The Effect of Elevated Air Pressure on the Oxidation Properties of the Nickel-based Superalloy, RR1000, at 650°C with Different Surface Modifications

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Materials at High Temperatures

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**The Effect of Elevated Air Pressure on the Oxidation Properties of the
Nickel-based Superalloy, RR1000, at 650°C with Different Surface
Modifications.**

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The Effect of Elevated Air Pressure on the Oxidation Properties of the Nickel-based Superalloy, RR1000, at 650°C with Different Surface Modifications.

Samples of RR1000 with differing grain size and surface finish have been exposed to air at different pressures. Specimens were exposed for 4000 hours at 650°C with some exposed to atmospheric pressure air and some exposed to air at 40 bar pressure. Samples exposed to elevated pressure formed a surface layer of NiCr_2O_4 whereas that formed on samples tested at 1 bar pressure was chromia. The surface layer formed at 40 bar pressure was thinner than that at 1 bar pressure. At 1 bar pressure, some samples exhibited regions of convoluted buckled oxides but no spallation. In adjacent regions of planar oxides, spallation did occur. For the latter case, an estimate of 6 Jm^{-2} for the interfacial fracture energy has been made. None of the specimens tested at 40 bar pressure exhibited oxide spallation.

Oxidation, Pressure, Chromia former, Superalloy, Spinel, XRD

Introduction

It is well known that aero-engines require materials that can withstand the high temperatures, high pressures and corrosive nature of the internal conditions. RR1000, is an ideal candidate for the disc component and the alloy of interest in this project. The component is manufactured using a powder metallurgy route and has the nominal composition given in Table 1[1]. The alloy contains sufficiently high concentrations of chromium necessary to form a surface layer of chromia and provide the alloy with the required oxidation resistance at operating temperatures. Previous work conducted on this alloy at 1 bar pressure and temperature generally between 700°C and 800°C, has shown that a continuous chromia layer does form on the alloy surface along with sub-surface alumina penetrations[2–7]. The rate of chromia growth was shown to be enhanced compared with that formed on chromium or an austenitic steel [8]. The identification of titanium in the surface oxide led to the hypothesis that the enhancement was due to doping of the chromia by this element [4, 9].

1 The effects of exposures of chromia forming alloys to low pressures have been
2 reported in the literature [10–13], but very little information is available on the effect of high
3 pressure. Work by Baur, Bartlett [14] on pure nickel found that the oxidation rate of nickel is
4 insensitive to pressure above atmospheric pressure. However, on advanced alloys under CO₂
5 atmospheres Pint, Brese [15] found a complex dependence on pressure in that alloys of
6 similar composition to RR1000 showed a decrease in the gravimetric oxidation rate at 125
7 bar pressure compared with 1 bar pressure. At pressures above 125 bar, the oxidation rates
8 tended to increase with increasing pressure.

9 The work presented in this paper investigates the effect of increasing air pressure,
10 from 1 atmosphere (1.013 bar) to 40 bar, on the oxidation behaviour of two grain size
11 variants of a nickel-based superalloy. Also included in the study are two surface conditions,
12 polished and shot-peened. The influence of pressure on the oxidation behaviour of samples
13 exposed for 4000 hours to 650°C will be assessed.

14 **Experimental Method**

15 The material used in this experiment was RR1000 with nominal compositions given in Table
16 1. The composition was confirmed for all elements except carbon and boron by Energy
17 Dispersive X-Ray Spectroscopy (EDS) during analysis. Both fine grained (FG) and coarse
18 grained (CG) variants were used with different surface modifications summarised in Table 2.
19 Two of each variant were supplied ready prepared by Rolls-Royce plc.

20 Two long-term isothermal exposures were conducted in air both at 650°C for 4000
21 hours with one carried out under 1 bar and one under 40 bar pressure. Samples were cleaned
22 ultrasonically in ethanol before testing and placed into clean alumina crucibles. For the test at
23 1 bar pressure, samples were inserted into preheated tube furnaces calibrated to $\pm 1^\circ\text{C}$ using
24 an R-Type thermocouple and exposed under static laboratory air. Samples were removed

after 4000 hours and allowed to cool to room temperature in laboratory air. The samples tested under 40 bar pressure were inserted into a clean autoclave, and the internal pressure increased to 40 bar using synthetic air, the temperature was then raised to 650°C. After 4000 hours, the autoclave was allowed to cool down to room temperature under pressure over two days, after which the pressure was relieved and the samples removed.

The surfaces of samples were imaged using a macro camera and a Philips XL30 SEM to examine oxide surface morphology and the extent of spallation. Samples were prepared for cross-sectional analysis by mounting under vacuum in Struers epofix low viscosity resin. These were ground through by a thickness of 2mm using 120 grit SiC paper, to reveal the cross-section. Sample preparation was continued from 240 to 1200 grit paper using water as a lubricant. Polishing was performed using 9, 3, and 1 µm water-based diamond suspensions with a final stage using colloidal silica. Examination of the cross-sections was made using either the Jeol 7000F or TESCAN MIRA3 FEG-SEM with Oxford Instruments INCA EDS. Image analysis was completed using the Fiji image processing package [16, 17] to measure external oxide thickness and the depth of internal alumina penetration. XRD analysis was performed using a PANalytical Empyrean powder diffractometer with a Co K-alpha source at an accelerating voltage of 40kV and a current of 40mA. Standard Bragg-Brentano theta-theta scan and grazing incidence 2-theta scans with a fixed source angle of 2° were performed. Different scan rates and durations were used to optimise results. Scans were analysed using PANalytical HighScore Plus and the International Centre for Diffraction Data (ICDD) database for phase analysis.

Results

Surface Examination

Figures 1 to 5 show planar views of the surface of the samples outlined in Table 2. In each

figure (a) is a sample exposed at 1 bar and (b) is a sample exposed at 40 bar pressure.

Differences in the morphology of the oxidised surfaces were noted when comparing the effect of pressure on the polished samples of the fine-grained alloy, Figures 1(a and b).

Irregular oxide growth with whiskers of titanium-rich oxides formed at 1 bar pressure whereas isolated crystallites were seen distributed across the oxidised surface under 40 bar pressure. On the coarse-grained variant of the alloy, Figures 2 (a) and (b) a more uniform coverage of oxide was observed. Some contrast was observed which could be linked to the location of grain boundaries which was more evident on the samples exposed to 40 bar pressure, Figure 2 (b). EDS data revealed the grain boundary regions to be rich in aluminium whereas grain centres contained a higher concentration of chromium, Table 3. Cobalt and nickel signals come from the underlying substrate. Regions of spalled oxide were seen on the sample exposed to air at 1 bar pressure, Figure 2(a) but not on the sample tested at high pressure, Figure 2(b).

The effect of shot peening has a significant effect on the morphology of the oxides formed on the fine-grained, Figure 3, and coarse-grained variant, Figure 4. A marked difference occurred in the samples exposed at 1 bar pressure. Buckling of the surface oxide can be seen in Figures 3(a) and 4(a). The effect was more prevalent in the coarse grained sample compared to the fine grained sample. Little to no titanium rich regions were present on this sample surface, compared with the dispersed areas of titanium-rich whiskers in the fine grained samples (Figure 3a). Samples tested at 40 bar pressure did not exhibit this buckled structure in either grain size variant. In fact, the fine-grained peened samples tested under 40 bar pressure exhibited a more uniform oxide morphology, Figure 3(b). EDS analysis of the surface of the coarse-grained variant in this condition showed regions rich in chromium interspersed with some areas of the sample richer in aluminium, as indicated in Figure 4(b).

1 Fine-grained samples were also tested in the swaged condition, Figure 5. Swaging is a
2 technique where the material is compressed inwardly to produce a bulk sample with high
3 residual compressive stresses. Extensive spallation was seen in the sample tested under 1 bar
4 pressure, Figure 5(a), (~40% of the sample surface) whereas under 40 bar pressure a uniform
5 chromium-rich surface oxide was observed, Figure 5(b).
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11 Oxides of varied morphologies were observed on samples exposed to air at 650°C for
12 4000 hours at 1 bar pressure. Buckling and spallation were also observed. When exposed to
13 the same oxidising conditions at 40 bar pressure samples developed a more uniform surface
14 oxide, and no spallation was noted. In several, the samples tested under the elevated pressure
15 condition, most obviously, the fine-grained polished samples, crystallite growths were
16 observed. These were distinguished from surface contamination by EDS and identified to be
17 predominantly chromium-rich.
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31 *Oxide Thickness and Morphology*

32 Fine-grained polished samples tested under 1 bar (Figure 6) and 40 bar (Figure 7) pressure
33 exhibited a continuous chromium rich external oxide with internal penetration of alumina
34 down grain boundaries. Figure 6 and EDS analysis revealed a discontinuous layer of
35 aluminium-rich oxide under the outer oxide scale in contact with the alloy, Table 4. At 40 bar
36 pressure, Figure 7, the surface oxide consisted of a thin chromium rich oxide with isolated
37 larger crystallite growths. Larger amounts of sub-surface oxide were observed under the
38 crystallites. All fine-grained polished samples exhibited a generally planar interface.
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51 Figure 8 shows the oxide present on a sample of coarse-grained RR1000 tested under
52 1 bar pressure. Similarly, to the fine grained variant, this sample exhibited a predominantly
53 chromium rich external oxide. EDS analysis, Table 5, shows that the external oxide is dual
54 layered with a continuous aluminium-rich oxide adjacent to the alloy with a chromium-rich
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oxide overlying this. Internal oxide penetrations are in the form of intragranular penetrations. Samples exposed to 40 bar pressure formed a very thin oxide layer on the surface with crystallite growths. The thinnest of the oxides was at the limits of the resolution of the SEM.

The buckled oxide formed on the fine-grained peened RR1000 samples tested under 1 bar pressure can be seen in cross-section in Figure 9(a). A layer of chromium-rich oxide also existed on the alloy surface underneath the buckle showing that either the chromia layer itself had split part-way through its thickness but parallel with the alloy surface or, that if delamination occurred at the oxide alloy interface at temperature, the exposed alloy underwent further oxidation. In many of the cross-sections of this sample, cracks were observed within and through the layer of buckled oxide. Internal oxidation of aluminium has occurred similar to that seen in earlier work on this alloy [4], at sub-grain boundaries resulting from the shot peening process. A region of the sample where planar oxides had formed is shown in Figure 9(b). As noted in Figure 3 (a), titanium-rich oxides were identified on the outer surface of the chromium-rich oxide. These can be seen embedded in the mounting resin to the left in Figure 9(b) which enabled a qualitative confirmation of the composition using EDS.

The samples tested under 40 bar pressure formed an adherent external oxide, Figure 10. In some regions, the oxide had pulled away from the alloy during mounting; a problem often found with very thin oxides. EDS analysis of the oxides showed a significant reduction in titanium concentration in the external oxides formed at 40 bar pressure compared with those formed at 1 bar pressure, Table 6. The concentration of aluminium is similar in both samples and is attributed to the internal oxidation process. The higher nickel and cobalt readings can be attributed to the proximity of the alloy and the interaction volume of the electron beam.

1 Coarse-grained peened RR1000 samples tested under 1 bar pressure, Figure 11,
2 exhibited similar morphology to the fine-grained variants with regions of buckled oxide
3 adjacent to regions of adherent oxides. However, cracking was not seen in the buckled oxides
4 in contrast to the fine-grained peened samples. Interestingly, no discernable oxide was seen
5 on the surface of the alloy underneath these buckles. In regions where adherent oxide was
6 present, the contrast in the BSE image indicated a variation in the composition of the oxide
7 (Figure 11b). EDS analysis indicated a continuous aluminium-rich oxide between the alloy
8 and the chromium-rich outer oxide.
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10 Under 40 bar pressure, see Figure 12, Figure 12a shows a thin continuous oxide layer
11 formed, rich in chromium and nickel with an internal oxidation zone. Also, regions
12 characterised by a thicker oxide layer with distinct outgrowth from the surface occurred. EDS
13 analysis revealed that the large crystallite oxide growths were predominately rich in
14 chromium and oxygen indicating that these are a chromium-rich oxide, presumed to be
15 chromia.
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17 Measurements of external oxide thickness taken from 50 measurements per sample
18 are shown in Table 7. On samples where isolated crystallites formed, e.g. coarse-grained
19 peened and fine-grained polished samples both tested under 40 bar pressure, these features
20 were excluded and thus only the continuous more uniform oxide was recorded. The means
21 and standard deviations of these thicknesses are presented in Figure 13. In all cases, the
22 thickness of the external oxide growth is significantly lower on samples exposed to 40 bar
23 pressure compared to those exposed to 1 bar pressure. The sizes of the crystallite oxide
24 regions vary in size between 0.5 and 6 μm on the same sample making a statistical
25 appreciation of the scale of these crystals impractical.
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XRD Analysis

XRD was conducted on these samples to establish the nature of the oxide phases formed at both high and low pressures. Indexed diffraction patterns, both with Bragg-Brentano and grazing-angle incidence geometries for fine-grained polished samples tested under 1 bar pressure are shown in Figures 14 and 15. The corresponding spectra for specimens tested at 40 bar pressure are shown in Figures 16 and 17. The results at 1 bar pressure agree well with previous studies [4]. They confirm the presence of rutile and chromia although the results of the Bragg-Brentano geometry suggested that the chromium-rich oxide was titanium-doped chromia with the chromia structure [4]. At 40 bar pressure, the XRD results have shown the formation of a chromite-type oxide with either nickel or cobalt. As the lattice parameter of the tetragonal NiCr_2O_4 and CoCr_2O_4 phases are similar XRD cannot distinguish between them with sufficient confidence. This change in dominant oxide phase formed appears to be a pressure effect, but other factors such as heating rate and moisture levels of test gas are being investigated. Further testing is necessary for clarification.

Discussion

A significant difference was found between samples tested under 1 bar pressure compared with those tested under 40 bar pressure. In all cases, the oxide formed at 40 bar was thinner as can be seen in Table 7. XRD analysis of the fine-grained variant of the alloy showed that the dominant oxide formed at 1 bar was Cr_2O_3 , albeit titanium doped. At 40 bar pressure, a $(\text{Ni},\text{Co})\text{Cr}_2\text{O}_4$ chromite spinel was found to be the dominant oxide. Cr_2O_3 was also identified at 40 bar which, using SEM and EDS analysis, was found to be in the form of isolated crystallites protruding from the surface of the samples. It should be noted that the spinel, NiCr_2O_4 , has previously been identified forming on this alloy at higher test temperatures [3]. Under the conditions tested in that study, i.e. $>700^\circ\text{C}$ under 1 bar pressure in laboratory air,

the phase constituted only a minor oxide component of the surface oxide.

Spinel oxides are generally regarded as faster growing oxides, and less protective than oxides such as Cr_2O_3 . Oxygen diffusion rates for nickel chromite spinel and Cr_2O_3 have been reported in the literature as $8 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ and $3 \times 10^{-23} \text{ cm}^2 \text{ s}^{-1}$, respectively [18].

Evidence of slow-growing protective spinels has been previously reported [19]. The chromite formed here showed slower growth kinetics than the titanium-doped Cr_2O_3 formed at 1 bar pressure. In addition, the internal oxide penetration appeared shallower in the case of samples exposed at 40 bar pressure suggesting a more protective oxide had formed.

It is, therefore, reasonable to assume that this spinel may grow slower than the titanium-doped Cr_2O_3 formed on RR1000. The evidence here shows that at 40 bar pressure a more protective surface oxide forms. Further work is on-going to fully characterise the oxides formed on each sample using XRD analysis and transmission electron microscopy to allow a more detailed investigation of these very thin oxides.

Another significant difference between samples in this study is the buckling observed of the external oxide. Buckling only occurred on samples that had undergone shot-peening and which were tested under 1 bar pressure (Figures 9 and 11). Caplan and Sproule [20] showed evidence of buckling in chromia layers grown on pure chromium and a Fe-26Cr alloy. Failure of the buckled layer, in that study, led to additional oxidation occurring to the exposed alloy surface, similar to that seen in the fine-grained shot peened sample of this study, Figure 9. Caplan and Sproule attributed the buckling of the oxides to the development of a fine-grained oxide structure, facilitating anion diffusion down oxide grain boundaries and continued Cr_2O_3 growth at these sites. The resulting lateral growth of oxide generated in-plane compressive growth stresses which were relieved by buckling of the external oxide. Localised surface contamination resulting from the shot peening process may also contribute

to this buckling behaviour. Buckling had not been seen on testing conducted on this alloy at higher temperatures [2–5], in the polished or peened condition.

Surface SEM imaging has highlighted that spallation of the surface oxide had occurred on a number of samples tested under 1 bar pressure. Coarse-grained polished and fine-grained peened samples exhibited small levels of spallation, but fine-grained swaged specimens showed extensive spallation. The absence of oxide spallation on the high-pressure specimens and its occurrence in specimens tested at 1 bar pressure is consistent with a spallation process driven by the strain energy developed in the oxide layer during cooling. A notable feature of the present results is the thicker oxide layer formed in the samples tested at 1 bar pressure compared with those tested at 40 bar pressure, Figure 14. Thus, the specific strain energy developed in the oxide layer during cooling will be appreciably higher for the thicker oxides. This strain energy in an oxide layer of thickness ξ is given as [21]:

$$\gamma_F = (\Delta T_c)^2 \xi E_{ox} (\Delta \alpha)^2 (1 - \nu) \quad (1)$$

where ΔT_c is the critical temperature drop required to initiate spallation, γ_F is the fracture energy of the interface between the oxide and alloy, ξ is the thickness of the oxide layer, E_{ox} is the Young's Modulus of the oxide (250 GPa [22]), $\Delta \alpha$ is the difference in thermal expansion coefficients between the alloy and the oxide ($\alpha_{alloy} = 14.2 \times 10^{-6} \text{ K}^{-1}$, $\alpha_{ox} = 7.2 \times 10^{-6} \text{ K}^{-1} \therefore \Delta \alpha = 7.3 \times 10^{-6} \text{ K}^{-1}$ [22]) and ν is the Poisson's Ratio of the oxide (0.2 [22]). (Note that these parametric values are for chromia but do not differ greatly for NiCr_2O_4).

Assuming that spallation in the 1 bar tests occurred at room temperature, i.e. $\Delta T_c = 620^\circ\text{C}$, and that the critical oxide thickness to initiate spallation, ξ , is $1.3 \mu\text{m}$ (a typically observed value), then the interfacial fracture energy of the oxide is calculated to be 5.6 J m^{-2} .

1 This value is comparable to that found previously (6 J m^{-2}) for chromia spallation on an
2 austenitic stainless steel [23].
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5 If this value of fracture energy, i.e. 5.6 J m^{-2} , holds for both chromia and the nickel
6 chromite spinel then the thinner oxide formed on the samples exposed to elevated pressure
7 will not have the required strain energy under the available ΔT_c to initiate spallation.
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11 Work by Evans and Taylor [24], however, has postulated a significant effect of
12 cooling rate on the spallation of oxide layers, where samples that are cooled slowly can
13 experience localised creep in the sub-surface region. Slower cooling would, therefore, lead to
14 a higher value of the effective γ_F to initiate spallation due to energy dissipation by the creep
15 relaxation process at interfacial cracks. In the present work, the cooling rate in the high-
16 pressure tests was indeed appreciably less than in the tests at 1 bar pressure and this
17 difference may also have contributed to the resistance to spallation found for the specimens
18 tested at 40 bar pressure. Further experimental work is planned to try and clarify this issue.
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32 33 **Conclusions**

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35 A thicker oxide layer formed on samples exposed to 1 bar pressure compared with that
36 formed on samples exposed to 40 bar pressure. XRD and EDS showed that Cr_2O_3 was
37 dominant under 1 bar pressure but $(\text{Ni},\text{Co})\text{Cr}_2\text{O}_4$ formed at 40 bar pressure. This thinner
38 oxide showed no delamination, buckling or spallation and also showed reduced alumina
39 penetration into the alloy.
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48 Buckling of the surface oxide was observed on samples where a surface preparation
49 of shot-peening had been performed, and the test conditions were at 1 bar pressure. This was
50 not observed on the polished samples tested under the same conditions where a more
51 continuous layer of alumina was seen at the interface between the alloy and the external
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Oxide spallation occurred on fine-grained peened and swaged samples tested under 1 bar pressure. An estimated fracture energy of 5.6 J m^{-2} was determined from the calculation of the oxide strain energy, assuming that the oxide spalled at a critical value of strain energy. This value compares well with literature values for the spallation of a chromia layer from an austenitic steel.

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Table 1- Nominal composition of RR1000[1].

	Ni	Cr	Co	Mo	Al	Ti	Ta	Hf	Zr	C	B
wt. %	bal.	15	18.5	5	3	3.6	2	0.5	0.06	0.027	0.015
at. %	bal.	16.5	17.9	3	6.4	4.3	0.63	0.16	0.04	0.13	0.08

Table 2 – RR1000 sample specifications.

Surface Finish	Grain Size (µm)
FG Polished	4-6
FG Shot peened	4-6
FG Swaged	4-6
CG Polished	30-50
CG Shot peened	30-50

Table 3 – EDS data (at.%) taken from the surface of the coarse-grained polished sample tested under 1 bar pressure, Figure 2 (a). Aluminium enhancement is seen at the grain boundaries.

Region	O	Al	Ti	Cr	Co	Ni	Mo	Ta
Grain Boundary	60.8	10.2	1.5	6.3	4.9	14.9	1	0.2
Grain Centre	59.2	2.1	1.8	22.2	8.6	5.7	0.3	0

Table 4 – EDS data (at.%) taken from a cross-section of fine-grained polished RR1000 tested at 1 bar pressure, Figure 6, showing aluminium-rich oxide at the interface between external oxide and alloy.

Region	O	Al	Ti	Cr	Co	Ni
Alloy	0	6.5	3.9	14.3	20	55.3
Interface	36.4	32	2.8	12.2	5.3	11.4
External Oxide	51.6	5.4	9.6	22.9	1.7	8.8

Table 5 - EDS data (at.%) taken from a mounted cross-section of coarse-grained polished RR1000 tested at 1 bar pressure showing aluminium-rich oxide at the interface between external oxide and alloy.

Region	O	Al	Ti	Cr	Co	Ni	Ta
Subsurface	14.0	13.3	2.2	11.9	16.1	41.9	0.7
Interface	28.9	16.6	3.7	31.4	4.9	13.1	1.4
External Oxide	39.3	8.5	3.1	37.5	3.2	7.9	0.5

Table 6 – EDS data (at.%) taken from the oxides formed on the fine-grained peened samples showing effect of pressure.

	O	Al	Ti	Cr	Co	Ni	Ta	Mo
1 bar Pressure	59.4	8.2	12.9	14.9	1.9	2	0.7	0
40 bar Pressure	51.3	8.7	2.2	11.5	7.8	16.3	0	0.8

Table 7 – Mean and standard deviation for external oxide thicknesses at 1 bar and 40 bar pressure. The isolated crystallites formed on the surface of samples tested at 40 bar are excluded from these measurements.

	1 bar Pressure (µm)	40 bar Pressure (µm)
FG Polished	1.18 ± 0.27	0.40 ± 0.16
CG Polished	1.26 ± 0.48	0.35 ± 0.13
FS Peened	2.39 ± 1.29	0.24 ± 0.09
CG Peened	1.01 ± 0.54	0.33 ± 0.19

(a)

(b)

Figure 1 – SEM images of the surface of fine-grained polished RR1000, at (a) 1 bar, and (b) 40 bar pressure, showing surface coverage of oxide. Titanium-rich whiskers were identified in (a) and isolated chromium-rich particles in (b). No spallation was observed.

(a)

(b)

Figure 2 - SEM images of the surface of coarse-grained polished RR1000, at (a) 1 bar, and (b) 40 bar pressure. Titanium-rich whiskers and areas of delamination and spallation were identified in (a). Grain boundaries were visible in (b) and tended to be rich in aluminium, but no spallation was seen.

(a)

(b)

Figure 3 - SEM images of the surface of fine-grained peened RR1000, at (a) 1 bar, and (b) 40 bar pressure. (a) Shows two oxide morphologies: buckled (top left and bottom right) and planar. Spallation associated with the planar regions is present. At 40 bar pressure a more uniform oxide forms with no spallation.

(a)

(b)

Figure 4 – SEM images of the surface of coarse-grained peened RR1000, at (a) 1 bar, and (b) 40 bar pressure, showing extensive buckling of the oxide in (a), in contrast to (b) where no buckling or spallation was observed, although some regions high in aluminium content were noted.

(a)

(b)

Figure 5 - SEM images of the surface of fine-grained swaged RR1000, at (a) 1 bar, and (b) 40 bar pressure, showing significant spallation in (a) in contrast to a uniform oxide formation with no spallation in (b).

(a)

(b)

Figure 6 –BSE images of a cross-section through the fine-grained polished samples exposed at 1 bar pressure showing uniform, continuous external oxide with (a) intergranular penetrations of internal oxide at spacings similar to the grain size (4 – 6 μm) and, (b) a near continuous layer of aluminium oxide at the alloy/chromium-rich oxide interface.

Figure 7 – BSE image of a cross-section through the fine-grained polished sample tested under 40 bar pressure showing continuous but occasionally non-uniform surface oxide formation and intergranular internal penetrations at grain boundaries.

Figure 8 - BSE image of a cross-section through the coarse-grained polished RR1000 tested under 1 bar pressure showing continuous surface oxide formation. A continuous layer of aluminium-rich oxide was identified at the interface between the alloy and the surface chromium oxide with some intragranular penetration of alumina.

(a)

(b)

Figure 9 – BSE images of a cross-section through fine-grained RR1000 in the peened condition tested at 1 bar pressure showing (a) buckled oxide, and (b) adherent oxide, sub-surface alumina formation occurs in both regions. Also present in (b) are titanium-rich oxide whiskers projecting above the surface and embedded in the resin.

Figure 10 – BSE images of a cross-section through fine-grained RR1000 in the peened condition tested under 40 bar pressure. A thin adherent oxide with intragranular penetration of alumina has formed.

(a)

(b)

Figure 11 – BSE images of a cross-section through coarse-grained RR1000 in the peened condition tested under 1 bar pressure showing (a) buckled region, no through-oxide cracks and no oxide attached to the alloy surface, and (b) an adherent region with a continuous alumina layer at the alloy chromia interface.

Figure 12 – BSE image of a cross-section through coarse-grained peened RR1000 tested under 40 bar pressure showing a thin surface oxide with crystallite growths found to be rich in chromium.

Figure 13 – Mean and standard deviation of the external oxide thicknesses for fine and coarse-grained alloys in both polished and peened condition, showing the effect of pressure. Values based on 50 measurements.

Figure 14 – XRD diffraction pattern for fine-grained polished RR1000 tested under 1 bar pressure. 30-minute Bragg-Brentano scan over $25 \leq 2\theta \leq 120$. The peaks indicated correspond to the following entries in the ICDD database: 04-017-1422 (square) γ' -Ti_{0.61}Ni₃Al_{0.39}, 01-077-3085 (circle) nickel, 04-015-9779 (triangle) Ti_{0.24}Cr_{1.76}O₃.

Figure 15 - XRD diffraction pattern for fine-grained polished RR1000 tested under 1 bar pressure. 30-minute grazing incidence scan ($\omega = 2^\circ$) over $25 \leq 2\theta \leq 80$. Peaks indicated correspond to the following entries in the ICDD database: 04-001-9278 (circle) Cr₂O₃, 01-071-4809 (triangle) TiO₂.

Figure 16 - XRD diffraction pattern for fine-grained polished RR1000 tested under 40 bar pressure. 30-minute Bragg-Brentano scan over $25 \leq 2\theta \leq 120$. Peaks indicated correspond to the following entries in the ICDD database: 04-003-3904 (square) $\text{Ta}_{0.08}\text{Ni}_{0.92}$ (This is the fcc gamma matrix), 01-078-0711 (triangle) CoCr_2O_4 (this has a very similar pattern to other MCr_2O_4 phases and so could not be definitely identified).

Figure 17 - XRD diffraction pattern for fine-grained polished RR1000 tested under 40 bar pressure. 30-minute grazing incidence scan ($\omega = 2^\circ$) over $25 \leq 2\theta \leq 95$. Peaks indicated correspond to the following entries in the ICDD database: 04-016-4592 (square) Ni (This is the fcc gamma matrix), 01-088-0109 (circle) NiCr_2O_4 (this has a very similar pattern to other MCr_2O_4 phases and so could not be definitely identified), 04-004-7761 (triangle) γ' - Ni_3Al .

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Fig2(a)

Fig4(a)

Fig14

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Fig15

Fig16

Fig17