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- The empirical c_{Al} based criterion is unable to properly predict the formation of a continuous α -alumina in MCrAlY coating.
- An Al-activity based MCrAlY coating life criterion is proposal and validated.
- Interdiffusion between coating and substrate during oxidation had a strong effect on coating microstructure evolution.

Long-term oxidation of MCrAlY coatings at 1000 °C and an Al-activity based coating life criterion

Pimin Zhang^{*1}, Kang Yuan¹, Ru Lin Peng¹, Xin-Hai Li², Sten Johansson¹

1 Department of Management and Engineering, Linköping University, SE-58183 Linköping, Sweden

2 Siemens Industrial Turbomachinery AB, SE-61283 Finspång, Sweden

*Corresponding author: pimin.zhang@liu.se

Abstract

MCrAlY type (M=Ni and/or Co) coatings are widely used for the protection of components in the hot sections of gas turbines at high service temperatures by forming a continuous α -alumina. A reliable criterion to estimate the capability of coating to form α -alumina is of great importance to accurately evaluate coating lifetime. However, some coatings retain the ability to form a continuous α -alumina scale when the concentration of Al in coatings decreases to a critical level, therefore, the empirical Al-concentration based criterion is inadequate to properly predict the formation of a continuous α -alumina. Thus, a new life criterion, namely the critical Al-activity criterion, is proposed.

In this work, the critical Al-activity to form a continuous α -alumina was validated by Al-activity calculation using Thermo-Calc software based on survey of research results of critical Al-concentration to form α -alumina on binary Ni-Al and ternary Ni-Cr-Al system. Long-term oxidation tests were performed to support the criterion: three different MCrAlY coatings coated on

IN-792 superalloy substrates were oxidized at 1000 °C for various periods of time up to 10,000 hours. The microstructural evolution of MCrAlY coatings was investigated using Scanning Electron Microscope. The near-surface Al concentration and interdiffusion behavior between substrate and coating were measured using Energy Dispersive X-ray Spectroscopy. The new critical Al-activity criterion has been successfully adopted in α -alumina formation prediction, showing a good agreement with experiment results. Therefore, it can be concluded that the extrapolation of new criterion from binary and ternary systems to multi-alloyed MCrAlY system is reasonable. Furthermore, the partial pressure of oxygen (P_{O_2}) in atmosphere has been taken into consideration by combination with Al-activity to calculate the critical chemical reaction constant (K) of formation of α -alumina. The potential applicability of the methodology to predict MCrAlY life is also discussed.

Keywords: MCrAlY, Al-activity, α -alumina, life criterion, long-term oxidation.

1. Introduction

MCrAlY (M=Ni and/or Co) coatings have been widely used to protect blades and other hot gas path components in gas turbine engines made of Ni- and Co-based superalloys, and they also provide protection as bond coat in thermal barrier coating (TBC) systems [1–5]. During high temperature exposure, a thin layer of protective α -Al₂O₃ formed on the coating surface, which serves as a diffusion barrier between the environment and underlying alloy [6]. A slow growth of dense α -Al₂O₃ layer and its adhesion to the bulk coating without spalling excessively are the key factors to provide protection against oxidation. The β -NiAl phase in MCrAlY coating is considered as Al-reservoir and its presence can supply Al needed to maintain the α -Al₂O₃ scale. Two reactions

contribute to the depletion of β -NiAl phase in coating during oxidation, including: (1) the growth of α -Al₂O₃ in coating/gas interface; (2) inward diffusion of Al from MCrAlY coating to substrate due to the chemical difference of Al between MCrAlY coating and superalloy substrate.

The depletion rate of β phase in MCrAlY has been used as a criterion by many investigators [7–11] to evaluate the end of coating lifetime. However, the complete depletion of β phase doesn't necessarily mean the end of coating life. It was indeed observed that some Ni-Al and Ni-Cr-Al alloy systems with no beta phase presence maintain the ability to provide protection [12–14]. Some researchers have found from empirical studies that the concentration of Al in a range of 4-6 wt. % is often sufficient to maintain α -Al₂O₃ scales and thus to provide adequate oxidation resistance [15–17]. In such cases, the complete depletion of β phase is obviously not an adequate coating life criterion. Furthermore, the empirical Al concentration criterion also has its limitation; the minimal Al concentration required by a continuous α -Al₂O₃ scale varies with coating composition. A more sophisticated model is therefore required. Sato et al. [18] developed and validated a model to predict the ability to form a continuous Al₂O₃ scale on nickel-based single-crystal superalloys during thermal exposure. The model using Gibbs free energy of oxide formation as criterion can be adapted to different Ni-based superalloy systems, which overcomes the limitation using the critical concentration criterion. Considering the chemical composition of superalloys, MCrAlY coatings are also Ni and/or Co based alloy system, similar criterion could be applied in the case of MCrAlY coating. A new approach using critical Al activity calculated from the Gibbs free energy of alumina formation can be used to predict the formation of a continuous Al₂O₃ scale on MCrAlY coating. The Ellingham diagram is useful to derive the Gibbs free energy of alumina formation. The Al activity in different alloy system can be calculated by Thermo-Calc software [19].

In this paper, the performance of several MCrAlY coatings for long-term oxidation was investigated to study the coating behaviour near the end of coating life. The microstructural development in the MCrAlY coatings for long oxidation time is described. A new criterion to evaluate the oxidation life of MCrAlY coatings was presented and compared with empirical Al-concentration based criterion. The predictions using new Al-activity criterion are compared with experimental data reported here and also with those available in the literature.

2. Experiments

The material systems studied in this work were three MCrAlY coatings deposited on Inconel 792 substrate (composition by wt. %: 12.5 Cr, 9 Co, 4.2 W, 4.2 Ta, 4 Ti, 3.4 Al, 1.9 Mo 0.08 C, 0.03 Zr+B, balanced by Ni), using the High Velocity Oxygen-fuel (HVOF) spraying technique. The HVOF coatings were produced using JP5000 HVOF spray system. The composition of the coatings measured by EDS is listed in Table 1. The thickness of the coatings was in a range from about 150 to 200 μm . The heat treatment performed on the samples included a 2 hours solution treatment at 1120 °C in vacuum and an ageing process at 845°C for 24 hours in air. Such a heat treatment, which is intended for strengthening the IN-792 substrate by refining γ' precipitates distribution and size [20], also increases the bond strength between the coating and substrate and produces dense coatings with porosity less than 1% [21].

Long-term oxidation of the samples was carried out at 1000 °C up to 10,000 hours in lab air. The samples were cross-sectioned and carefully polished to investigate the microstructures in the materials. Optical microscope and scanning electron microscope (SEM) Hitachi SU70 were used. Energy-dispersive spectroscope (EDS) equipped in the SEM was applied to measure the chemical

composition in the samples. For the acceleration voltage, 20 KV, used in this work, the spatial resolution of point EDS measurement for aluminium is around 3 μm but less than 3 μm for other elements with higher atomic number.

The Al activity of given compositions in different alloy systems investigated in this study is calculated using Thermo-Calc software [19,22]. In thermodynamic, activity is a measure of the “effective” concentration of a species in the system which can be used to define equilibrium constant [23]. The calculation of element activity in equilibrium is identical to evaluating partial derivatives of total Gibbs energy with respect to variables at thermodynamic equilibrium as described in ref [24]. This is performed by solving Lagrangian multipliers of the equilibrium calculation optimization problem in Thermo-Calc software [23]. And it is worth to mention that total Gibbs energy is a function of all elements in the system, indicating Al activity calculation in Thermo-Calc software also depends on other elements in the system. The workflow used in this study are described in Fig. 1: 1) EDS measurement of composition in interested area; 2) define alloy system with composition obtained from step 1 and temperature as a condition in equilibrium module ‘POLY’; 3) calculate equilibrium of current system by minimization of total Gibbs energy derived from thermodynamic database (TCNI8) using Thermo-Calc software; 4) calculate Al activity based on the equilibrium from step 3. For the evaluation of Al activity as a function of oxidation time, the time dependent composition changes are also considered.

3. Results and Discussion

3.1. Microstructural evolution in coating A, B, and C

High temperature oxidation behaviour of the MCrAlY coatings (coating A, B and C) has been studied in our previous work [25], but only in short time (less than 5000 hours at 1000 °C). This

section will discuss the microstructural evolution in the coatings for a longer oxidation time up to 10,000 hours.

Microstructure of the as received coatings contains a solid solution phase, γ , and an intermetallic phase, β , while the main phases in the substrate are γ and an intermetallic γ' . Due to the consumption of Al in coating during oxidation, the β phase (high Al content) transforms into γ' (medium Al content) or γ (low Al content) following:

while the stability of γ' phase in coating depends on coating composition. If the γ' phase is not stable in the coating, the β phase would transform into γ -phase directly. Al consumption generates an outer- β -depletion zone (OBDZ) below the oxide scale, whereas loss of Al through diffusion to the substrate results in an inner- β -depletion zone (IBDZ) next to the coating-substrate interface.

General microstructure of coatings A, B, and C oxidized for 2,000 and 10,000 h are illustrated in Figs. 2-4, respectively. The average compositions of main elements (Ni, Co, Cr and Al) of various areas indicated by the square bracket using EDS area measurement are displayed on the right side of the figures. Coatings A-C have a disordered FCC γ -phase matrix containing precipitates such as ordered BCC β -phase, ordered FCC γ' -phase, MC-type carbides rich in Ti and Ta (denoted “c”), and detrimental TCP σ -phase. The original coating and substrate interface are marked by dash line.

Near the coating and substrate interface, a complex interdiffusion process occurred. The activity gradient of elements between coating and substrate induced element interdiffusion, including inward diffusion of Co, Cr and Al from coating to substrate and outward diffusion of Ni, refractory elements such as Ta, Mo, W, and γ' -stabilizer Ti from substrate to coating. The

microstructure near interface evolved as the interdiffusion occurred, whose development in the current systems was highly related to the content of Co and Cr in the coatings [26,27]; the high concentration of Co and Cr in coating enhances the diffusion of Co and Cr from coating into substrate. It also destabilizes γ' and stabilizes β phase [25,28].

As shown in Fig 2a, with the low-Co-Cr coating A, no obvious γ' depletion was found in the substrate near the coating/substrate interface, thus, γ' was stable in the substrate. As the oxidation process continued, γ' was even stabilized in the IBDZ in coating A. These observations again prove the above mentioned effect of the Co and Cr activities. In contrast, as shown in Fig. 3a and 4a, β phase reprecipitated in the substrate near coating/substrate interface due to the inward diffusion of Co and Cr from the high-Co-Cr coating B and C.

As shown in Fig. 3a and 4a, β phase reprecipitated in the substrate near coating/substrate interface due to the inward diffusion of Co and Cr from the high-Co-Cr coating B and C. While with the low-Co-Cr coating A, no γ' depletion was found in substrate near coating/substrate interface, thus, γ' was stable in the substrate (Fig. 2). As the oxidation process continued, γ' was even stabilized in the IBDZ in coating A.

With coatings B and C, the inward diffusion of the relatively larger amount of Co and Cr added to the formation of (Ta,Ti)C carbides in the γ' -depletion zone in the substrate, and according to

(Ta,Ti)C carbides were observed to distribute along splat boundaries as shown in Fig. 5.

The formation of the carbides in the coatings was due to the outward diffusion of Ta, Ti and C from the substrate, and the low solubility of Ta and Ti in the Co-Cr-rich γ phase in coating B

and C contributed to the carbides formation as well [29,30]. In coating A, the outward diffusion of Ta and Ti also occurred, but the elements Ta and Ti can be fully dissolved into the Ni-rich γ and γ' phase in the IBDZ of coating A. Other elements from substrate like W and Mo were detected in γ phase in the coatings and the concentration of those refractory elements near the coating surface reached about 1 to 2 wt. % after 10,000 hours.

3.2. Al-activity based criterion

3.2.1. Empirical Al-concentration based criterion and Al-activity based coating life criterion

Fig. 6 gives the development of the Al concentration near the coating surfaces in the oxidation process measured by EDS. At the beginning of the oxidation, due to the consumption of Al in oxidation, the microstructure near coating surface transformed from a mixture of β and γ phases to single γ phase. The Al concentration near coating surface quickly dropped down to about 3~5 wt. % (Al content in γ phase) from the original coating Al content (average Al content of β and γ phases mixture). Later then, the Al concentration became stable when the γ phase reached equilibrium statues. After 2000 hours oxidation, the β phase near coating surface was depleted completely, forming an OBDZ zone with a thickness around 20 microns. The Al concentration in coatings A, B and C near coating surface was about 4.4 wt. %, 3.9 wt. % and 3.4 wt. %, respectively, which mainly depended on the equilibrium composition of γ phase at 1000 °C. In this case, the Co and Cr contents are the main factors that decided the Al content in γ phase. The Al activity calculated using Thermo-Calc software in Fig. 7 shows that coating C with a lower surface Al concentration, however, owned a higher Al activity. D. Renusch [31] suggested ~3 wt. % as the critical Al content, $c_{Al,cri}$, marking the end of MCrAlY coating life; $c_{Al,cri}$ can be defined as the Al content below which a continuous alumina scale can no longer be formed. The value of $c_{Al,cri}$, however, was alloy

composition dependent. For instance, the $c_{Al,cri}$ for Ni-Al alloys was about 20 wt. %, while the $c_{Al,cri}$ value decreased to about 5 wt. % in Ni-Cr-Al alloys with 5 wt. % Cr [32].

The oxidation of Al from the MCrAlY coatings can be represented by

and the Gibbs free energy of formation of alumina can be expanded consistent with the Van't Hoff isotherm [19,33] according to

$$\Delta G = \Delta G^0 - RT \times \ln \left(\frac{a_{Al_2O_3}^{\frac{2}{3}}}{a_{Al}^{\frac{4}{3}} \times \frac{P_{O_2}}{P_{O_2}^0}} \right) = \Delta G^0 + RT \times \ln \left(a_{Al}^{\frac{4}{3}} \times \frac{P_{O_2}}{P_{O_2}^0} \right), \quad \text{Eq.4}$$

where ΔG is Gibbs energy change of the reaction in kJ/mol, ΔG^0 is standard Gibbs energy formation of alumina in equilibrium reaction, R is gas constant, T is temperature in Kelvin, a_{Al} is Al activity, $a_{Al_2O_3}$ is Al_2O_3 activity (commonly taken to be unity), P_{O_2} is oxygen partial pressure of oxidizing atmosphere, and $P_{O_2}^0$ is the standard pressure, equals to 1 bar. Eq. 4 can be transformed into a simplified Arrhenius type equation to calculate the critical Al activity of alumina formation

$$a_{Al} = A * \exp \left(-\frac{\Delta G}{RT} \right), \quad \text{Eq. 5}$$

where A is a mathematic constant.

For the oxidation of pure Al, ΔG^0 can be derived from Ellingham diagrams [34]. However, the Ellingham diagrams are not applicable to complicated systems such as quaternary alloys [35] as ΔG^0 also depends on the existence of other alloy elements. In the case of oxidation of Al in MCrAlY alloy system, the construction of a more general criterion is necessary. Normally, activities are used to define equilibrium constants of a system but, in practice, concentrations are often used instead

[36]. Using Al concentration c_{Al} to replace a_{Al} in Eq. 5 is equivalent to the use of aforementioned empirical $c_{Al,cri}$ based criterion. To further test the criterion defined by $c_{Al,cri}$, oxidation results of Ni-Al and Ni-Cr-Al alloys from literature [12–14,37–40] are collected (Table 2) and examined. Fig. 8 shows the Al concentration of the alloys (plotted on a log scale) in relation with their ability (able or unable) to form continuous alumina scales at high temperatures. The data are categorized into three groups: □ Y) alloys able to form a single scale of alumina, △ M) alloys able to form an alumina scale with other oxides outside, ◇ N) alloys unable to form a continuous alumina but with the formation of severe internal alumina. Note that some of the included oxidation tests were not performed in ambient air. The critical Al content for forming a continuous alumina scale can be as low as 2 to 4 wt. %, however for some alloys while for some others it can be much higher. Thus, it's difficult to mark a boundary of critical Al concentration of alumina formation, indicating temperature and compositional effects are not represented in $c_{Al,cri}$ criterion and an empirically critical Al concentration alone is not sufficient for evaluating the life of the wide composition range of nickel based coatings.

On the other hand, the work by Hughes [41] and Nicoll [35] indicated that the Al activity which is temperature and chemical composition dependent, appeared to be a more suitable criterion for oxidation life in multiple component systems. Hughes [41] showed that boundary between the formation of a continuous scale and internal oxidation can be characterized by the activity of the oxidizing element in the alloy. Nicoll et al. [35] interpreted the Gibbs energy of oxide formation boundary between the continuous alumina in MCrAlY and mixed oxide scales. Al activities are calculated for those alloys shown in Fig. 8 and plotted in Fig. 9. It should be noted that as a considerable oxidation life still remains for some alloy systems (they did not approach the end of their oxidation life) the data appeared to be scattered in group 'Y'. The Al-activity criterion

obviously shows a better ability to define the boundary separating the zones to form continuous or discontinuous alumina scales than the Al-concentration criterion. Due to the limitation of the data from literature, the real boundary of minimum activity of alumina formation at certain temperature could not be reached yet, thus, a more reasonable approach is to use a strict criterion to evaluate coating life, i.e., the lower boundary (the minimal Al activity) for the formation of a continuous alumina scale. Corresponding data points were then identified in Fig. 9, as indicated by arrows, and a linear function was fitted to those points to determine the lower boundary. From the fitting, the critical Al activity is expressed as following:

$$a_{Al,cri} = \exp(-10235/T - 11.1). \quad \text{Eq.6}$$

The determined lower boundary is plotted in Fig. 9 as dash line. The result suggests that nickel-based coating life is controlled by Al activity; when the Al activity near the coating surface drops below a critical Al activity, $a_{Al,cri}$, a continuous alumina scale is unable to form, meaning the end of coating life. This approach to use Al-activity as a coating life criterion is therefore more reasonable.

Using the same approach used for Ni-Cr-Al alloys in Fig. 9, the boundary to form a continuous α -Al₂O₃ based on Al activity was derived from experimental results in the literature for Co-Al alloys [42] and superalloys [43]. Their comparison with the previously derived boundary for the Ni-Cr-Al alloy in Fig. 10 indicates that Eq. 6 could not be applied to alloys whose chemical composition is too different from Ni-Al and Ni-Cr-Al systems. In general, the activity depends on the factors that alters the chemical potential including: concentration, temperature, interaction between chemical species, etc. [23]. Due to the large difference of chemical composition between Ni-(Cr)-Al alloys, Co-Al alloys, and superalloys system, the interaction of Al with other elements

differs in different systems, which alters the critical Al activity boundaries accordingly, as shown in Fig. 10. In the Co-Al alloy system, the influence of Co on Al shifts the chemical potential of alumina formation, which drives the critical Al activity boundary upward. As for Ni-based superalloys system, the presence of many other refractory elements in different superalloys modifies chemical potential of alumina. Thus, the critical Al activity boundary for Ni-based superalloys becomes a broad area instead of a line. Therefore, Eq. 6 which is obtained mainly based on data of Ni-Al and Ni-Cr-Al alloys is expected to be applicable for nickel based alloys like NiCrAlY and MCrAlY.

Some researchers have suggested that the formation of a layer of continuous alumina scale was also affected by the oxygen partial pressure (P_{O_2}) of oxidizing atmosphere for MCrAlY [44–46]. In the equation (Eq. 4) which was used to calculate the critical aluminum activity for the formation of alumina in the equilibrium reaction, P_{O_2} was taken into account. $a_{Al}^2 * P_{O_2}^{3/2}$ or $a_{Al} * P_{O_2}^{3/4}$ can be integrated as chemical equilibrium constant $K = a_{Al} * P_{O_2}^{3/4}$. The critical chemical equilibrium constant K can be derived. Since some oxidation test from literature were not performed in ambient air, the boundary of $a_{Al} * P_{O_2}^{3/4}$ product slightly shifted and the critical chemical equilibrium constant K is then expressed as following:

$$K_{Al,cri} = \exp(-9441/T - 13.05). \quad \text{Eq.7}$$

The result suggests that the incorporation of oxygen partial pressure with Al activity into the critical chemical equilibrium constant may also be used as life criterion to predict the MCrAlY coating life when the oxygen partial pressure during oxidation is different from the atmospheric oxygen partial pressure.

3.2 An application of the Al-activity based coating life criterion

To test the Al-activity based MCrAlY coating life criterion, the oxidation time should be long enough to reach the near end of coating life. Our previous research has suggested that the addition of hafnium in MCrAlY coating can accelerate the aluminum oxidation [25]. As shown in Fig. 11, the near-surface aluminum concentration of two Hf-containing coatings (A1 and B1) was compared with their reference coatings (A and B). By focusing on the longer time range of these curves from 2000 to 10000 hours, coating A1 and B1 have a clear aluminum concentration drop with time, however, the aluminum concentration in the coatings reaches a threshold value of 4.3 wt. % for coating A and 3.1 wt. % B. If using 3 wt. % as the critical aluminum concentration for chemical-failure based coating life evaluation, the lifetimes of coating A1 and B1 were about 6000 hours and 4000 hours, respectively. However, according to the shape of the curves of coating A1 and B1, the decreasing trend of aluminum concentration near the coating surface was smooth at 6000 hours and 4000 hours. Furthermore, the result in Fig. 12 which presents how deep aluminum oxidation penetrated into the MCrAlY coatings from the original coating surface, shows that the internal oxidation was not heavy in coating A1 up to 10,000 hours. In coating B1, from about 8000 to 10,000 hours a quick coating degradation occurred. The microstructure of coating A1 and B1 oxidized for 10,000 hours is shown in Fig. 13.

By applying Eq. 6, the critical aluminum activity for the end of coating life is $4.7\text{E-}9$ at 1000 °C. The evolution of Al activity with oxidation time was calculated from chemical compositions measured right below the oxide scale for the different oxidation times given in Figure 12. The results in Fig. 14 shows that Al activity in coating B1 reaches such activity level for the end of coating lifetime at about 8000 hours, which agrees with the microstructure of the severe degradation occurred in coating B1 at 8000 hours (Fig. 13b). According to the result in Fig. 14, the

lifetime of coating A1 and the two reference coatings (A and B) should be longer than 10,000 hours.

4. Conclusions

An Al-activity based coating life criterion for MCrAlY coatings was established, and the microstructure evolution of several coatings after long term high temperature exposure was examined. The results from analysis of literature oxidation data showed that the Al-activity based coating life criterion marked a clear boundary of critical Al-activity for the formation of a continuous α -alumina in binary Ni-Al and ternary Ni-Cr-Al systems when the empirical Al-concentration criterion failed. The incorporation of partial pressure of oxygen into Al-activity based coating life criterion was also in a good agreement with experiment results from literature survey. The long term oxidation results of several MCrAlY coatings shown complicated interdiffusion behaviour near coating and substrate interface. The inward diffusion of Co and Cr from coating to substrate destabilized γ' in substrate and the outward diffusion of Ti and Ta from substrate to coating stabilized γ' in both substrate and coating. The Al activity criterion proposed in this study explained reasonably the end life of a coating with Hf addition and remaining life of other long term oxidized MCrAlY coatings. The results demonstrate that the use of Al-activity based coating life criteria are benefit for the optimization of MCrAlY coating.

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Table 1. Nominal coating composition (wt. %).

Table 2. Ni-Al, Ni-Al-Si and Ni-Cr-Al alloy systems included in Fig. 8 and 9 from references.

Fig. 1. Workflow of Al activity calculation method in this study.

Fig. 2. The cross sections of coating A after the oxidation for (a) 2000 hours and (b) 10,000 hours.

The Ni, Co, Cr and Al concentration of corresponding microstructure zones (in order) **measured by EDS** are listed beside each zones.

Fig. 3. The cross sections of coating B after the oxidation for (a) 2000 hours and (b) 10,000 hours.

The Ni, Co, Cr and Al concentration of corresponding microstructure zones (in order) **measured by EDS** are listed beside each zones.

Fig. 4. The cross sections of coating C after the oxidation for (a) 2000 hours and (b) 10,000 hours.

The Ni, Co, Cr and Al concentration of corresponding microstructure zones (in order) **measured by EDS** are listed beside each zones.

Fig. 5. SEM images showing the microstructure in the substrate and the three coatings (coating A, B and C) after 10,000-hour oxidation. The dash lines denote the original coating-substrate interfaces. The arrows denote the (Ta,Ti)C carbides shown as bright particles in the SEM images.

Fig. 6. The Al concentration (in wt. %) in coatings beneath alumina scales after oxidation measured by EDS.

Fig. 7. Comparison of the Al activity and Al concentration in coatings under alumina scales after oxidation for 10,000 hours. The Al activity is calculated using Thermo-Calc software.

Fig. 8. A summary of oxidation results based on literatures: □ Y: alloys are able to form a single scale of alumina; △ M: alloys are able to form an alumina scale with other oxides outside; ◇ N: alloys are unable to form a continuous alumina, the formation of severe internal alumina occurs.

Fig. 9. A summary based on literatures: □ Y: alloys are able to form a single scale of alumina; △ M: alloys are able to form an alumina scale with other oxides outside; ◇ N: alloys are unable to form a continuous alumina, the formation of severe internal alumina occurs. Noted that the Al activity was calculated based on the same alloy systems in Fig. 8, some points in Fig. 8 overlapped with each other. Data reached the minimal Al activity required for continuous alumina formation are selected and marked with arrow. The dash line marks the boundary of Al activity in Ni-Al and Ni-Cr-Al alloys to form continuous alumina scale are from linear fitting of selected data marked with arrow.

Fig. 10. Comparison of the critical Al activity boundary of Ni-Cr-Al alloys (including Ni-Al alloys) with the critical Al activity boundaries of some superalloys and Co-Al alloys. The Al activity values are derived from the literatures or Thermo-Calc calculation.

Fig. 11. Near-surface Al concentration during the oxidation process: a comparison among some coatings. About 0.3 wt. % Hf is added in coating A1 and coating B1 comparing with their reference coatings – coating A and B, respectively. Addition of Hf in coatings accelerates the alumina scale growth, which enhances the Al consumption in coatings.

Fig. 12. (a) The through-coating oxidation-depth fraction (a ratio between the oxidation depth and coating thickness) in coatings. (b) Schematic illustration of how the oxidation depth is measured.

Fig. 13. The cross sections of coating A1 and B1 after oxidation for 10000 hours. The addition of Hf in these two coatings accelerated the growth of alumina.

Fig. 14. The development of Al activity near coating surfaces in oxidation. The Al activity is calculated using Thermo-Calc software.

Composition of interested
area measured by EDS

Define alloy system with composition and temperature
as a condition in equilibrium module 'POLY'

TCNI8
database

Solve Lagrangian multipliers of the
equilibrium calculation optimization problem

Calculate Al activity

Coatings	Ni	Co	Cr	Al	Y	Si	Ta
A	Bal.	28	15	11	0.4	0.25	0.5
B	30	Bal.	20	10	0.6	0.25	0.5
C	30	Bal.	28	7.5	0.6	0.25	0.5

Alloy systems	x (wt.%)	y (wt.%)	Ref.
Ni-xCr-yAl	0~30	1~9	[12]
Ni-xAl-ySi	4	0~5	[13]
Ni-xAl	1.15~12.8	-	[14,37,38,40]