as a criterion for the continuing hot corrosion. The fluxing mechanism in hot corrosion would lead to the re-precipitation of non-protective oxide particles [17, 18].

In the current study, the effects of salt observed are not believed to be associated with the acidic fluxing mechanism. Firstly, when only NaCl salt was used, there were no SO_4^{2-} species available for acidic fluxing to occur, yet the effects of the salt on the cyclic oxidation was still observed in Fig. 2, albeit somewhat delayed, compared to that of synthetic sea salt. In addition, the application of MgSO_4 alone, despite the low absolute amount used, would have caused a significant mass loss if acidic fluxing were occurring. Secondly, the parabolic TGA kinetic curve seen in Fig. 1 for the salt deposited samples, as well as the flat mass gains observed in Fig. 3 after salt application, and in Fig. 5 in the 4th cycle and beyond, would not be expected if acidic fluxing were occurring. Acidic fluxing leads to self-sustaining and continuous dissolution of any protective Al_2O_3 formed, resulting in continuous oxidation in the absence of a protective oxide layer.

The current study shows that the presence of salt is highly detrimental when a high number of thermal cycles are experienced. Thus, in applications such as land-based gas turbine engines which experience fewer thermal cycles, and depending on the types and dosages of the salts ingested during service, the detrimental effects of salt on oxidation attack may be smaller. Even where turbine blades are operated with protective coatings, alloys should be designed to have some intrinsic resistance to cyclic oxidation in the presence of salt, to allow for potential coating failure.

The current study has revealed many aspects of the mechanism by which salt affects the elevated temperature oxidation behavior of CMSX-4 at 1100 $^\circ\text{C}$, however we do not yet know the chemical form in which the salt is retained close to the oxide-substrate

interface, and why this leads to enhanced oxide formation and loss. This is the area in which considerable further work should be concentrated. Nevertheless, the ability of the salt-accelerated cyclic oxidation tests to closely reproduce the degradation seen in actual turbine components [9] highlights the relevance of this approach as a testing method, and allows the degradation mechanism of turbine components at temperatures well above those characteristic of Type I corrosion to be studied.

Summary and Conclusions

- Sea salt accelerates the oxidation processes in CMSX-4 at 1100 °C, resulting in the formation of thicker, less ordered oxide layers, leading to increased oxidation attack prior to the formation of a protective Al₂O₃ scale.
- After conditions for Al₂O₃ formation had been attained, the thick, non-compact alumina oxides formed in the presence of salt are fully protective, equivalent or even superior to those of the compact alumina formed without salt deposition.
- However, these thick oxides are extremely prone to fracture and spallation when subjected to thermal cycling. This is the key detrimental effect of salt on the elevated temperature cyclic oxidation of CMSX-4.
- Pre-oxidation to produce protective alumina provides little benefit against the effects of salt during subsequent isothermal and cyclic oxidation.
- A continuous cycle of oxide layer disruption, spallation and regeneration occurs once the steady-state mass change behavior was established after the first 8-9 cycles of cyclic oxidation with salt deposition.
- During cyclic oxidation, up to a critical salt dosage, a dynamic equilibrium exists between the oxide spallation and the supply of aluminum to the surface to provide limited degree of protection.
- The components of the sea salt, NaCl and MgSO₄ on their own, were less detrimental during cyclic oxidation compared to the synthetic sea salt. MgSO₄ has synergetic effects in accelerating the oxidation processes in combination with NaCl.

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