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Numerical modelling of diffusion coupled with cyclic oxidation. Application to alumina-forming coatings used for industrial gas turbine blades.

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Abstract. A model using a finite elements code is developed to simulate degradation due to combined cyclic oxidation and interdiffusion in materials used in high temperature components of gas turbines. Coating recession due to cyclic oxidation (oxide growth and spalling) is also modelled using a statistical approach. Interdiffusion between coating and superalloy is modelled to predict total Al depletion in the coating. The phase transformations in the alumina-forming coating and the effects of the precipitates at the coating / superalloy interface are investigated. The results of simulations are compared with experimental data. Effects of diffusion parameters and of cyclic oxidation kinetics are discussed.

Introduction

Materials used in high temperature components of land-based gas turbines are subjected to mechanical stresses, high temperature oxidation and corrosion when low-grade fuels are burnt. Gas turbine efficiency requires the highest possible temperature but blade degradation due to creep and oxidation shortens its life. Ni based superalloys are widely used as turbine blades materials because of their good mechanical properties (creep and creep-fatigue). A protective coating is added at their surface to improve high temperature oxidation resistance. So far, coatings used for turbine blades are chosen for their oxidation-corrosion resistance: they form a protective oxide scale at the air/coating interface which decreases oxidation kinetics. During cooling, the large mismatch between oxide and coating thermal expansion coefficients induces stresses. The amount of stresses depends on many factors (temperature drop, temperature rate, oxide scale thickness...). The adherence of the oxide onto the coating is also difficult to assess depending on surface roughness, sulphur content... During thermo-mechanical cycling of the blade, spalling of the oxide is observed, accelerating oxidation kinetics. Different coatings are used on blades: overlay MCrAlY, diffusion aluminides or more recently thermal barrier coatings. For these systems, aluminium content in the coatings is large enough to ensure alumina formation and then to slow down oxidation kinetics. When spallation occurs, overlay MCrAlY and diffusion aluminides coating act as an aluminium reservoir and a new alumina scale is formed. Cyclic oxidation models have been developed [1-10] with simple assumptions to calculate the Al consumption due to cyclic oxidation (spalling and re-oxidation). The use of gas turbines for energy production or aeronautical applications, requires to identify, to understand and to model the mechanisms of degradation which take place in service conditions in these coating/Ni based superalloy systems. Many studies have been devoted to this subject [11-18]. The objectives of the European program ALLBATROS (Advanced Long Life

Blade Turbine Coating Systems) [19] were to increase the efficiency, reliability and maintainability of industrial gas turbine blades. The hot parts (900-1100°C) of these turbines are subjected to strong thermal and mechanical requests. Innovative coatings proposed during this program were characterized and compared to existing coating/superalloy systems. Long term cyclic oxidations (35*300h at 1050°C) have given valuable information on the chemical and microstructural evolution of the studied systems. Degradation due to long term cyclic oxidation tests have been investigated [20-23]. For the studied systems, it was shown that Al depletion in the coating was due to oxidation and spalling of the protective oxide but also that the contribution of Al diffusion from the coating toward the substrate was a key element in life assessment. That is the reason why the present study focuses on numerical modelling of combined diffusion and cyclic oxidation of alumina forming systems. Coupled oxidation-diffusion calculations using the finite difference methods have already been performed by Whittle in 1972 [25], then by Nesbitt [26-27]. Finite element calculations of oxidizing zirconium alloy have already been carried out taking into account diffusion [28]. However, the originality of the simulations presented here is to model in the same calculations cyclic oxidation (oxide growth and spalling), interdiffusion between the coating and the substrate, coating recession (mobile boundary) and precipitates effects. Furthermore, calculations are compared to experimental data.

Materials and experimental results

The materials of the present study are composed of two different Ni-base superalloys coated with two Pt modified aluminides (RT22 developed by pack cementation and CN91 developed by chemical vapour deposition). These systems are RT22/IN792, RT22/CMSX-4, CN91/CMSX-4, and CN91/IN792. IN792 is a polycrystal alloy whereas CMSX-4 is a single crystal. The experimental database for these systems comes from long term cyclic oxidation tests performed in laboratory air at 1050°C. Cycle duration was 300 h.

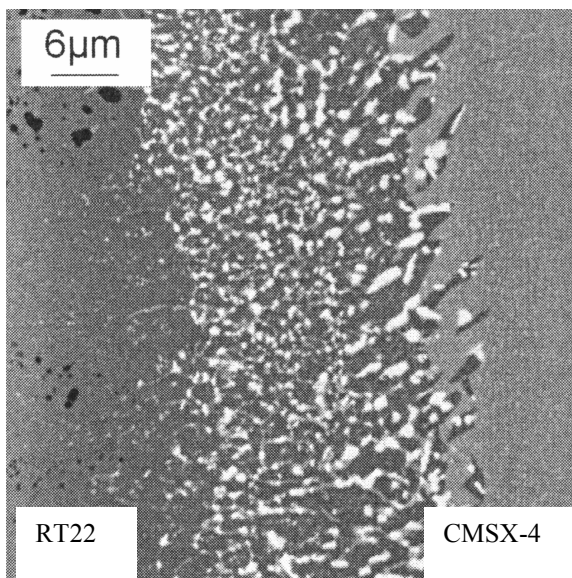


Fig. 1. SEM observation of RT22/CMSX-4 cross section before cyclic oxidation showing precipitates at the coating/superalloy interface[21]

The Net Mass Change (NMC) curves of these oxidation tests have been reported elsewhere [20-23]. The shape of these curves is characteristic of the competition between oxidation (mass gain) and spallation (mass loss). The microstructure of the oxides formed as well as the evolution of the microstructure of the coating have been studied at different stages during the cyclic oxidation, including SEM, XRD and cross-section observations followed by chemical analysis (EDS: Energy Dispersive X-ray Spectroscopy). These concentration profiles came from different samples of each studied system removed from the furnace after 6 cycles, 17 cycles or 35 cycles of 300 h. Concentration profiles are available for each system and their evolution during cyclic oxidation were used to test the accuracy of the model.

Methods applied for the numerical simulations

The nickel base superalloys of this study have a smaller Al content (8-12at%) than the coating (>45at%). Turbine blades operate in temperature range where interdiffusion cannot be neglected. During coating processing, Ti, Ta, Cr and Mo diffusion from the substrate towards the coating leads to the formation of precipitates at the coating/superalloy interface (Fig. 1). We will not take into account the influence of platinum content on interdiffusion. In the numerical simulations detailed in this paper, the problem of the diffusion of Ti, Ta, Cr has to be considered. In fact, as long as the coating is not transformed into γ -Ni, these species are primarily present in precipitates (Fig. 1) at the coating/superalloy interface. As long as these precipitates remain stable, there is no need to calculate the diffusion of these various elements. So, diffusion simulation will take into account only Al and Ni. However, we will show how simulations confirm the active role of these precipitates during interdiffusion. Then, simulations will be modified as detailed later to take this phenomenon into account.

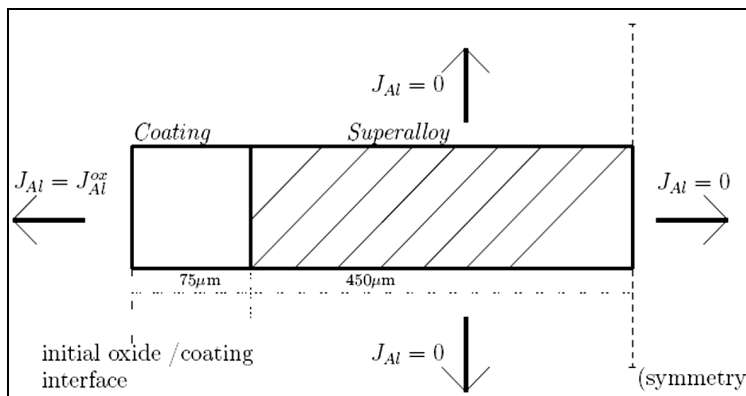


Fig. 2.: Scheme of the boundary conditions used for FE diffusion calculations

The numerical simulations carried out in the present study also need to take into account coating recession due to oxide formation and partial oxide scale spallation during cycles. The cyclic oxidations of the systems observe during this study induced significant Al consumption at the oxide/coating interface. To illustrate that point, 7 μ m of the 75 μ m thick coating is consumed in the RT22/IN792 system after 6 cycles of 300h at 1050°C.

A probabilistic model [7] is chosen to model the cyclic oxidation kinetics. This model is used as a boundary condition (Al flux lost by the coating due to cyclic oxidation) in the finite element calculations. The 2-D Finite Element simulations are performed with the Finite Element code CAST3M [24]. Fick's equation is solved for Al with an interdiffusion coefficient (\tilde{D}_{Al}) depending on Al content in order to take into account the dependence of interdiffusion coefficient on Al content in β -NiAl and phase transformations.

Initial conditions. Heat treatments are carried out during coating processing and these treatments give the initial microstructure of the system. This microstructure and chemical composition associated have been characterised using SEM and EDS. These initial profiles (reduced to Al/ Ni ratio) are introduced in the model as initial condition.

Boundary conditions. As the effect of the precipitates will be investigated, a 2-D Finite Element (FE) simulation is chosen with the boundary condition illustrated in Fig. 2: Fluxes equal zero at the centre of the superalloy and on each side. At the coating / oxide interface, Al flux is given by the cyclic oxidation model so oxide is not meshed.

Cyclic oxidation modelling

The experimental NMC curves are given in Fig. 3 [21-22]. For the four systems reported in this study, during the first 30 cycles, oxide scale is mainly (but not only) α -alumina. The p - k_p cyclic oxidation model [7] is used. Only two parameters are to be identified (Table 1), a spalling probability p corresponding to the mass proportion of the oxide scale spalled at each cooling and the parabolic constant k_p , which characterizes the oxidation kinetics during high temperature dwells. This model is relevant when the nature of the oxide formed remains constant. It allows us to calculate not only the Net Mass Change but also the metal consumption as a function of the number of cycle ($Met(n)$). These values are the fourth boundary condition of the FE calculation.

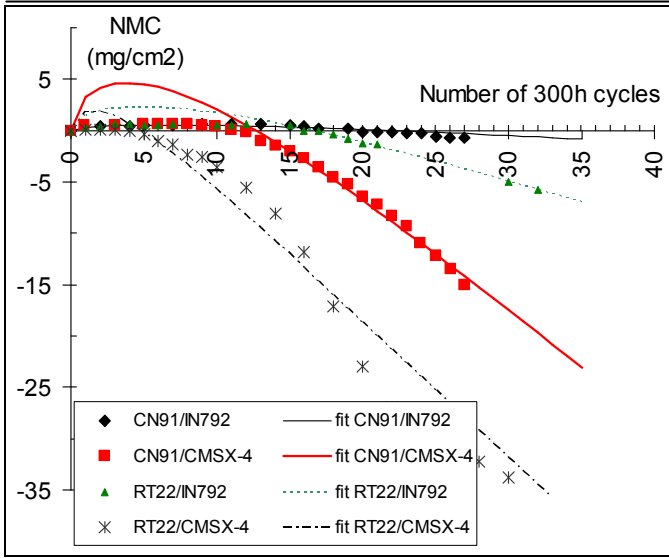


Fig. 3. Net mass change at 1050°C of each coating systems during cyclic oxidation in laboratory air (35 cycles of 300h corresponding to 10,500h)

The p - k_p model gives the values of Al consumption per cycle (mass per unit of area in mg/cm^2) at each cycle.

In the FE simulations (see Fig. 2), the outgoing Al flux $J_{\text{Al}}^{\text{ox}}(n)$ due to cyclic oxidation is taken constant during each cycle and equals the Al consumption at the cycle n , i.e. $Met(n)$ divided by the duration of the cycle Δt ($\Delta t = 300\text{h}$). So $J_{\text{Al}}^{\text{ox}}(n) = \frac{Met(n)}{\Delta t}$.

Table. 1 Cyclic oxidation modelling for several systems

System	CN91/IN792	CN91/CMSX-4	RT22/IN792	RT22/CMSX-4
p	0.05	0.11	0.065	0.185
k_p [$\text{mg}^2\text{cm}^{-4}\text{s}^{-1}$]	$1.1 \cdot 10^{-7}$	$8 \cdot 10^{-6}$	$1.8 \cdot 10^{-7}$	$8.3 \cdot 10^{-6}$

During the simulations, the calculation of the Al consumption is carried out once at the beginning of the program and the results used during the former steps (See Fig. 4).

Coating recession. Re-meshing is time consuming and error generating, so the re-meshing step has to be optimised.

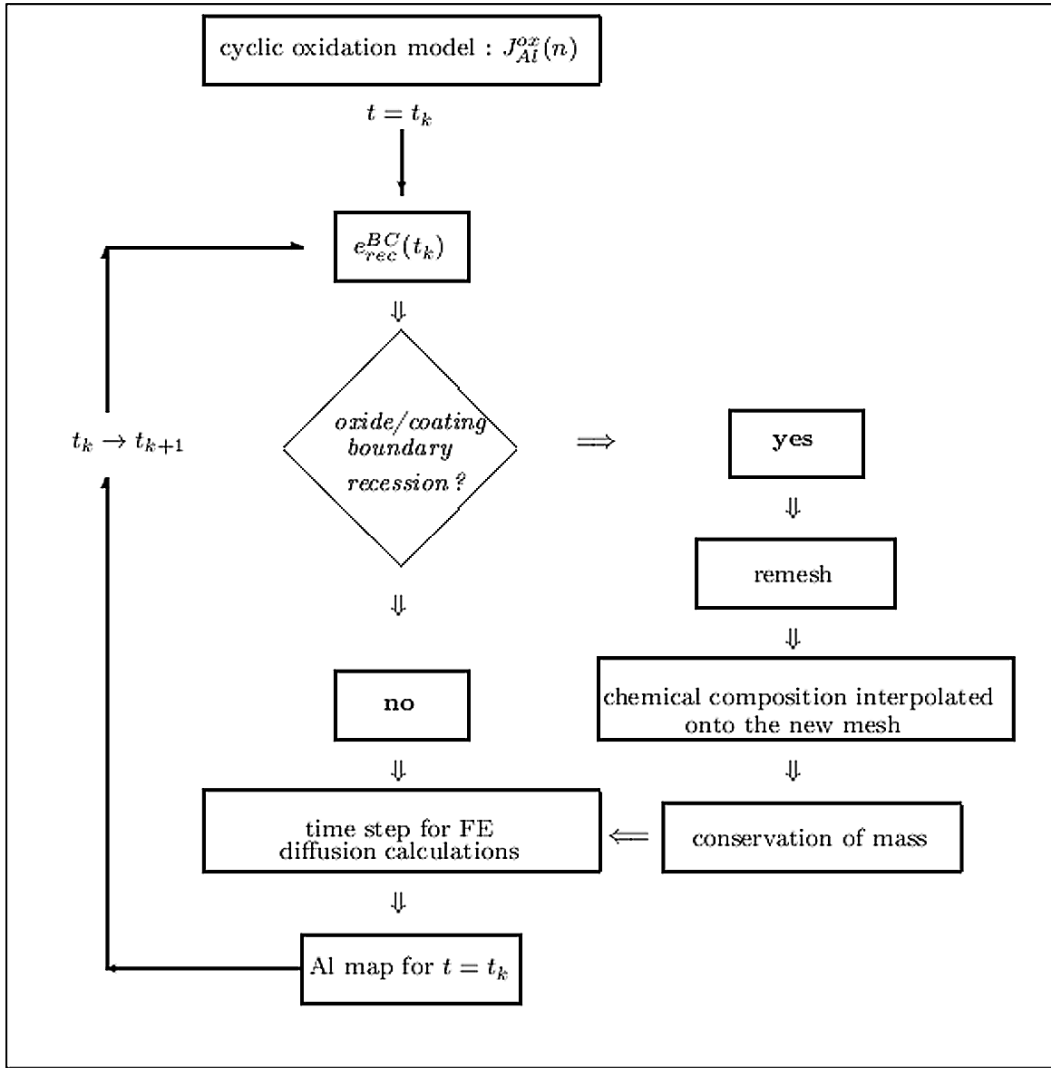


Fig. 4. Scheme of the algorithm used to model coating recession

To limit the numerical errors during remeshing due to the interpolation of Al content at each node of the new mesh, coating recession (and then remeshing) occurs for a chosen step $\Delta\epsilon$. Different values from $0.2 \mu\text{m}$ to $2 \mu\text{m}$ have been tested for $\Delta\epsilon$. The simulation is carried out with the same mesh until the coating recession is more than the chosen step. The value $\Delta\epsilon=0.5 \mu\text{m}$ was chosen for the simulations, offering a good compromise between precision and computation time. Fig. 4 summarizes the algorithm used for these combined simulation of interdiffusion and cyclic oxidation.

The coating recession $e_{\text{rec}}^{\text{BC}}(t)$ is calculated as follows using the input of the cyclic oxidation model:

$$e_{\text{rec}}^{\text{BC}}(t) = A \left\{ \sum_{j=1}^{j=n} J_{\text{Al}}^{\text{ox}}(i) + \frac{t - n\Delta t}{\Delta t} J_{\text{Al}}^{\text{ox}}(n+1) \right\} \quad (1)$$

with $A=2.84 \cdot 10^{-7} \text{m}^3 \text{s g}^{-1}$. This value is calculated using the theoretical density for stoichiometric β -NiAl as an approximation for the coating density.

Diffusion calculations. The approach was very simplified as it takes into account only Al and Ni contents. Nevertheless, Fick's equation is solved for Al with a diffusion coefficient depending on Al content. Indeed, diffusion of Al in β -NiAl and γ' -NiAl is strongly dependent of Al content. Data are available in the literature [29-31]. A simplified piecewise linear function for Al interdiffusion coefficient was chosen. Data are given in Table 2. This way was chosen in order to take into account phase transformations through severe \tilde{D}_{Al} variations.

Table.2 Piecewise linear function for Al interdiffusion coefficient

Al at%	0	7	19	29	36	40	48
\tilde{D}_{Al} [$10^{-14}m^2/s$]	2.	2.	0.3.	0.3	0.3	0.1	0.03

Results

Without taking into account precipitates at the coating/superalloy interface. Simulations were carried out on CN91/CMSX-4 system. Comparisons between calculated Al profile and experimental data shows (Fig. 5, curve "simu1") that simulation did not manage to account for the profile (strong decrease) at the coating/superalloy interface. In fact, the precipitates evidenced (Fig. 1) act as a diffusion barrier. For the 4 systems studied, EDS analyses carried out for 6 and 15 cycles show that Al distribution does not follow a classical fickian diffusion profile. It was then necessary to take into account this diffusion barrier.

Taking into account precipitates

The first method consists in introducing holes in the mesh with a surface fraction (30%) and a localisation corresponding to the SEM cross section observations (Fig. 6). In fact the size and distribution of precipitates evolve during the oxidation but the surface fraction measured with the SEM on cross section remains roughly constant as long as Al content in the coating is not lower than 7at% [21]. When the simulations are performed with this diffusion barrier, results (Fig. 5 curve "simu2") are in better agreement with experimental data. However, meshing the precipitates did not seem to be sufficiently simple to be used by industrial partners. We thus propose an intermediate solution easier to implement. The precipitates zone acts as a diffusion barrier for Al. As the precipitates increase the tortuousness of diffusion path, we simply applied a penalization coefficient on

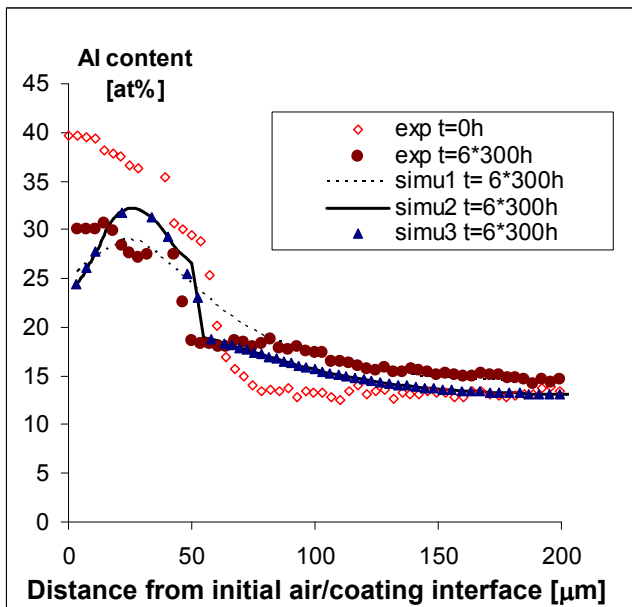


Fig. 5. CN91/CMSX-4, Al profiles from simulations compared with experimental data.

the diffusion coefficient in the zone where precipitates are located. So a particular zone has been defined in the mesh between 55 and 75 μm from the initial coating surface where a reduction of the interdiffusion coefficient (shadow mask effect) was imposed (ratio \times so \tilde{D}_{Al} becomes $\times \tilde{D}_{Al}$).

Different values of x have been tested in order to get the same results than previously. The value $x=0.3$ has given good results on systems CN91/CMSX-4 (Fig. 5 curve “simu3”) and RT22/IN792 after 6 cycles of 300h. This value and this method have been chosen for all the other simulations. A more detailed study might be undertaken to correlate x with the volume fraction of precipitates in each system.

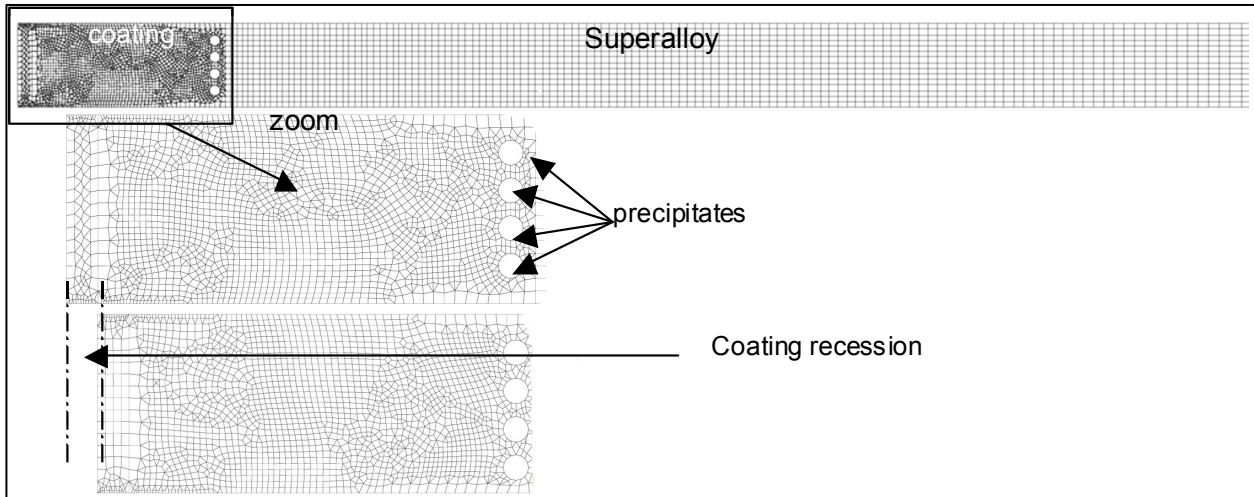


Fig. 6. Mesh used for 2D FE simulation taking into account precipitates at the coating/superalloy interface and coating recession.

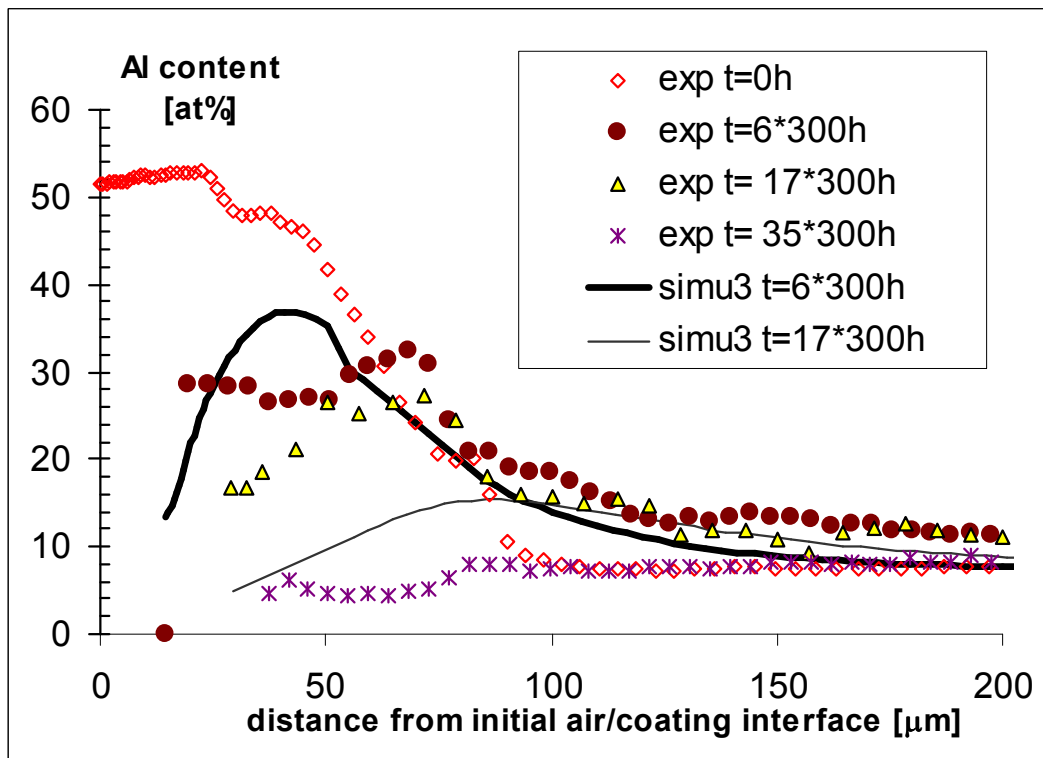


Fig. 7. RT22/IN792, calculated Al profiles compared with experimental data

Discussion

Haynes *et al.* [32] and Vialas *et al.* [20-23] have shown that the superalloy substrate influences the oxidation behaviour of aluminide bond coating. These observations are related to coating composition changes due to interdiffusion and to related phase transformations. Simulations may help to understand these effects. However, comparison between the calculated results obtained in the present study and the experimental data shows that improvements are still required. Al depletion

due to cyclic oxidation kinetics (J_{Al} flux on Fig. 2) is modelled using the p- k_p model and tends to overestimated oxidation kinetics and spalling during the first ten cycles as seen on see Fig. 3. As the outward flux of Al is overestimated, the Al concentration decreases faster to the γ composition and \tilde{D}_{Al} , the diffusion coefficient of Al increases drastically (Table 2). In reality, the coating remains β phase with slow Al diffusion during a longer time than in the simulation. Furthermore, experimental results reveal an increasing amount of spinels in the oxide scale. These changes in oxidations kinetics are not yet taken into account in the simulations. As the nature of oxide formed depends on the Al contents just beneath the oxide scale, such simulations could be performed with the present simulation code. Diffusion calculations have also been extremely simplified: the materials composition was reduced to a Al-Ni binary system. Phase transformations have been taken into account only through sharp variation of Al interdiffusion coefficient (\tilde{D}_{Al}). For the four studied system, experimental data on Al profiles in the coating are always flatter than the calculated ones. This is partly due to the fact that phase transformation and equilibrium between phases is not simulated. Both CN91 and RT22 coatings contain a large amount of Pt. Several studies [33-37] have been devoted to the effect of Pt contents on diffusion and/or oxidation in PtNiAl alloys. Taking into account Pt content effects requires to take into account the diffusion under an activity gradient in the ternary system PtNiAl. The use of Al content does not take into account that Pt decreases the chemical activity of Al [36] because the chemical bond between Al and Pt is stronger than that between Al and Ni.

Conclusion

Numerical simulations have been carried out to predict Al content in the coating and especially, beneath the oxide scale in four different superalloys coated platinum modified aluminide systems. These coupled simulations of cyclic oxidation kinetics and interdiffusion include many simplifying assumptions. They can now be refined by removing the more penalizing ones. Improvements are to be tested like refining the modelling of the outgoing aluminium flow i.e. cyclic oxidation kinetics and improving diffusion calculations. However, to our knowledge, this type of calculations taking into account cyclic oxidation kinetics, coating recession, interdiffusion and the effects of precipitates at the coating/superalloy interface represent an improvement on existing oxidation/interdiffusion modelling. Later on, only a flexible approach as that permitted by CAST3M will enable us to introduce the mechanical stresses that intervene on the diffusion and the transformations of phases and on oxide scale spalling. These points would be perhaps to take into account. A good knowledge of the thermomechanical loadings and properties of the materials (superalloy, coating in its various phases and alumina) are then necessary

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