Advanced burner-rig test for oxidation–corrosion resistance evaluation of MCrAlY/superalloys systems

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Abstract

Protective coatings are used on gas turbine components to enable them to survive in engine-operating conditions. This study presents a recently developed cyclic burner-rig test that is used to simulate helicopter engine conditions and to assess the oxidation and hot corrosion behaviour of MCrAlY coatings on nickel-base superalloys. A diluted sea-salt solution is atomised into the burner-rig to simulate hot-corrosion. Each cycle lasts 1 h with temperatures varying in the range of 900 °C to 1000 °C followed by 15 min cooling to room temperature. Specimens are tested up to 1000 such cycles. Three different NiCoCrAlYTa coating thicknesses are used to determine the influence of the Al reservoir on the lifetime of the coated MC2 superalloy. The evolving microstructural features are identified using high resolution scanning electron microscopy and energy dispersive spectroscopy and compared with isothermal testing in pure oxidising conditions. The NiCoCrAlYTa microstructure obtained after the burner-rig test has typical features of a Type 1 hot corrosion degradation, with internal oxidation and nitruration and a front of chromium and yttrium-rich sulphides. This type of advanced burner-rig test cycle is successful in reproducing the accelerated combined hot-corrosion/oxidation damage.

1. Introduction
2. Materials and experimental procedures
2.1. Samples

1. Introduction

The working environment of gas turbines is extremely harsh. The hot-section components such as turbine blades must endure various stresses and severe environmental conditions at operating temperatures of 900 °C to 1000 °C. Because of the specific properties of each chemical element, it is extremely difficult to develop structural alloys capable of providing the desired high temperature mechanical properties, as well as achieving an acceptable resistance to environmental attack. Structural alloys have thus been developed for optimal mechanical properties [1] and coatings have been developed to provide the environmental resistance [2] and [3] including diffusion coatings, overlay coatings and thermal barrier coatings. MCrAlY coatings have been studied extensively [4], [5], [6], [7], [8], [9], [10] and [11] and show adequate oxidation and hot corrosion properties. Nickel-based superalloy blades with MCrAlY coatings are typically used in gas turbines [12].

Cyclic oxidation testing is used to assess high temperature environmental resistance [13], but regular laboratory tests in air are not able to fully simulate the engine environment. This study presents a recently developed cyclic burner-rig test that is used to simulate TURBOMECA's engine conditions and to assess the oxidation and hot corrosion behaviour of MCrAlY coatings on nickel-based superalloys. The specificity of this test is highlighted by comparison with pure oxidation tests at 900 °C, 950 °C and 1000 °C. The results of this study are compared with the degradation observed in service-exposed blades.

2. Materials and experimental procedures

2.1. Samples

The system used in this study is a nickel-based single-crystal superalloy MC2 [14] coated with NiCoCrAlYTa coating. Rectangular bars of dimensions 30 $*$ 10 $*$ 1 mm^3 were machined from a MC2 rod specimen. The coating was provided by Praxair Surface

Technologies (Oldmixon Crescent, England) and made by the Tribomet™ process, where CrAlY particles are entrapped in a growing Ni–Co electroplate layer to produce a uniform dispersion. Samples were plated in two steps in order to coat the whole surface, resulting in a slight overlap. Three different MCrAlY coatings thicknesses (30 µm, 70 µm and 110 µm) have been studied. The nominal composition of superalloy MC2 and NiCoCrAlYTa coating are given in Table 1.

Table 1.

Nominal composition of the superalloy and the MCrAlY coating used in this study (wt.%)

Alloy	Ni	Cr	Co	Al	Ta	Mo	Ti	W
MC2	Bal	7.8	5.2	5.0	5.8	2.1	1.5	8.0
NiCoCralYTa	Bal	20.6	19.3	8.6	4.3	–	–	–

The full heat-treatment consisted of a two step ageing treatment, 6 h at 1080 °C and 20 h at 870 °C in an argon atmosphere. The resulting microstructure of NiCoCrAlYTa coating after heat-treatment is shown in Fig. 1. The three different thicknesses give similar coatings as far as the structure and composition are concerned.

Fig. 1. SEM back scattered electron image of 110-µm thick NiCoCrAlYTa coating on MC2 superalloy after vacuum heat treatment.
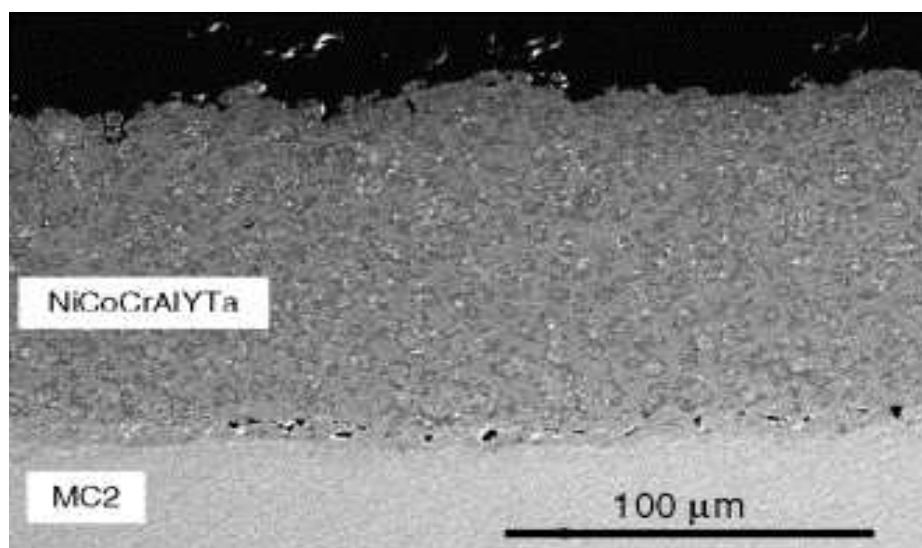
2.2. Burner-rig experiments and oxidation tests

These coated samples are subjected to oxidation and sulphidation tests on the new TURBOMECA burner-rig. Most conditions in a gas turbine can be accurately simulated in this low-velocity burner-rig, with the exception of gas velocity and pressure. This one-zone rig is able to test specimens at varying temperatures under a kerosene/air combustion environment. The fuel used is standard aviation kerosene with 0.2 wt.% sulphur content. The TURBOMECA burner-rig is operated in a cyclic mode, heating the specimens in a rotating holder. In the present case, specimens are tested under oxidising conditions and Type I hot corrosion conditions [12]. A salt-water solution is atomised into the flame to reproduce hot-corrosion. Specimens are ramped from 900 °C to oxidising conditions (1000 °C, 5 min) similar to those present during take off and climb, then dropped to 950 °C (25 min dwell). One cycle thus corresponds to 1 h at varying temperatures in the range of 900 °C to 1000 °C followed by 15 min air cooling to room temperature. The typical thermal cycle is shown in Fig. 2. Two specimens of each system are tested up to 950 such cycles.

Fig. 2. Typical thermal cycle of the TURBOMECA burner-rig.
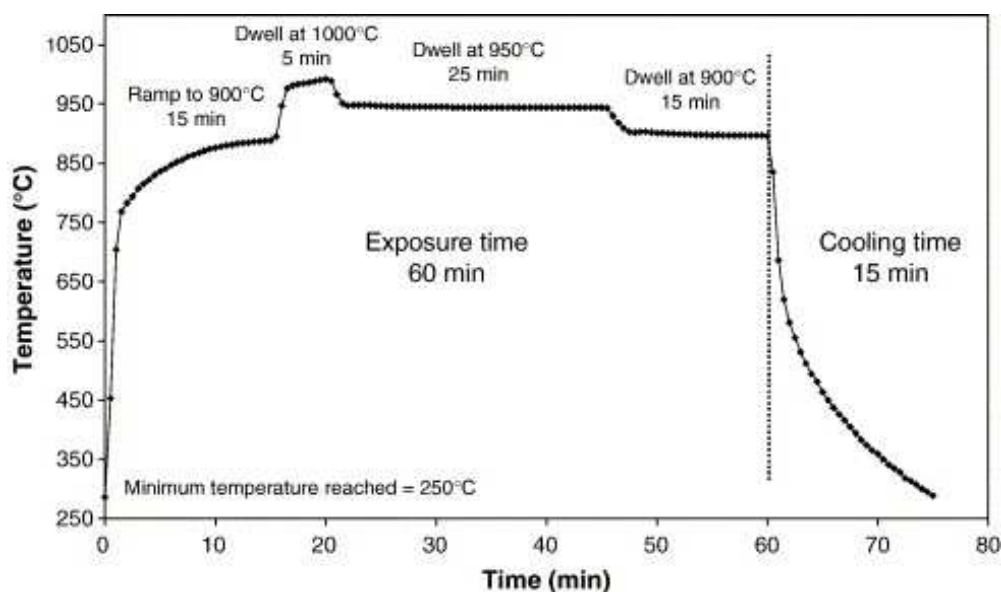
As a complementary test, other samples are also heat treated in laboratory air environment at 900 °C, 950 °C and 1000 °C during 900 h.

2.3. Observation

Specimens were examined at regular intervals for both burner-rig tests and oxidation tests. Both optical and scanning electron microscopy (SEM) with X-ray energy-dispersive

spectroscopy (XEDS) studies were carried out before and after oxidation testing. Attention has been paid to the evolution of microstructure from the as-coated condition through to subsequent thermal exposure.

3. Results and discussion

3.1. Isothermal oxidation

To highlight the specificity of the burner-rig test, samples have been heat treated in a laboratory air environment at 900 °C, 950 °C and 1000 °C during 900 h. Fig. 3 shows 110-μm thick NiCoCrAlYTa coating deposited on the MC2 superalloy after isothermal exposure at 1000 °C for 900 h. The microstructure of a MCrAlY coating is well documented [4], [5] and [6] and is known to consist of a γ-solid solution (Ni, Co, Cr rich phase with fcc structure) containing a dispersion of β-NiAl (B2 structure) and γ′-(Ni,Cr)$_3$Al (L1$_2$ structure). The microstructure of the NiCoCrAlYTa coating, identified with XEDS [6], consists of β-NiAl and γ′-(Ni,Cr)$_3$Al islands in a γ-Ni matrix. As the NiCoCrAlYTa coating oxidises, grains of the aluminium-rich β phase gradually convert to islands of γ′ by consumption of the aluminium to form the oxide scale. Dissolution of the β phase near the coating/alloy interface is also observed because of the interdiffusion with the substrate.

Fig. 3. SEM back scattered electron image of 110-μm thick NiCoCrAlYTa coating on MC2 superalloy after 900 h isothermal exposure at 1000 °C.
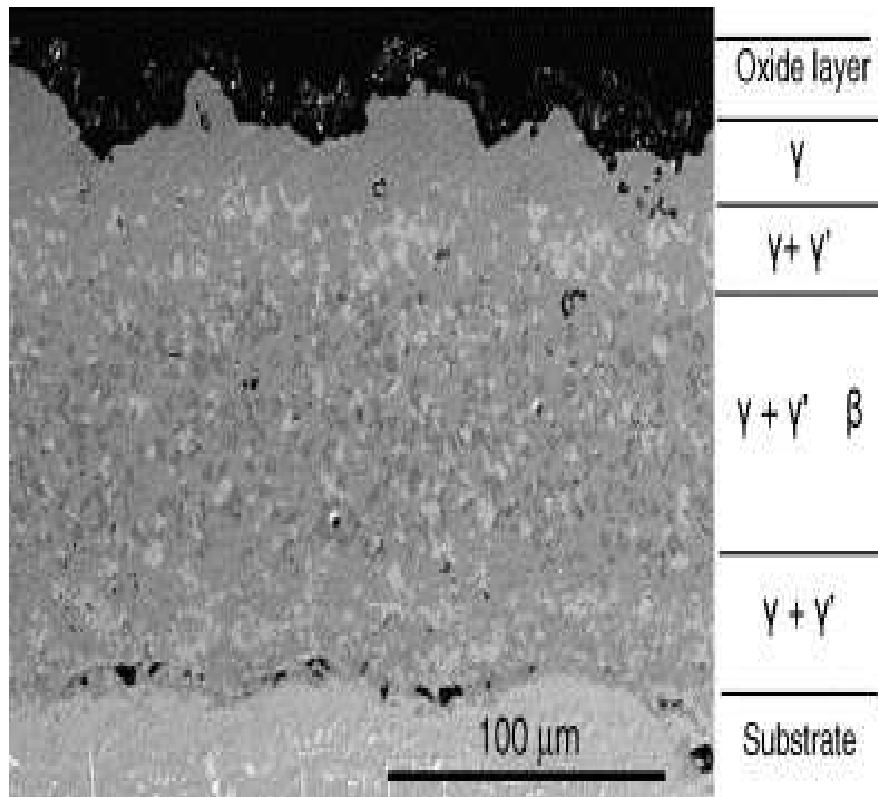
The microstructure of the oxidised coatings after 900 h depends on the coating thickness and on the exposure temperature, as shown in Table 2. Thicker coatings at lower temperatures remain three-phased whereas the thinnest coating at highest temperature experienced full transformation to a single γ phase. Two-phased γ/γ′ microstructures are observed for intermediate conditions.

Table 2.

Exposure temperature dependence of NiCoCrAlYTa coatings microstructure

Coating thickness	Exposure time	Temperature	Phases	Aluminium content (wt.%)
30	900 h	900 °C	γ′–γ	3.8

Coating thickness	Exposure time	Temperature	Phases	Aluminium content (wt.%)
70	900 h	900 °C	β–γ′–γ	7.2
110	900 h	900 °C	β–γ′–γ	8.2
30	900 h	950 °C	γ′–γ	3.1
70	900 h	950 °C	β–γ′–γ	6.8
110	900 h	950 °C	β–γ′–γ	7.9
30	900 h	1000 °C	γ	3.0
70	900 h	1000 °C	γ′–γ	5.4
110	900 h	1000 °C	β–γ′–γ	7.0
30	413 cycles	Burner-rig test	γ′–γ	–
70	950 cycles	Burner-rig test	γ′–γ	4.4
110	950 cycles	Burner-rig test	γ′–γ	5.4

Increasing the temperature from 900 °C to 1000 °C induces no modification in the oxide scale microstructure but a small increase of the oxide scale thicknesses, ranking from 3.2 μm to 4.5 μm after 900 h for a 110-μm thick NiCoCrAlYTa coating. Two continuous layers of oxides can be detected under the scanning electron microscope according to the analysis carried out using the electron microprobe. A dark-contrast inner layer is identified as alumina, and a lighter layer at the top of the scale corresponds to a mixed spinel-type oxide $(Ni(Cr,Al)O_4)$ [11].

Increasing the temperature causes further changes in the microstructure, with aluminium loss at the coating surface due to oxide scale formation, and at the coating/substrate interface due to interdiffusion. As a result of the decrease of the aluminium content, the depletion of the β-NiAl phase and possibly of the γ′ phase occurs in the coating. Fig. 4 shows the influence of the exposure to high temperatures on Al concentration–distance profile after 900 h, as determined by EDX. More extreme changes in the microstructure are observed following exposure for 900 h at 1000 °C, where extensive interdiffusion with the substrate occurs. The depleted zone width is thus a function of the temperature of exposure, as expected for a diffusion controlled process [8].

Fig. 4. Influence of exposure temperature on Al concentration-distance profile after 900 h for a 110-μm thick NiCoCrAlYTa coating on MC2 superalloy.

Fig. (chart)
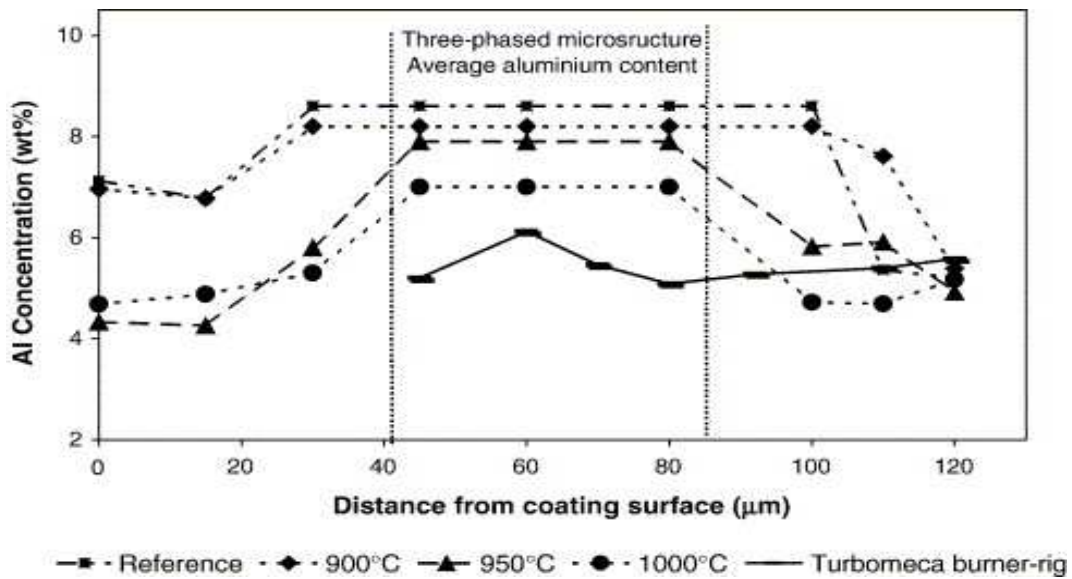
The different coatings are characterised by the same depletion zone thicknesses (Fig. 5), both at the oxide/coating interface and at the coating/substrate interface. The 30-μm thick NiCoCrAlYTa coating is γ single-phased after exposure at 1000 °C for 900 h, containing 3 wt.% Al. Only a small region in the centre of the 110-μm thick NiCoCrAlYTa coating is still three-phased, and the 20-μm thick depletion zone of the coating is γ/γ′. As can be seen on Fig. 6, the increasing coating thickness provides a larger Al reservoir which is beneficial for the formation of a protective alumina scale. There is still sufficient Al in the 110-μm thick coating to confer oxidation protection and the average residual aluminium content decreases with decreasing coating thickness after 900 h at 1000 °C. The evolution of the average aluminium content as a function of temperature and coating thickness is given in Table 2.

Fig. 5. SEM back scattered electron image of 30-, 70- and 110-μm thick NiCoCrAlYTa coating on MC2 superalloy after 900 h at 1000 °C.
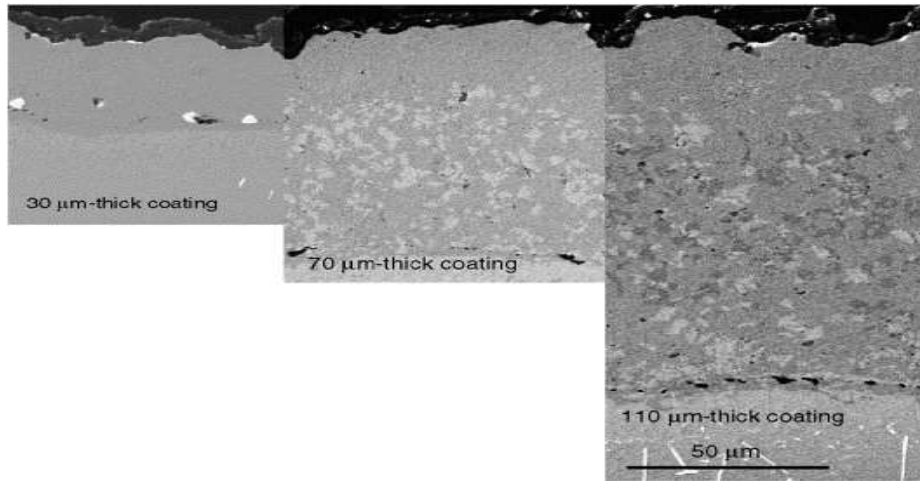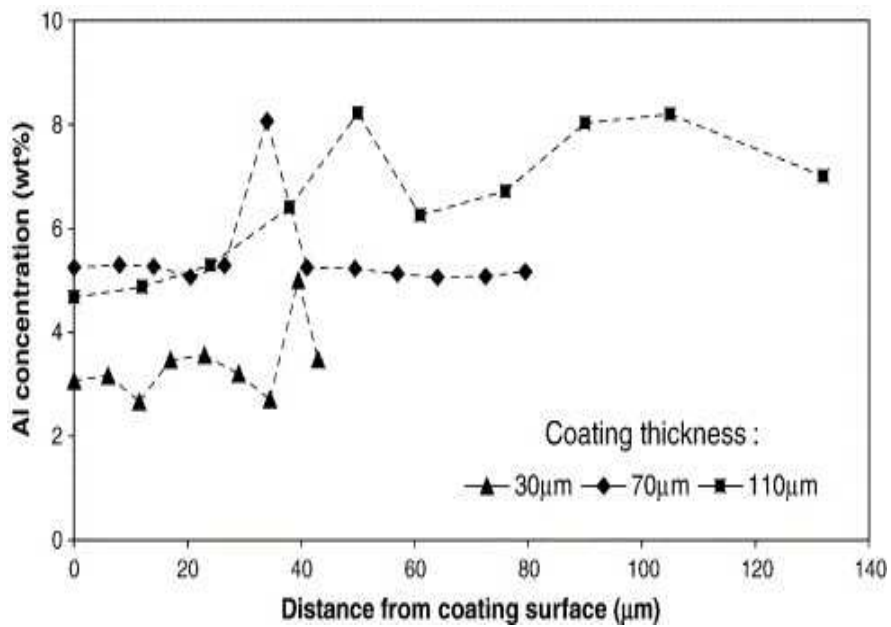
Fig. 6. Influence of the coating thickness on Al concentration–distance profile after 900 h exposure at 1000 °C.

3.2. Burner-rig tests

Optical images of samples after burner-rig experiments are shown in Fig. 7. The two specimens of the 30-μm thick NiCoCrAlYTa coated MC2 samples have been removed from the burner-rig after 413 cycles, because of an accelerated degradation due to corrosion. The other samples have been tested up to 950 cycles. The accelerated damage of the 30-μm thick NiCoCrAlYTa coating was detected after an incubation period of about 270 cycles.

Fig. 7. Optical images of NiCoCrAlYTa-coated MC2 samples after burner-rig experiments.

30 µm-thick coating, 413 cycles   70 µm-thick coating, 950 cycles   110 µm-thick coating, 950 cycles
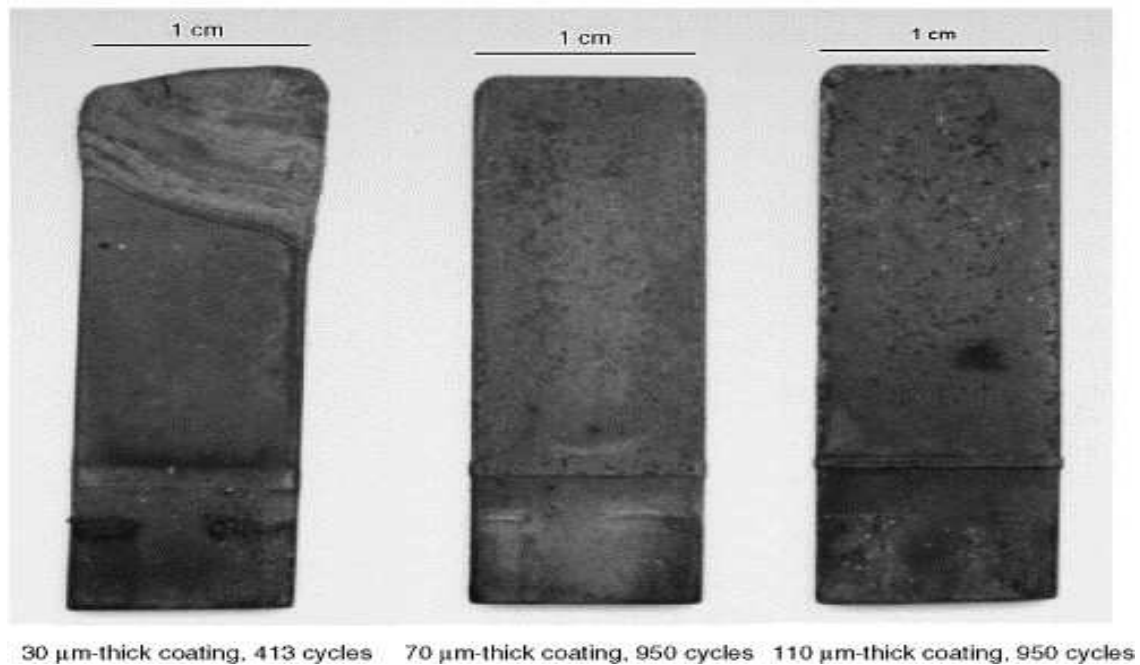
A post test examination of the NiCoCrAlYTa coated samples revealed that all had undergone significant modification of the coating composition and microstructure. Three distinct zones can be seen on cross sections in Fig. 8 (left):

– A thick oxide scale consisting of a mixture of alumina (Al_2O_3, inner layer) and rich Ni, Cr, Al spinel-type oxide.

   – An internal oxidised zone (alumina) in the upper part of the coating with a front of internal nitridation (AlN) above chromium-rich sulphides and yttrium-rich sulphides, identified with EDX (Fig. 8 and Fig. 9).

Fig. 9. SEM images of the corrosion front for a 110-μm thick NiCoCrAlYTa coating on MC2 superalloy after burner-rig exposure for 950 cycles.
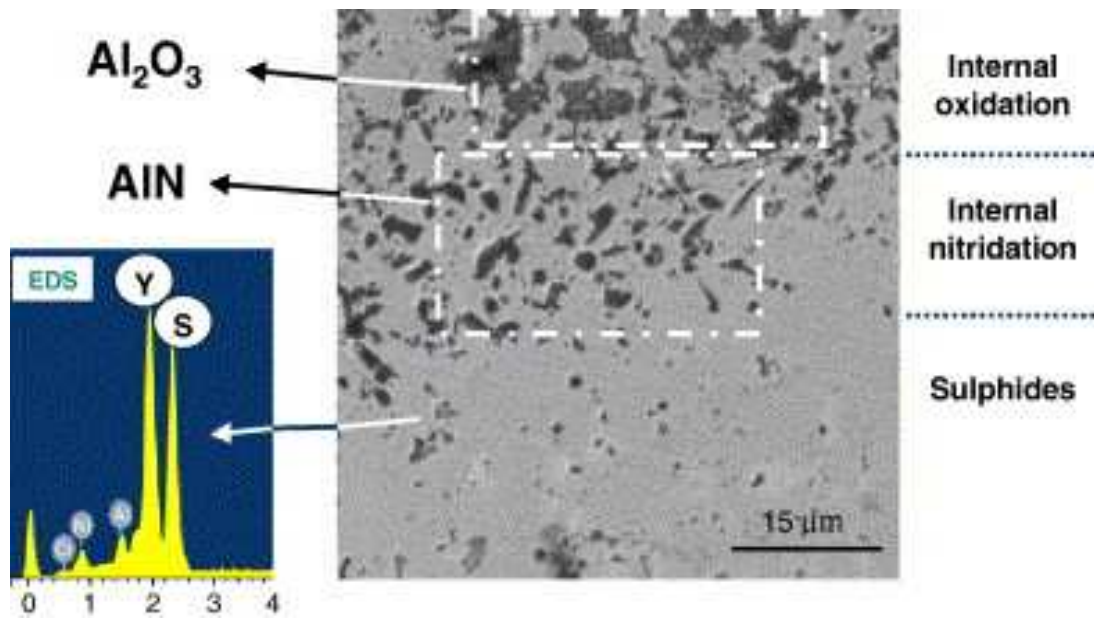
– A γ/γ′ zone formed by Al depletion at the coating/substrate interface.

Fig. 8. SEM images of 110-μm thick NiCoCrAlYTa coating on MC2 superalloy after (left) burner-rig exposure for 950 cycles, (right) service-exposed for 3000 h.
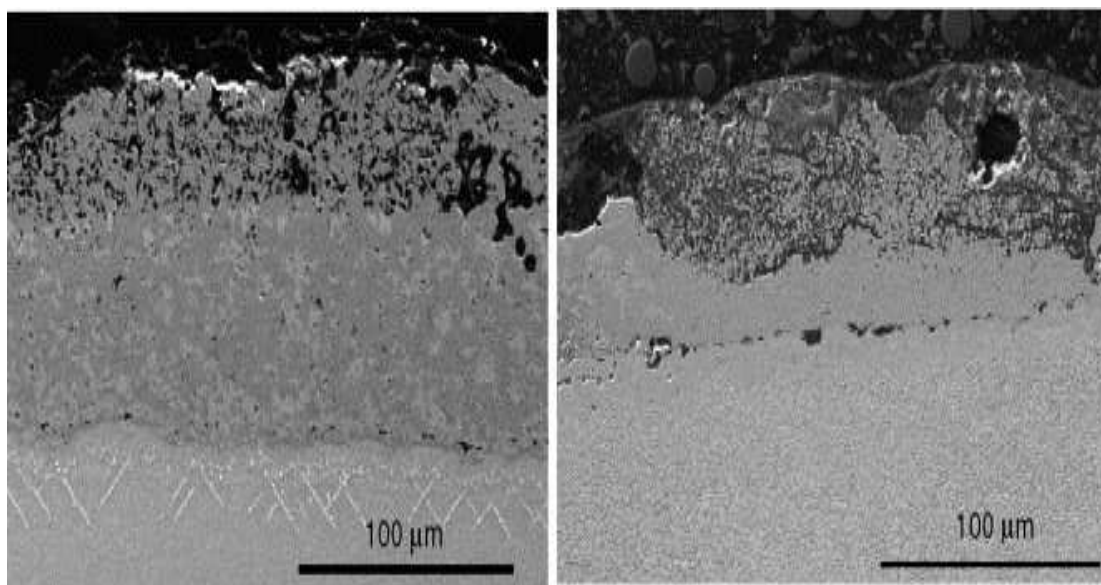
This microstructure has typical features of a Type I hot corrosion microstructure [15]. Internal oxidation in the coating results from a non-adherent oxide scale. Molten salts such as Na_2SO_4 can effectively dissolve the protective scale formed on the coating [16]. The re-forming scale is no longer protective and rapid hot corrosion damage ensues by internal diffusion of sulphur and oxygen. SEM investigations reveal that the upper part of the coating contains less than 1 wt.% of aluminium.

3.3. Comparison between oxidation tests, burner-rig experiments and a service-exposed blade

The isothermally oxidised samples are characterised by an adherent and protective oxide scale. It should be noted that no internal oxidation has been observed either during the 900-h tests, or by Vialas et al. [17] during a 1800×1 h cyclic oxidation test. On the contrary, the degradation of a NiCoCrAlYTa coating in the burner-rig is characterised by the presence of internal oxides within the coating.

The internal diffusion zone under the coating/substrate interface seems to be temperature dependent. The γ' zone is 9.5-μm thick at 900 °C, 16-μm thick at 950 °C and 25-μm thick at 1000 °C for isothermal tests. As far as the interdiffusion is concerned, the equivalent temperature during the burner-rig test can be roughly estimated at 950 °C with a 17-μm thickness of the internal zone.

Depletion zones at the coating/oxide and coating/substrate interfaces have almost the same thickness in isothermal oxidation tests, whereas the internal oxidation zone is thicker than the diffusion zone in the burner-rig test. The internal oxide formation depletes the aluminium content and causes further phase transformation in the coating. Despite its large reservoir of Al, the 110-μm thick NiCoCrAlYTa coating undergoes microstructural evolution and is two-phased after the burner-rig test. The resulting microstructures of the different coatings are given in the phase diagram in Fig. 10. It shows the influence of coating thickness on its degradation during a high temperature exposure. The large aluminium reservoir and the potential to form a protective scale under oxidising condition are not sufficient to provide the same lifetime under Na_2SO_4-induced hot corrosion. The rapid propagation of a corrosion attack inside the coating may degrade the substrate protection before the transformation in a γ single phase (low aluminium content).

Fig. 10. Coating microstructure diagram, function of temperature and coating thickness (after test of 900 h).
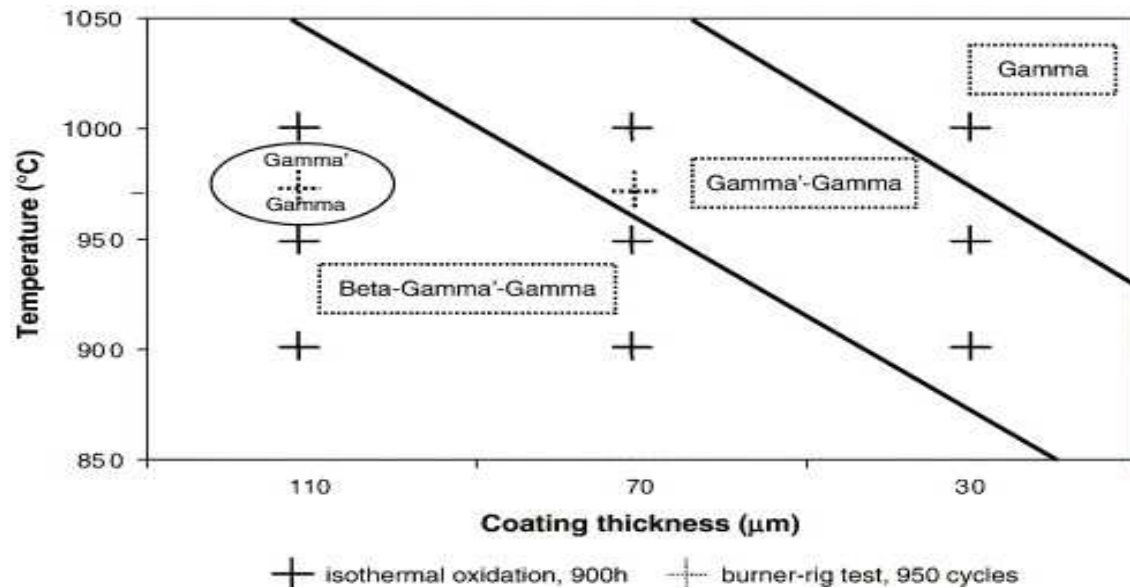
A vacuum plasma spray (VPS) NiCoCrAlYTa coating microstructure after 3000 h of service in corrosive operating conditions is shown in Fig. 8 (right). The degradation is similar to that observed after a burner-rig test, with internal oxidation and nitridation, and chromium-rich sulphides. The burner-rig is successful at reproducing the accelerated combined hot-corrosion/oxidation attack. Parallelepipedic samples are also representative of a blade geometry, with an accelerated degradation on the edges, as can be observed on a blade leading and trailing edge (Fig. 11). The influence of curvature radius relating to the oxidation and diffusion phenomena is then brought to the fore.

Fig. 11. Comparison of degradation between (left) a burner-rig tests sample and (right) a blade trailing edge.
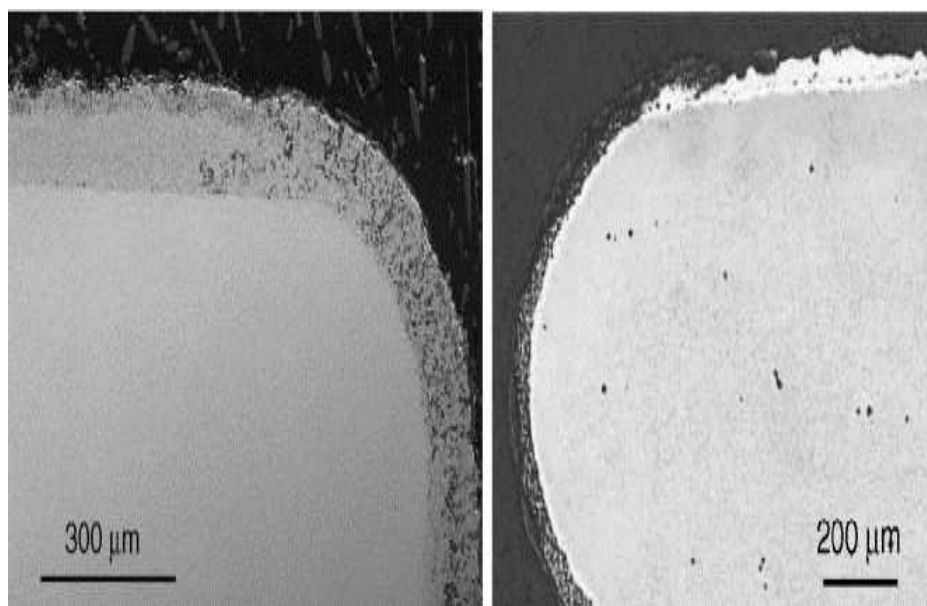
4. Conclusion

A recently developed cyclic burner-rig test, used to assess the oxidation and hot corrosion behaviour of MCrAlY coatings on nickel-based superalloys, is successful at reproducing the accelerated combined hot-corrosion/oxidation attack. The microstructure of the degraded sample, which consists of a mixed oxidised/metallic zone on the initial γ–γ′ NiCoCrAlYTa coating, is somewhat different from the isothermal oxidation tests, and similar to the degradation observed in service-exposed blades. Laboratory tests in simplified conditions show the influence of coating thickness on the aluminium content. The 110-μm thick NiCoCrAlYTa coating provides a larger Al reservoir which is beneficial for the formation of a protective alumina scale. In oxidation conditions, it increases the coating lifetime, controlled by aluminium loss by oxidation and diffusion. In more complex conditions, where corrosion, oxidation and interdiffusion interact, the coating end-of-life may be reached before the transformation into a γ single phase.

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Original text : <u>Elsevier.com</u>