



## Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <http://oatao.univ-toulouse.fr/>  
Eprints ID : 2962

**To link to this article :**

URL : <http://dx.doi.org/10.4028/www.scientific.net/MSF.461-464.747>

**To cite this version :** Vialas, Nadia and Monceau, Daniel and Pieraggi , Bernard ( 2004) [\*Effect of Cycle Frequency on High Temperature Oxidation Behavior of Alumina-forming Coatings Used for Industrial Gas Turbine Blades.\*](#) Materials Science Forum , vol. 461 - 464 . pp. 747-754. ISSN 0255-5476

Any correspondence concerning this service should be sent to the repository administrator: [staff-oatao@inp-toulouse.fr](mailto:staff-oatao@inp-toulouse.fr)

# Effect of Cycle Frequency on High Temperature Oxidation Behavior of Alumina-forming Coatings Used for Industrial Gas Turbine Blades

Nadia Vialas<sup>1</sup>, Daniel Monceau<sup>1</sup> and Bernard Pieraggi<sup>2</sup>

<sup>1</sup> CIRIMAT UMR 5085, ENSIACET-INPT, 31077 Toulouse Cedex 4, France

<sup>2</sup> ENSTIMAC-CROMEPE, Campus Jarlard, 81013 Albi CT Cedex 9, France

Daniel.Monceau@ensiacet.fr

**Keywords:** high temperature cyclic oxidation, cycle frequency, alumina-forming coatings, Pt-modified nickel aluminide, MCrAlY, modeling of cyclic oxidation, long term oxidation, interdiffusion.

**Abstract.** Oxidation kinetics of platinum modified aluminide and overlay coatings on nickel base superalloys were investigated. Isothermal oxidation tests were carried out at 1050°C in synthetic air. Cyclic oxidation tests were performed with 2 cycle frequencies :

- Short term cycles : 1h dwells at 1050°C in synthetic air ×1800 cycles
- Long term cycles : 300h dwells at 1050°C in laboratory air × 6 cycles (experiment planned to totalize at least 10 000 hours at high temperature)

The mass gain curves point out a large effect of the cycle frequency at 1050°C for overlay NiCoCrAlYTa coating whereas the effect is less significant for Pt-modified nickel aluminide coating. Scanning electron microscopy combined with energy dispersive X-ray spectroscopy was used to evaluate the effect of cycle frequency on microstructural evolution. A simple statistical spalling model [1,2], assuming that the parabolic rate constant  $k_p$  and the spalling probability  $p$  are constant, is tentatively applied and discussed in view of the microstructural evolution complexity.

## Introduction

Single crystal nickel-base superalloys are widely used as turbine blades components in aero and industrial gas turbines since they combine good mechanical properties with microstructural stability at relatively high temperature [3]. In order to improve the high temperature oxidation resistance, diffusion aluminide or overlay MCrAlY, or more recently thermal barrier coatings, are deposited [4,5]. Turbine blades are subjected to severe service conditions particularly during thermal cycling. Then cyclic oxidation tests are widely used to assess high temperature resistance of the materials. During cooling, stresses induced by thermal expansion mismatch between metal and oxide and growth stresses lead to oxide scale spalling. Spallation depends on many factors such as surface roughness, surface preparation, material composition, but also cycle duration. Cycle duration for aircraft are shorter than for land-based gas turbines, consequently, materials may have different cyclic oxidation behaviour when used for aero turbines or land-based gas turbines. Several numerical models were developed to assess the effect of successive spallation and re-oxidation on protective element consumption kinetics (i.e. aluminum). A statistical model was proposed in 1978 by Smialek [6] and numerically developed in 1991 (COSP) by Lowell et al. [7]. More recently, Poquillon et al. developed a simple statistical spalling model [1,2] in which the oxide scale protectiveness is quantified throughout two parameters : a spalling probability  $p$  and an apparent parabolic rate constant  $k_p$ , which can be determined from mass changes recorded during cycling oxidation test. In this paper, effects of cycle frequency on high temperature oxidation behaviour of two alumina-forming coatings have been examined throughout mass gain curves, microstructural observations, Al concentration profiles and data provided by the

fitting of experimental kinetics results with the  $p-k_p$  model. Experimental results and data given by the model were also compared to discuss the  $p-k_p$  model. Then, a  $p-k_p$  map containing Al consumption lines allows to classify the systems according to their cyclic oxidation resistance.

## Materials and Experimental Procedures

**Materials.** Three Ni-base superalloys were used as substrates: single crystal alloys CMSX-4<sup>TM</sup> and SCB444<sup>TM</sup> (developed in the framework of an European program [8]) and polycrystal alloy IN792<sup>TM</sup> containing 0.5wt% of Hf. Discs specimens (9 mm in diameter and 2 mm thick) were coated with a Pt-modified aluminide coating CN91<sup>TM</sup> or with an overlay coating NiCoCrAlYTa, both manufactured by Chromalloy France. The CN91<sup>TM</sup> process involved an electrolytic deposition of Pt to a thickness of  $7\pm 2$   $\mu\text{m}$  (this stage requiring an electrical contact, a MCrAlY rod was laser welded but cut just before the oxidation test) and a vapour phase aluminization. The NiCoCrAlYTa was vacuum plasma sprayed only on IN792 using Amdry997<sup>TM</sup> powder. With this last process, coatings were thinner at the edges of the discs. After heat treatments, as-coated specimens were oxidized.

### Experimental procedures.

**Isothermal oxidation.** specimens were oxidized in a Setaram TGA24S thermobalance for 100 hours at 1050°C in synthetic air. Mass gain data were analysed using local fitting of general parabolic law [9] in order to determine the stationary stage parabolic rate constants allowing for extrapolation of mass gain curves for longer test duration.

**Short term cyclic oxidation.** tests were performed using a horizontal tube furnace and under controlled atmosphere during cooling and heating. The specimens hang on a Pt/Rh wire, were inserted and removed from the hot furnace with a heating rate of approximately 2°C/s (calculated according to COTEST instructions [10]) and natural cooling rate inside the cooling chamber. One cycle consists of 1 hr at 1050°C in synthetic air and 15 min down to 65°C in the cooling chamber also under synthetic air. 1800 cycles were performed.

**Long term cyclic oxidation.** The specimens were hung with a platinum wire on an alumina rod to be introduced in a Carbolite furnace at 1050°C in laboratory air with a heating rate of 3°C/s. After 300 hours exposure, specimens were removed from the furnace to be placed in front of fans at room temperature, which results on an initial cooling rate of 9 °C/s. Six cycles of 300 hours were performed to compare with the 1800 cycles of 1 hour. Additional samples were cycled up to 5200hr and 10800hr.

For short and long term cyclic oxidation tests, the net mass gain per unit area (NMG) was followed as function of cycle number using a Sartorius microbalance with 10  $\mu\text{g}$  accuracy, spalled oxide is not included in the measure of NMG.

Surface and cross-sections of the samples were examined using a Leo435 scanning electron microscopy (SEM) equipped with a PGT energy dispersive X-ray spectrometry system (EDS). Concentration profiles were obtained from EDX elemental maps. The average concentration of 9 elements was given by quantitative analysis inside  $14\times 364\mu\text{m}$  (for NiCoCrAlYTa) and  $4\times 182\mu\text{m}$  (for CN91<sup>TM</sup>) area parallel to the interface and translated from the metal/oxide interface to the substrate. Oxide phases present in the scale were identified using a Seiffert X-ray diffraction apparatus (XRD).

## Results.

**Effect of cycle frequency on gravimetry results.** Cycle frequency has a large effect on gravimetry results for the overlay NiCoCrAlYTa coating whereas this effect is less significant for the platinum aluminide coating CN91. (Fig. 1). For CN91 systems (Fig. 1b,c,d), after

approximately 800 cycles of 1 hour, acceleration of the oxidation kinetics was observed. This acceleration is not due to the formation of oxides, such as spinel,  $\text{Cr}_2\text{O}_3$ , less protective than alumina but results from crack formation at the welding between the MCrAlY rod and the sample and oxidation inside this crack (Fig. 4a).

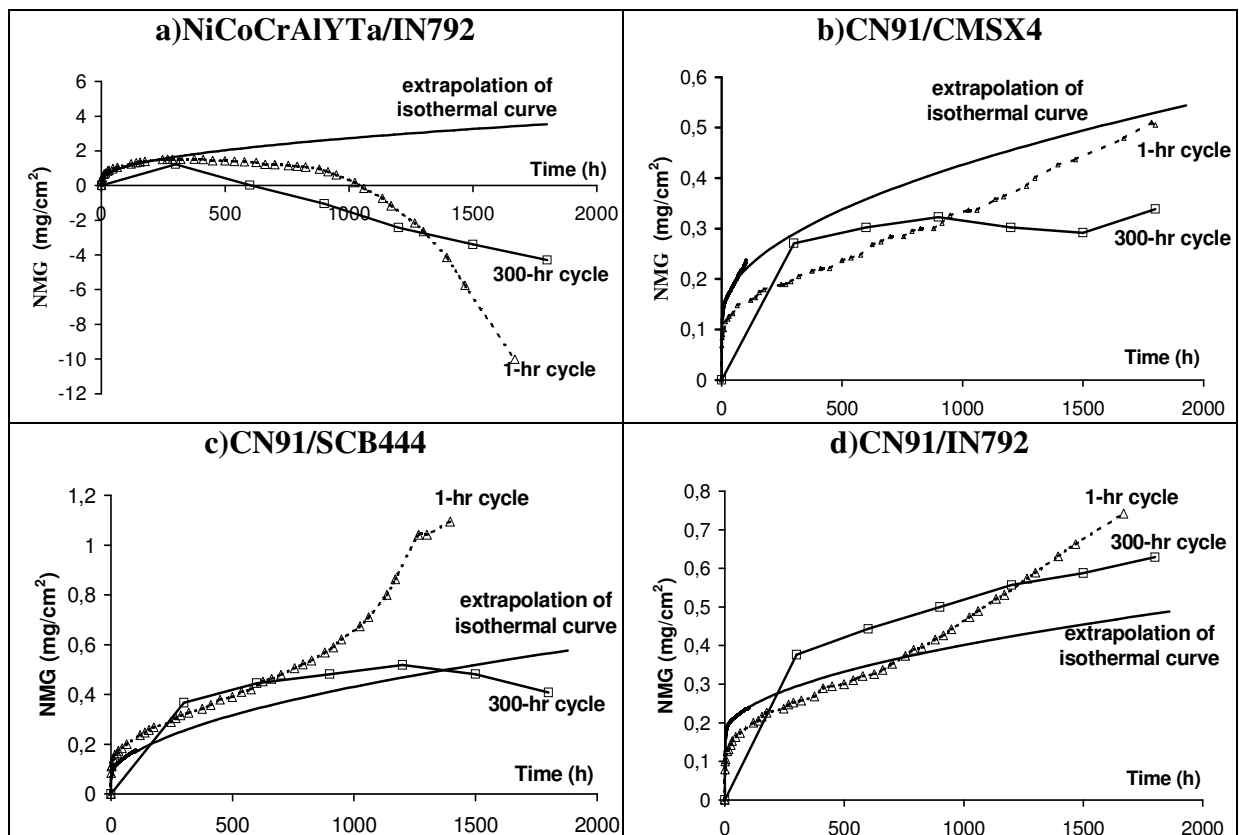


Fig. 1. Net Mass Gain vs time for NiCoCrAlYTa/IN792 (a), for CN91/CMSX-4 (b), /SCB444 (c) and /IN792 (d) oxidised 1800 hr at 1050°C : 1-hr cycle in synthetic air, 300-hr cycle in laboratory air.

### Effect of cycle frequency on spallation, oxide thickness, microstructural evolution and Al diffusion.

**NiCoCrAlYTa/IN792.** The backscattered electron images of the surface of the system NiCoCrAlYTa/IN792 are reported in Fig.2a. Percentage of freshly spalled (bright zones) area and size dispersion were quantified by image analysis. After long term cycles, 5% of the total surface is spalled whereas after short term cycle only 1% is spalled. Freshly spalled zones are less numerous and smaller after short term cycles than after long term cycles. Cross-section observations (Fig. 2b) showed that the average oxide scale thickness are similar whatever the cycle duration, with a large dispersion for 1-hr cycles because one specimen face was more oxidized than the other one. The oxide scale consists of about 40%  $\alpha\text{-Al}_2\text{O}_3$  and 60% spinel type  $(\text{Ni},\text{Co})(\text{Al},\text{Cr})_2\text{O}_4$  whatever the cycle duration. Backscattered electron images of the cross-section and the aluminum concentration profiles (Fig. 2c) indicate that cycle duration has limited effect on microstructure evolution, on aluminum consumption to form alumina and on Al diffusion from the coating to the substrate. Initially, the coating consisted of 110  $\mu\text{m}$  thick  $\gamma\text{-Ni}$  phase with small amount of  $\beta\text{-NiAl}$  and  $\gamma'\text{-Ni}_3\text{Al}$  phases. After 1800 cycles of 1-hr, the coating consists of 70  $\mu\text{m}$  thick single phase  $\gamma\text{-Ni}$  (Al 7at.%) with Ti,Ta-rich precipitates and 30  $\mu\text{m}$  thick  $\gamma\text{-Ni}$  phase with  $\gamma'\text{-Ni}_3\text{Al}$  particles. After 6 cycles of 300-hr the coating is single phase  $\gamma\text{-Ni}$  (Al 7at.%), without any  $\gamma'\text{-Ni}_3\text{Al}$ .

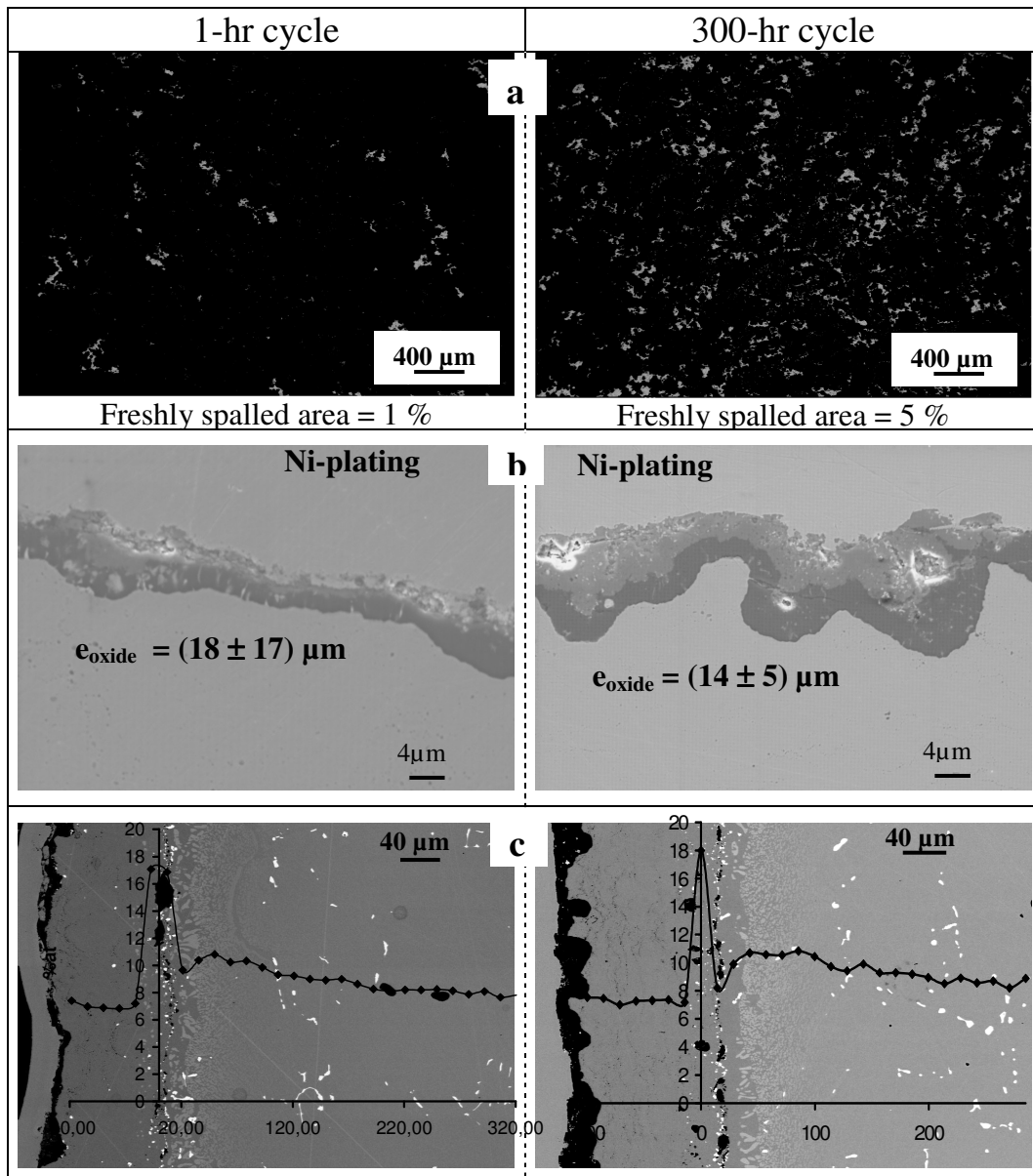


Fig. 2. NiCoCrAlYTa/IN792 oxidised 1800h at 1050°C (1-hr and 300-hr cycles): surface, bright zones are spalled zones (a), cross section (b, c) with corresponding Al concentration profiles in at% (c). a and c : BSI-SEM; b: SEI-SEM

**NiPtAl/CMSX-4.** As for the system NiCoCrAlYTa/IN792<sup>TM</sup>, the freshly spalled area (Fig. 3a) on NiPtAl/CMSX-4<sup>TM</sup> is larger after 6 cycles of 300-hr (9 %) than after 1800 cycles of 1-hr (0.04 %). After short term cycles there are few freshly spalled zones with a small size ( $< 50\mu\text{m}^2$ ), after long term cycles freshly spalled zones are numerous and larger (up to  $0.01\text{mm}^2$ ). The oxide scale (Fig. 3b) is thicker after long term cycles than after short term cycles and it essentially consists of  $\alpha$ -alumina. Initially, the coating was constituted by a  $35\mu\text{m}$  thick zone containing single phase  $\beta$ -NiAl enriched with Pt and a  $20\mu\text{m}$  thick interdiffusion zone containing Cr,W,Co,Re-rich precipitates of  $\mu$  phase [11]. After cyclic oxidation (long term or short term), because of Al consumption to form  $\alpha$ -alumina and Al diffusion from the coating to the substrate, the  $\beta$ -NiAl transforms to  $\gamma'$ -Ni<sub>3</sub>Al in some zones of the coating (Fig. 3c). Volume fraction of  $\gamma'$  phase is larger after long term cycling consistent with aluminum concentration profiles. Overall Al consumption is larger after long term cycles. The interdiffusion zone precipitates coarsen.

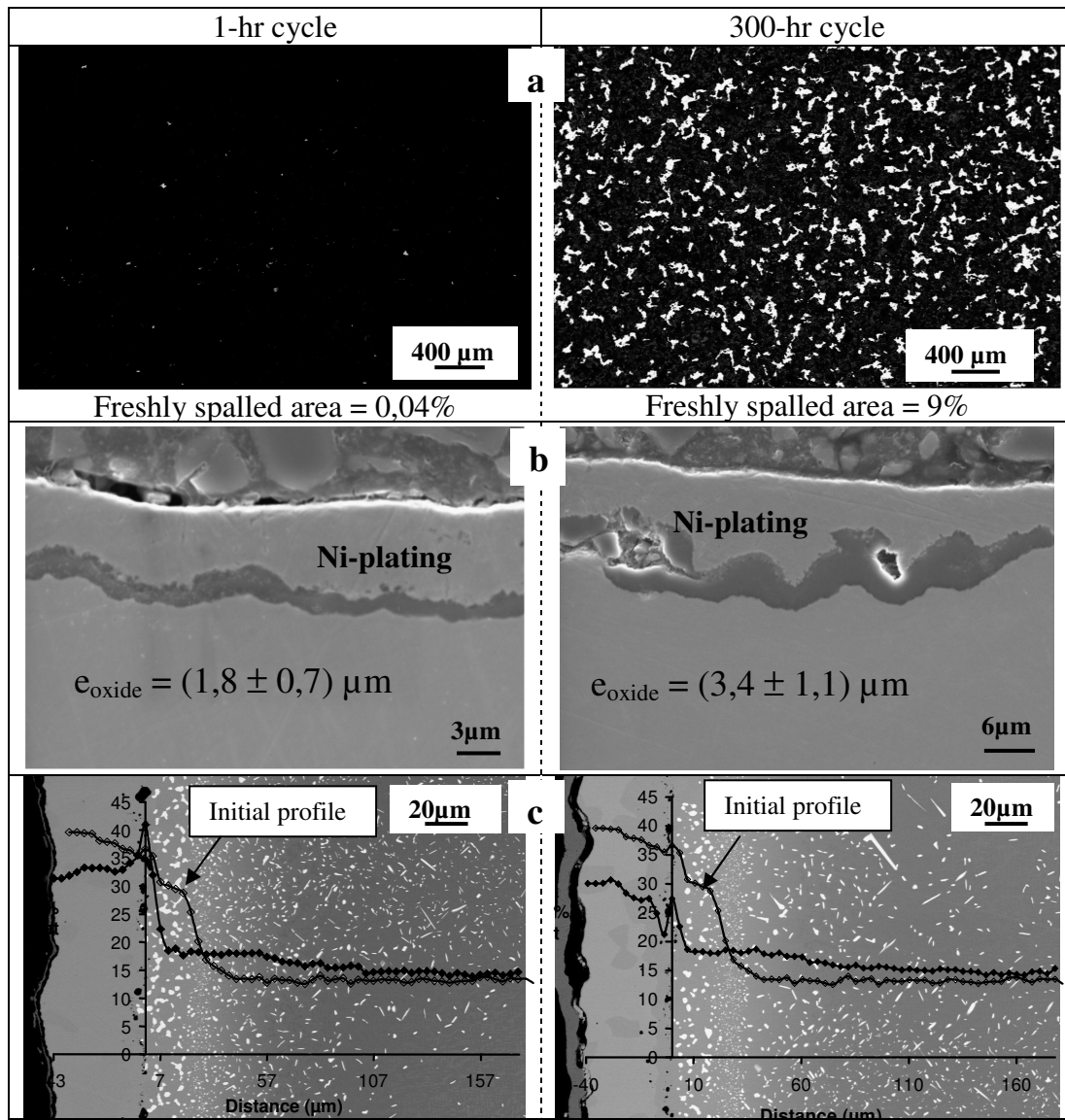


Fig. 3. NiPtAl/CMSX-4 oxidised 1800h at 1050°C (1-hr and 300-hr cycles) : surface, bright zones are spalled zones (a) and cross section (b, c) with Al concentration profile in at% (c). a and c : BSI-SEM; b: SEI-SEM

**Application of the simple statistical spalling model “p-k<sub>p</sub>” [1].** The simple statistical spalling model p-k<sub>p</sub> [1] was used to fit the mass gain curves obtained after short term cycles (Fig. 4a) and long term cycles (Fig. 4b). Despite the strong assumptions made in the model (p and k<sub>p</sub> constant at each cycle during all the experiment), it was possible to closely fit the mass gain curves. After 1000 cycles of 1-hr, a deviation between the experimental curve for NiCoCrAlYTa/IN792 and the fit is observed. As seen on the SEM image (Fig. 4a, image on the left), this deviation can be attributed to a local mass loss at the edges of the specimen, where the coating was initially thinner (due to the coating process). In the same way, the small deviation observed after 800 cycles of 1-hr for the NiPtAl/CMSX-4 system can be attributed to the acceleration of the mass gain due to oxidation inside the crack which was formed at the welding between the MCrAlY rod and the specimen (Fig. 4a, image on the right). By fitting gravimetric curves before these deviations, the model permitted calculation of p and k<sub>p</sub> constants (spalling probability and the apparent parabolic rate constant k<sub>p</sub><sup>app</sup>), but also the average oxide thickness e<sub>oxide</sub> and the aluminum consumption after 1800 cycles of 1-hr or 6 cycles of 300-hr. These data are reported in the Table 1 and compared to the experi-

mental results.

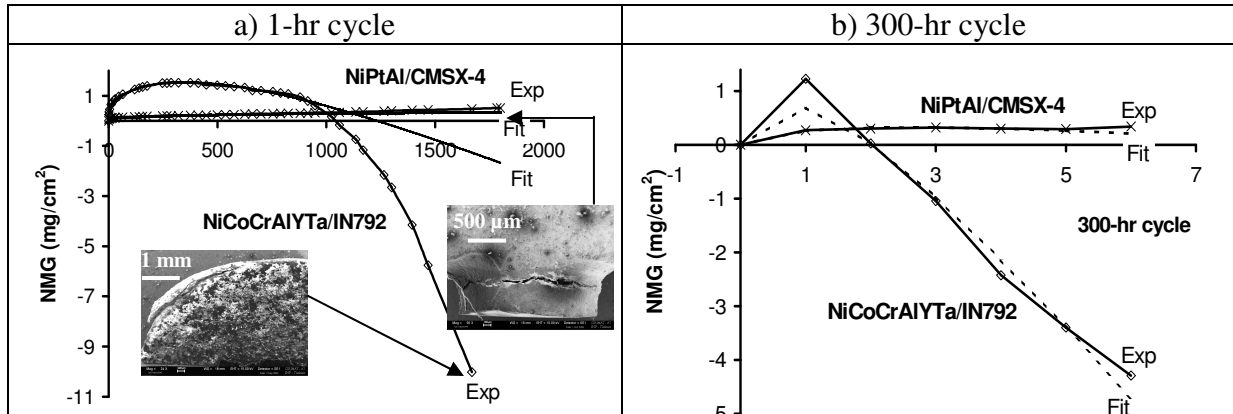


Fig. 4. Fit of experimental net mass gain curves of NiPtAl/IN792 and NiCoCrAlYTaN/IN792, with short term (a) and long term (b) cycles.

		Isothermal		Cyclic		Model p-k <sub>p</sub>			
		$\Delta m/S$ at t=300hr (extrapolated using [9])	$k_p^{app} = (\Delta m/S)^2/t$ [ $mg^2/cm^4s$ ]	spalled area [%]	measured $e_{oxide}$ [ $\mu m$ ]	p [%]	$k_p^{app}$ [ $mg^2/cm^4/s$ ]	$e_{oxide}$ [ $\mu m$ ]	Al consumption due to oxidation [ $mg/cm^2$ ]
1-hr cycle	NiPtAl/CMSX-4	0.287	$7.6 \cdot 10^{-8}$	0.04	$1.8 \pm 0.7$	0.01	$2.1 \cdot 10^{-8}$	2.1	0.51
	NiCoCrAlYTaN/IN792	1.65	$2.5 \cdot 10^{-6}$	1	$18 \pm 17$	0.1	$3.8 \cdot 10^{-6}$	17.2	8.5
300-hr cycle	NiPtAl/CMSX-4	0.287	$7.6 \cdot 10^{-8}$	9	$3.4 \pm 1.1$	11	$1.1 \cdot 10^{-7}$	3.4	1.14
	NiCoCrAlYTaN/IN792	1.65	$2.5 \cdot 10^{-6}$	5	$14 \pm 5$	32	$7.4 \cdot 10^{-6}$	16	12

Table 1. Comparison between the model and the experimental results.

**Materials performance chart.** In order to classify the coating/substrate systems, p and k<sub>p</sub> are plotted in a p-k<sub>p</sub> map [1,2] (Fig. 5). Al consumption lines of 0.5, 1, 2.5, 5, 10, 15 and 20 mg/cm<sup>2</sup> were added to this map, following Smialek idea [12], calculated for 1800 cycles of 1-hr and 6 cycles of 300-hr. Each map allows classification of the systems studied in view of their performance for a particular cycle oxidation test. For 300-hr cycles, for a constant value of k<sub>p</sub>, life-time does not increase when p decreases whereas Al consumption is very sensitive to spalling extent for 1-hr cycles.

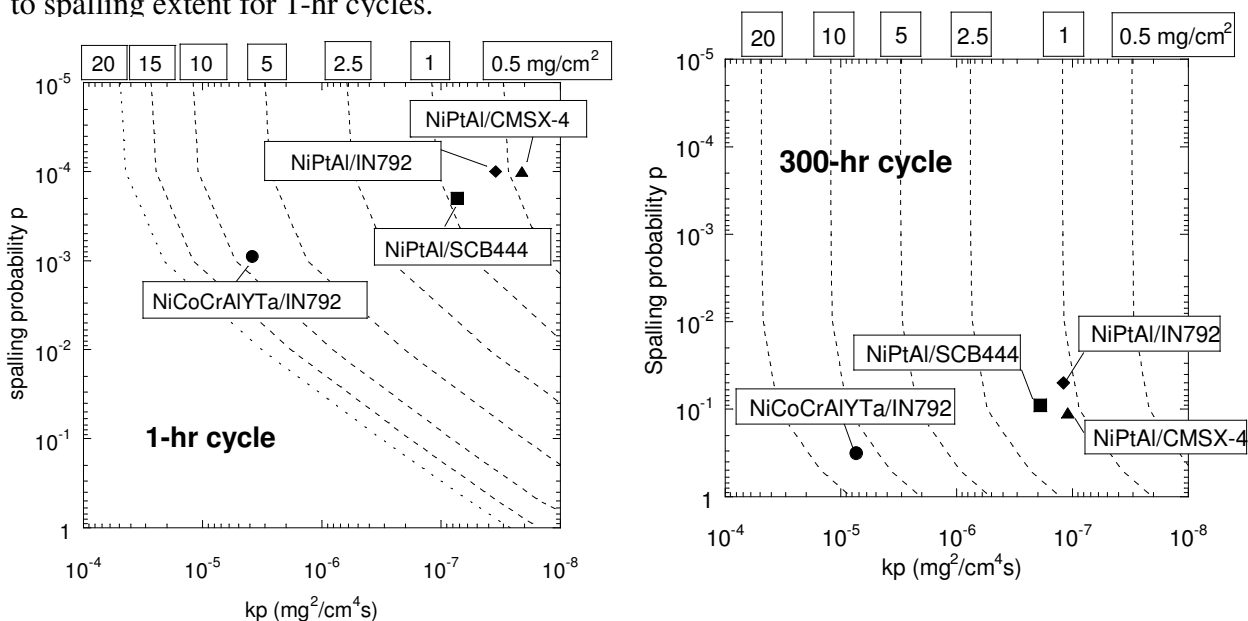


Fig. 5. p-k<sub>p</sub> maps with Al consumption lines after 1800 cycles of 1-hr and 6 cycles of 300-hr.

## Discussion

**Systems classification.** According to Fig. 5, Pt aluminide coatings are better than NiCoCrAlYTa coatings, with an Al consumption 10 times smaller whatever the cycle duration. The worse performance of NiCoCrAlYTa is first due to the large  $k_p$ . As CN91™ is the best cyclic oxidation resistant system, 1800hr exposure time was perhaps too short to observe an effect of cycle frequency on thermogravimetry results. The present results also point out a substrate effect on Pt-aluminide coating performances : CN91™ seems better when applied on CMSX-4™ and IN792™ than on SCB444™. This classification was found whatever the oxidation test (isothermal or cyclic), whatever the temperature (900°C, 1050°C or 1150°C) or the process to develop Pt-aluminide coating (pack cementation or vapor phase aluminisation) [13].

**Application of the p- $k_p$  model.** In the model, kinetics parameter  $k_p$  is considered constant during the experiment, that means that transient oxidation is not taken into account. However, during the first cycle, transient oxidation is preponderant but also occurs during new oxide formation on freshly spalled areas. For the long term cycles curves, this discrepancy is not serious, since after 300hr, stationary oxidation is reached and the transient stage represents only 3% of the oxidation time. But for short term cycles, stationary oxidation is not reached at each cycle especially for the first one. So, in order to fit correctly 1-hr cycle curves, it can be necessary to impose the experimental value as the first  $\Delta$ NMG calculated value. Spalling probability  $p$  is also considered constant in the p- $k_p$  model. In particular  $p$  does not depend on oxide scale thickness. Despite this assumption the model fits quite well the experimental curves (Fig. 4) and data calculated using the p- $k_p$  model ( $p$ ,  $k_p^{app}$ ,  $e_{oxide}$  and Al consumption) are consistent with experimental data (Table. 1), except for spalled area measurement on NiCoCrAlYTa/ IN792. As explained in [1], the general good quality of the fit may be due to the fact that oxide scale thickness is constant during the steady-state linear mass decrease.

**For a same total exposure time, which cycle frequency is the most detrimental ?** The protectiveness of the alumina-forming coatings is assumed to be controlled by Al content (reservoir model). Al content decrease in the coating is due to oxidation and Al diffusion toward the substrate. Cycle frequency can affect Al loss in the coating due to oxidation if it affects spallation. But it should not influence Al diffusion to the substrate. Microstructural investigations and Al concentration profiles made on CN91/CMSX-4 (Fig. 3c) are in a good agreement with this statement. Al consumption by oxidation and diffusion leads to  $\beta$ -NiAl transformation to  $\gamma'$ -Ni<sub>3</sub>Al. Proportion of  $\gamma'$ -Ni<sub>3</sub>Al phase is larger after 6 cycles of 300-hr than after 1800 cycles of 1-hr (§3.2.2), indicating that for a same high temperature exposure time (1800hr), Al consumption is higher after long term cycles. Comparison between Al concentration profiles after oxidation and initial profile indicates that Al lost by diffusion in the substrate (difference of the surface under the curve from the interdiffusion zone to the centre of the sample) is the same whatever the cycle duration. On the other hand, Al lost by oxidation (difference of the surface under the curve from the surface to the interdiffusion zone) is higher after 6 cycles of 300-hr than after 1800 cycles of 1-hr. Moreover, the p- $k_p$  model indicates that Al lost after long term cycles is twice more important than after short term cycles (Table 1 and Fig. 5). Oxide scale measured after 300-hr cycles is thicker, so stresses on cooling should be higher leading to more spallation and faster scale growth rate. The  $k_p^{app}$  value calculated by the model, reflects an oxidation kinetics faster for long term cycles. The  $p$  value indicates that after 300 cycles of 1-hr only 3% (300×0.01%) of the surface has been spalled, which is small compared to 11% after 1 cycle of 300-hr. So for CN91/CMSX-4, 6 cycles of 300-hr are more damaging than 1800 cycles of 1-hr. Mass gain curves for CN91/CMSX-4 are close because during long term cycles mass loss due to spallation is compensated by faster growth rate. Effect of cycle frequency should be detected on mass gain curves after longer exposure time. Results for CN91/CMSX-4 are consistent



with ones reported by Pint et al. [14] for Pt-containing aluminides, showing at 1100°C that spallation increased as frequency decreased. For NiCoCrAlYTa, NMG curves seem to indicate a strong effect of cycle frequency (Fig. 1a). However, microstructural observations (oxide scale thickness, phase transformations, Al concentration profiles) are similar for 1 hr and 300 hr cycles conditions. The kinetics model applied to NMG results confirms the small effect of cycle frequency: similar calculated  $k_p$  and small effect of  $p$  leading to slightly larger value of Al consumption for 300-hr cycles (Table. 1 and Fig. 5). Then the apparent strong effect of cycle frequency on Fig.1a is certainly due to the local mass loss at sample edges after 1000 cycles of 1 hr. This highlights that for gravimetry measurements on coated samples, specimen elaboration (coating deposit, roughness) is critical.

## Conclusions

- Six cycles of 300-hr were more damaging than 1800 cycles of 1-hr for Pt-aluminide coatings. The mass gain curves did not point it out but it was shown by microstructural investigations, concentration profiles and calculated Al consumption using the  $p$ - $k_p$  model.
- For NiCoCrAlYTa coatings, there was no significant effect of cycle frequency on microstructure despite the apparent difference in the mass gain curves, due to coating problem on sample edges.
- Despite strong assumptions,  $p$ - $k_p$  model fits correctly the mass gain curves (except for NiCoCrAlYTa/IN792 because of the problem mentioned above) and permits to quantify the oxide scale protectiveness throughout the spalling probability  $p$  and the apparent parabolic rate constant  $k_p^{app}$ , which allow the calculation of Al consumption. Parameters  $p$  and  $k_p$  were plotted in a materials performance map containing Al consumption lines calculated for given exposure time and cycle frequency. It appeared that Pt-aluminide coating had a better cyclic oxidation behaviour than NiCoCrAlYTa and that Al consumption was more severe after 6 cycles of 300-hr than after 1800 cycles of 1-hr.

## Acknowledgements

The authors thank EEC for financial support through the European project Allbatros (N°ENK5-CT2000-00081) and all partners for their contribution. J. Lacaze, D. Oquab, D. Poquillon are acknowledged for their help in, respectively, image analysis, SEM and use of  $p$ - $k_p$  model automatic fitting.

## References

- [1] D. Poquillon and D. Monceau: *Oxid. Met.* Vol. 59 (2003), p. 409
- [2] D. Poquillon and D. Monceau: TMS Annual Meeting, San Diego, (2003), p.165
- [3] M. Durand-Charre: *The microstructure of superalloys*: Gord. and Breach Sc. Pub. (1997).
- [4] J.R. Nicholls, MRS bulletin (Sept2003), p.659.
- [5] R. Mevrel: *Mater. Sci. Eng.* Vol. A120 (1989), p. 13
- [6] J.L. Smialek: *Metall. Trans. A* Vol. 9A (1978). p.309
- [7] C.E. Lowell, C.A. Barrett, R.W. Palmer, J.V. Auping and H.B. Probst: *Oxid. Met.* Vol. 36 (1991), p. 81
- [8] P. Caron and A. Escalé: 5th Int. Charles Parsons Turbine Conf., Parsons 2000-Advanced Materials for 21st Century Turbines and Power Plant, Cambridge, UK, (2000), p. 847.
- [9] D. Monceau and B. Pieraggi: *Oxid. Met.* Vol. 50 (1998), p. 477
- [10] European program COTEST (RTD project N°: GRD1-2001-40037 M-T).
- [11] J. Angenete and K. Stiller: *Mater. Sci. Eng.* Vol. A316 (2001), p. 182
- [12] J.L. Smialek: to be published in *Acta Metall.* (2003).
- [13] N. Vialas: unpublished results, Deliverable WP4-D34, Allbatros program (2003).
- [14] B.A. Pint, P.F. Tortorelli and I.G. Wright: *Oxid. Met.* Vol. 58 (2002), p.73