



HAL
open science

The reactive element effect (R.E.E.): a tentative classification

J. Maximilien N'Gandu-Muamba, Roland Streiff

► **To cite this version:**

J. Maximilien N'Gandu-Muamba, Roland Streiff. The reactive element effect (R.E.E.): a tentative classification. *Journal de Physique IV Proceedings*, 1993, 03 (C9), pp.C9-281-C9-290. 10.1051/jp4:1993927 . jpa-00252365

HAL Id: jpa-00252365

<https://hal.science/jpa-00252365>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The reactive element effect (R.E.E.): a tentative classification

J. Maximilien N'gandu-Muamba and Roland Streiff

Université de Provence, 13331 Marseille Cedex 3, France

Abstract. — The oxidation resistance of many high temperature materials, especially gas turbine materials, can be enhanced by applying protective coatings. In this study, aluminide and chromaluminide coatings were applied on a number of superalloys, viz., IN738, René 80, B1900, IN100 and IN713, using both high and low activity pack cementation process, and subjected to cyclic oxidation. Oxidation behaviour of the coated material was found to be dependent on the type of pack used, i.e. low or high activity pack and also on the composition of the base alloy. It is well established that small additions of so-called "reactive elements" increase the oxidation resistance of alumina former superalloys. The beneficial effects of these "reactive elements" are currently regarded as being of two kinds: 1) an improvement in oxide to metal adhesion, and 2) a reduction in oxidation rate for some systems. The results on the effect of certain alloying elements, such as Mo, Ta, Ti and Hf on the oxidation behaviour of these aluminide coatings are presented in this paper and a classification of the "reactive elements" is proposed.

1. Introduction.

Early in the history of aircraft turbo-engines, diffusion aluminide coatings were designed to remedy the lack of surface stability of alloys in gas turbine hot components. During the last decade, because of the requirements of higher strength materials owing to increasing turbine inlet temperatures, ductile MCrAlY alloy overlay coatings have been developed. Both these types of coatings are oxidation resistant as a result of forming a protective alumina scale under high temperature conditions.

However this alumina scale is prone to spallation. Coatings on turbine blades are subjected to thermal cycling and mechanical strain. This results in stresses in the oxide formed during operation of the turbine hot components, and in cracking and spallation of the scale which loses protectivity.

The composition of the alloy to be coated is a relevant parameter regarding the protectivity of the coatings. The alloying elements from the Ni or Co base superalloys can diffuse into the coatings during the aluminising process and thus modify their oxidation resistance properties. It is well established that small additions of the so-called "reactive elements" (R.E.) increase the oxidation resistance of alumina former super-alloys. One method of introducing reactive elements into aluminide coatings to improve their oxidation resistance might be by diffusing these elements into the coating from the substrate.

The aim of this work was to investigate the effect of a number of substrate alloying elements in some commercial superalloys on the oxidation of aluminide coatings in order to identify which of these elements may be ranked in the family of the R.E. and then be beneficially added to the superalloys to improve the oxidation resistance of the coatings.

The effect of Hf addition in IN738, and of Hf addition with varying Ti content in René 80 along with the effect of some of the standard alloying elements, viz. Ti, Mo, and Ta, respectively in IN100, IN713 and B1900 superalloys was investigated.

2. Materials and experimental procedures.

2.1 SUBSTRATE ALLOYS. — Chemical compositions of the alloys, all commercial cast alloys, used for this study are given in table I. The IN738 and René 80 alloys were plates or rods. The other three alloys were pieces of actual cast turbine blades.

Table I.

SUBSTRATE ALLOYS															
IN738															
Ni	Co	Cr	Al	C	B	Mn	Si	Mo	W	Nb	Fe	Zr	Ta	Ti	Hf
Bal*	8,50	16,00	3,40	0,17	0,01	0,10	0,15	1,75	2,60	0,90	0,25	0,10	1,70	3,40	1
Bal*	"	"	"	"	"	"	"	"	"	"	"	"	"	"	2
René 80															
Ni	Co	Cr	Al	C	B	Mn	Si	Mo	W	Nb	Fe	Zr	Ta	Ti	Hf
Bal**	9,50	14,00	3,00	0,17	0,015	—	—	4,00	4,00	—	—	0,03	—	5	0
Bal*	"	"	"	"	"	—	—	"	"	—	—	"	—	3,5	0
Bal*	"	"	"	"	"	—	—	"	"	—	—	"	—	1,96	0
Bal*	"	"	"	"	"	—	—	"	"	—	—	"	—	5	1,2
Bal*	"	"	"	"	"	—	—	"	"	—	—	"	—	3,5	1,5
Bal*	"	"	"	"	"	—	—	"	"	—	—	"	—	1,96	1,2
** : standard René 80 composition															
IN100															
Ni	Co	Cr	Al	C	B	Mo	Nb	Fe	Zr	Ta	Ti				
Bal*	15,00	10,00	5,50	0,18	0,014	3,00	—	—	—	—	4,70				
IN713															
Ni	Co	Cr	Al	C	B	Mo	Nb	Fe	Zr	Ta	Ti				
Bal*	—	13,00	6,00	0,15	—	4,50	2,00	1,30	—	—	0,70				
B1900															
Ni	Co	Cr	Al	C	B	Mo	Nb	Fe	Zr	Ta	Ti				
Bal*	10,00	8,00	6,00	0,10	0,015	6,00	—	0,12	0,10	4,00	1,00				
* compositions in weight percent															

2.2 PACK ALUMINIDE COATINGS.

2.2.1 *Aluminide coatings* were fabricated by either one of the two classical aluminising processes:

– The high aluminium activity process, (also designated as LTHA for Low Temperature High Activity), which is a low temperature pack cementation process performed at 760 °C, resulting in a δ Ni₂Al₃ coating; this one is then further transformed into a β NiAl coating by a subsequent diffusion treatment at 1080 °C for 4 hours.

– The low aluminium activity process, (also designated as HTLA for High Temperature Low Activity), which is a vapour phase process performed at 1040 °C, resulting in a β NiAl coating. These coatings are also subjected to a subsequent diffusion treatment for 4 hours.

2.2.2 *Chromaluminide coatings*, also designated Cr-Al coatings, were prepared by a two step process, including: first a chromium deposition by pack chromising at 1060 °C for 40 hours,

followed by a high activity pack aluminising at 750 °C for 3 hours and then by the usual subsequent diffusion treatment for LTHA process.

2.3 OXIDATION TEST. — Cyclic oxidation was performed to assess the effect of the various alloying elements on the spallation resistance of the protective alumina scales. Samples of about 50 – 60 mm² surface area were used for the oxidation tests. The coated samples were cyclically oxidised at 1050 °C, in air, with a cycle of 20 h heating, i.e. heating up to 1050 °C in about 1 h and then maintaining at temperature, followed by 4 h non forced cooling to room temperature. Each sample was subjected to 10 such cycles. Kinetics was followed by weight change recording after each cycle. One series of samples, on IN738 substrate, was isothermally oxidised at 1000 °C.

2.4 SURFACE AND MORPHOLOGIE ANALYSIS. — At the end of the oxidation run, surfaces and cross-sections of the specimens were examined by optical microscopy. The oxide scales were characterised by X-ray diffraction, their morphologies were investigated by Scanning Electron Microscopy after dissolution of the subjacent metal by the deep etching method [1], and compositions were determined using Energy Dispersive X-ray Analysis (SEM/EDAX). The composition and element distribution in the as-coated coatings were determined by Electron Probe Micro Analysis (EPMA).

3. Experimental results.

3.1 COATING STRUCTURES.

3.1.1 Aluminide coatings with hafnium. — Aluminide coatings showed the same structure, with no visible differences, whether they were formed on a substrate with or without hafnium additions.

The high activity type coatings exhibited the archetypal three zone structure described by Goward and Boone [2] with:

- an external zone of hyperstoichiometric β NiAl with numerous precipitates;
- an intermediate zone of pure NiAl without precipitates, also called the “denuded zone”;
- an interdiffusion zone resulting from external diffusion of Ni from the substrate alloy with a coarse precipitation of intermetallics and carbides.

The hafnium distribution was determined by microprobe analysis of the coating. In the as-coated sample, before oxidation, the hafnium is concentrated in the cortical zone of the largest precipitates in the outer zone. In the rest of the coating it is at a solid solution level. The hafnium content is about 4 to 5 times higher in the precipitates than in the hyperstoichiometric NiAl matrix, and the content in solid solution is higher in the denuded zone than in the external hyperstoichiometric zone.

The low activity type coatings exhibited the archetypal two zone structure with:

- an external zone of hypostoichiometric NiAl which contains the substrate alloying elements up to the solid solution level; and
- the interdiffusion zone which again is formed by the external diffusion of the nickel from substrate.

In this coating, hafnium is detectable only in some sub-micron precipitates located at the interface between the NiAl zone and the interdiffusion zone, or in some carbide precipitates in the substrate.

3.1.2 Chrome-aluminide coatings. — Chrome-aluminide coatings showed the classical three zone structure, in agreement with the high activity aluminising second step of the process of formation, previously described by Streiff and Boone [3]. The main feature-interesting

for the present oxidation study- of that coating is the substrate alloying element distribution and the chromium distribution throughout the coating. No differences were observed in the coating structures for the three substrate alloys, i.e. IN100, IN713 and B1900. In the fully processed coatings, i.e. after diffusion treatment of the initially formed Ni_2Al_3 layer, chromium is concentrated in the outer zone in the form of fine precipitates of β Cr in a NiAl matrix saturated in chromium. The other substrate alloying elements are present in solution in the NiAl coating with a concentration corresponding to their solubility level in the Ni_2Al_3 as-formed coating. Owing to their high diffusivity in NiAl, elements like titanium and molybdenum were found at the outer surface of the coating. EDAX analyses of the coating surface of these chromaluminide coatings have demonstrated that the amount of alloying element can rise up to 10 wt% [3].

3.2 OXIDATION KINETICS OF THE COATINGS. — Oxidation kinetics of these coatings has already been published elsewhere [4,5]. We will therefore only briefly recall these results.

On standard IN738 substrate alloy (with no Hf addition) low activity aluminide coatings provided some better protectivity - in terms of scale and spallation evidenced by weight loss of the oxidised samples - than high activity coatings, although the thickness of the high activity coatings was greater. Kinetics curves showed the classical profile for cyclic oxidation, i.e. an initial period with increasing weight, reaching a maximum weight gain followed by a continuous weight loss regime.

High activity coatings deposited on IN738 with 1% Hf addition showed a marked improvement in both oxidation rate and protectivity, whilst on low activity coatings the effect of a 1% Hf addition was detrimental. A 2% Hf addition to the alloy had a beneficial effect on high activity coating protectivity, with, however marked increase in oxidation rate, but was deleterious for low activity coatings.

Coatings deposited on 1.5% Hf, low Ti, René 80 alloys exhibited definitively better oxidation behaviour over all other René 80 substrates for both type of coating. They showed continuous weight gain during the 200 hours tests. Conversely, coatings on titanium-containing alloys were very prone to oxide spallation. For instance, oxidation of René 80 without Hf and with 1.9% or 5.0% Ti coated by a high activity aluminide began losing weight after only 2 oxidation cycles. This deleterious effect of Ti on the oxidation resistance of aluminide coatings is in agreement with earlier observations by Dupré *et al.* [6].

Cyclic oxidation of chromium-modified aluminide coatings deposited on B1900, IN100 and IN713 superalloys confirmed the beneficial effect of chromium on the aluminide oxidation resistance. Although some spallation of the formed oxide scales was observed, no weight losses were recorded for any of the substrate alloys. Kinetics exhibited in all three cases two periods: an initial period with a high rate followed by a parabolic period, with slower oxidation rate. A substrate element effect was identified for both the initial period length and the parabolic oxidation constant. Titanium in IN100 results in a high initial rate and a parabolic constant almost twice that of the coating deposited on B1900. Molybdenum IN713 produces a longer initial period. Tantalum in B1900 results in the best oxidation resistance with a short initial period and the lowest parabolic oxidation constant.

3.3 OXIDE SCALE MORPHOLOGY. — As stated earlier [4] the increase of protectivity of coatings formed on substrates with hafnium additions can be ascribed to an increase in the formed oxide scale adhesion.

The scale morphology shows the formation of oxide pegs at the oxide/coating interface in number varying with the hafnium content of the substrate alloy. The samples with 0% Hf addition exhibit a rather planar interface with a wave-like undulation as shown in figure 1

which displays the oxide formed on *high activity coatings* deposited respectively on (a) René 80 with 5.0% Ti + 0% Hf and (c) IN738 with 0% Hf oxidised for 200 hours. The same features are observed in the case of low activity coatings.

Conversely, in the case of coatings deposited on substrate alloys containing hafnium additions the oxide interface shows a profusion of pegs as can be seen in figures 1b and d.

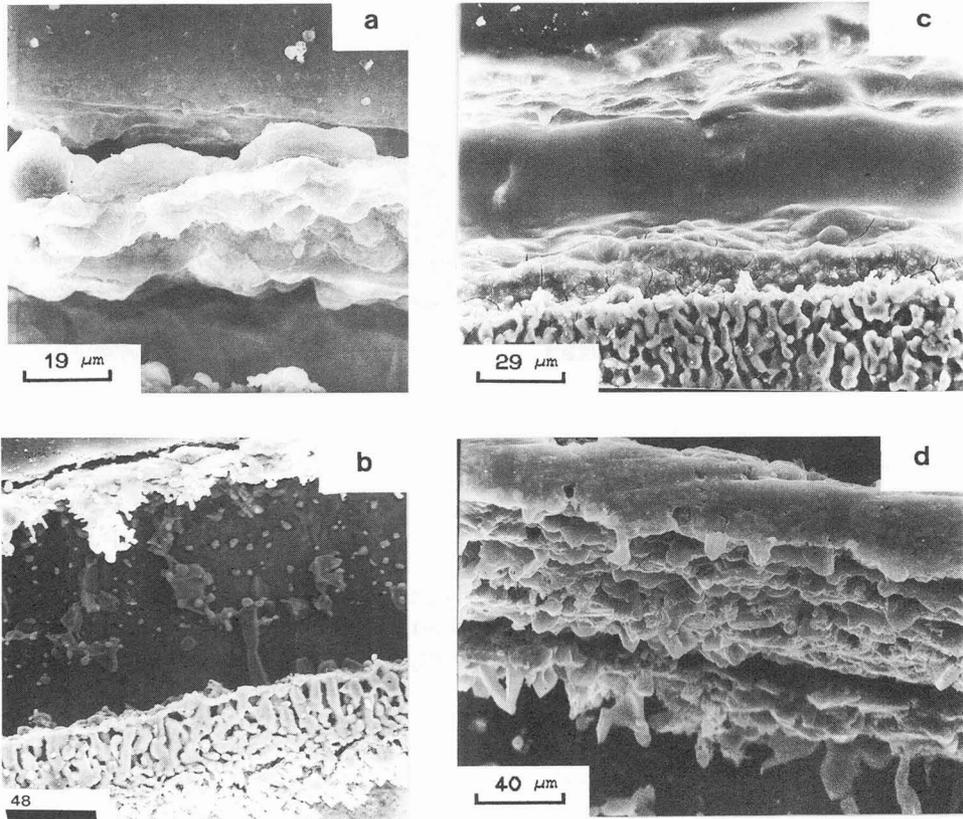


Fig. 1. — SEM under side views of oxide scales (after “deep etching”) formed on high activity aluminide coatings deposited on a) René 80 with 0% Hf and 5% Ti; b) René 80 with 1.5% Hf and 1.96% Ti; c) IN738 with 0% Hf; d) IN738 with 2% Hf.

Analysis of the small oxide pegs carpeting the interface was not easy because these were rather narrow for reliable counting. However, EDAX analyses indicated that there was some Hf content in the interface zone. Earlier RBS investigations [5] have demonstrated occurrence of hafnium at the surface of the coating with a content varying in the same way as the substrate hafnium concentration. This suggests a rapid and preferential diffusion of hafnium from the substrate through the coating and therefore explains the formation of these hafnium oxide pegs at the oxide surface.

In *low activity aluminide coatings* deposited on substrates containing hafnium, these oxide pegs develop into large protrusions or oxide sheaths (Fig. 2). EDAX analyse showed a high hafnium content, and X-ray imaging demonstrated that these sheaths were HfO_2 encapsulated in Al_2O_3 (Fig. 3). These hafnium oxide protrusions are similar to the HfO_2 sheaths

observed by Allam *et al.* [7] and by Stringer *et al.* [8] by oxidation of a CoCrAl alloy containing hafnium addition or hafnium oxide particles, and may grow by the same mechanism.

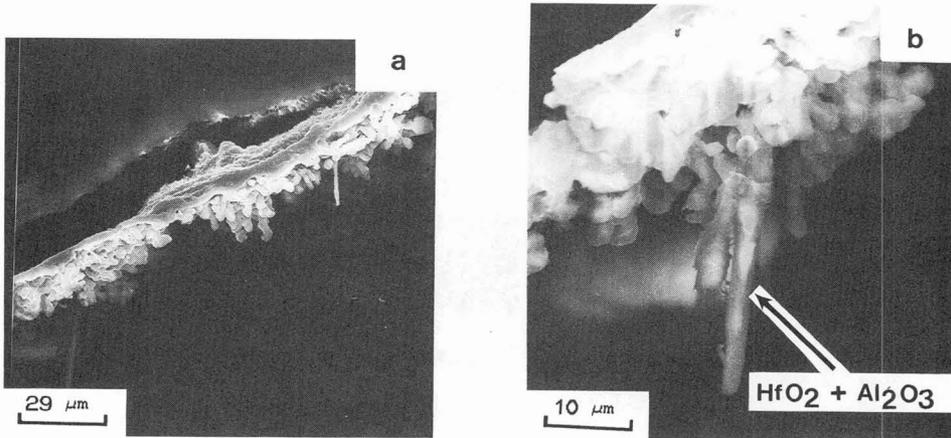


Fig. 2. — SEM under side views of oxide scales (after “deep etching”) formed on low activity aluminide coatings deposited on a) IN738 with 1% Hf; b) IN738 with 2% Hf.

The small oxide pegs which form at the oxide scale/coating interface develop in the whole volume of the coating and grow into the grains of β -NiAl while the large oxide sheaths grow along grain boundaries in the coating and may reach the interdiffusion zone of the coating, creating diffusion paths for the oxygen. This is certainly responsible for the absence of a beneficial effect of Hf addition in the low aluminide coatings observed in this study and previously reported by Smeggil *et al.* [9].

Surface and scale morphologies of oxides formed on IN100, IN713 and B1900, coated with high activity chromaluminide coatings, are presented in figure 4.

For all three coatings the oxide scale is formed of two layers:

- an outer layer of α alumina with a high Cr content, on which nodules of oxides of the substrate alloying element or alumina whiskers develop;
- an inner layer composed of a mixture of alumina and spinels. This layer shows also some oxide protrusions or pegs which may develop perpendicular to the coating/oxide interface or be imbedded in the alumina scale.

The oxide on the surface of the coating deposited on IN100 is fairly well crystallised with numerous large nodules emerging which were identified as TiO_2 by EDAX analysis. The formation of these nodules results from the rapid diffusion of Ti ions through the aluminide coating and the alumina scale. They cause the breaking of the oxide surface scale. On the coating deposited on IN713 numerous alumina whiskers were observed with some nodules which were found to contain molybdenum. On the coating deposited on B1900 only a thick carpet of alumina whiskers was observed.

The external alumina scale spalled off after two oxidation cycles revealing the inner layer, permitting an investigation of the nature and composition of that layer. On the coating formed on the IN100 alloy the inner oxide layer shows a high content of Ti mainly concentrated in large oxide protrusions which in some cases reach the coating/oxide interface causing accelerated oxidation, presumably by providing rapid oxygen diffusion paths. On

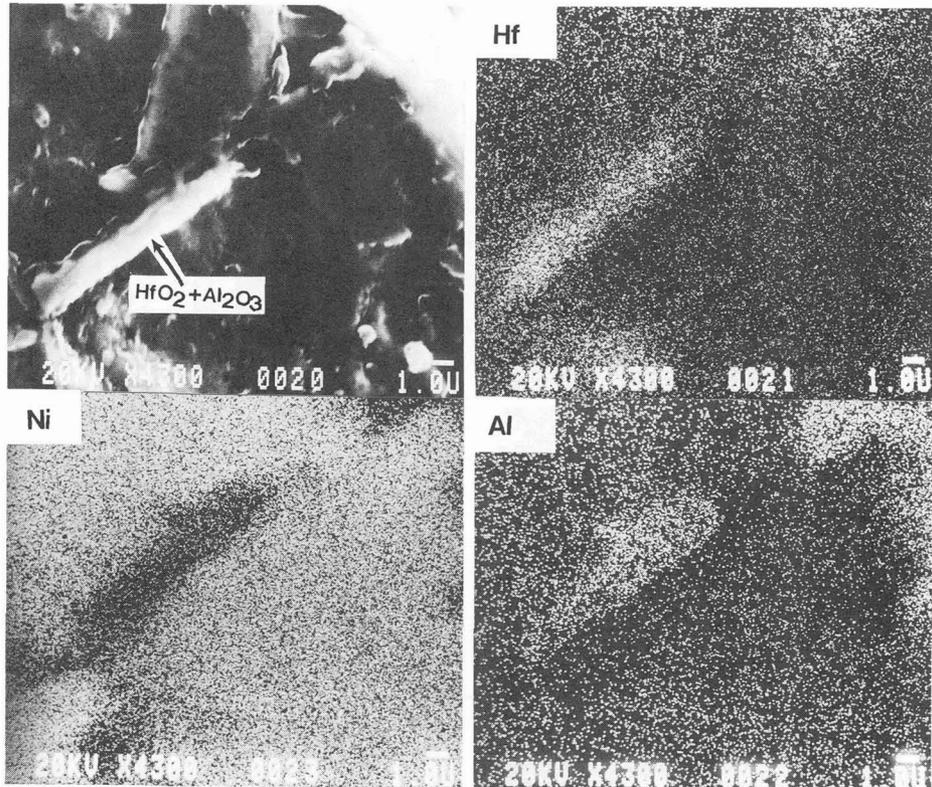


Fig. 3. — SEM view and X-ray images of Hf, Al and Ni of an HfO_2 sheath in the oxide scale formed on a low activity aluminide coating deposited on IN738 with 2% Hf.

coatings deposited on IN713 the occurrence of molybdenum was detected along with the Ni (Cr, Al) $_2\text{O}_4$ spinel in the inner oxide layer. Some small pegs containing Ti were also observed. On the coating deposited on B1900 no Ti was detected in either of the oxide layers; however a strong enrichment in tantalum was observed and the formation of the double oxide AlTaO_4 was evidenced by X-ray diffraction analysis.

4. Discussion.

The so-called “reactive element effect” is recognised by one the following features: decrease of the oxidation rate, modification in the oxidation mechanism, modification of the oxide morphology and improvement of oxide scale adhesion. This effect was first described for the addition of Ce mischmetall deoxidizer prior to vacuum melting of an Ni-20Cr alloy, but has been later observed for a number of other elements, especially yttrium in Fe-Cr-Al alloys and hafnium. This effect is usually ascribed to the increase of adhesion of the formed alumina scale.

Earlier explanations of the reactive element effect which have been reviewed by Whittle and Stringer [10], included:

- (1) enhanced oxide scale plasticity allowing accomodation of the thermally induced stresses;

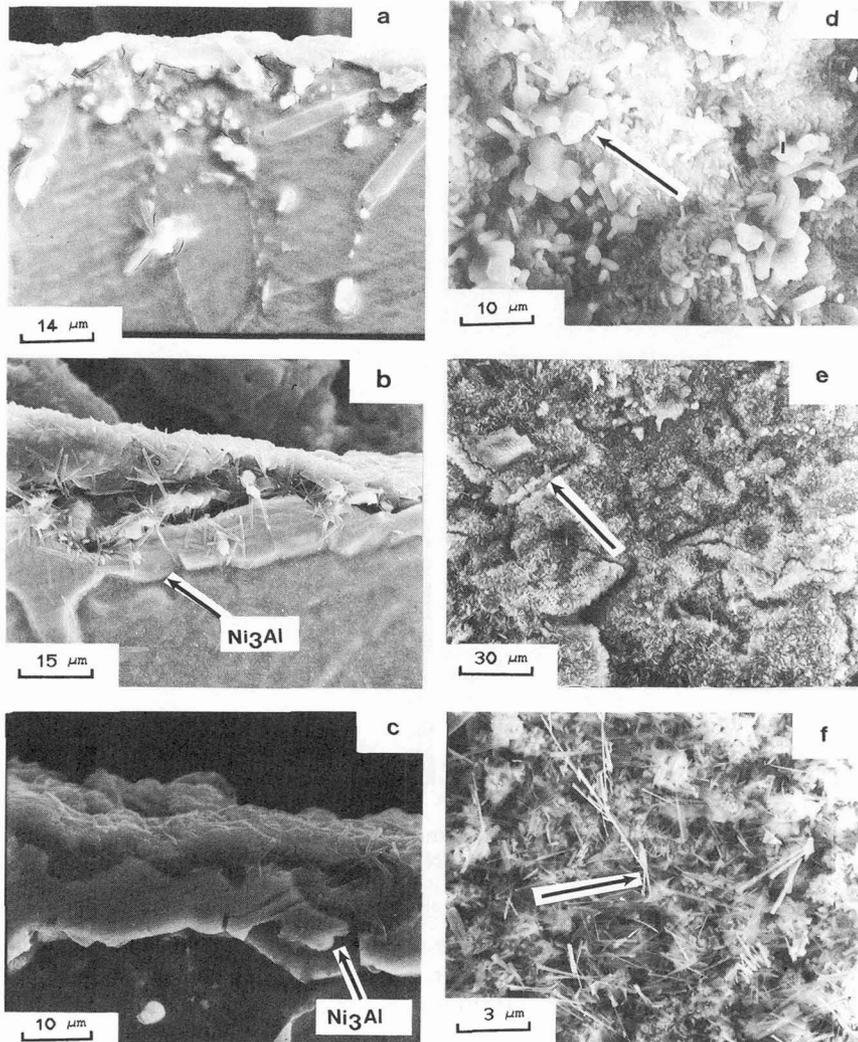


Fig. 4. — SEM views of cross sections (a, b, c) and of surfaces of the oxide scales formed respectively on a and d) IN100, b and e) IN713, c and f) B1900. Arrows show: on photo d) TiO_2 nodules, on photo e) molybdenum oxide nodules and on photo f) alumina whiskers.

(2) modification of oxide growth process by the suppression, due to the incorporation of the active element, of the cation contribution to the scale growth;

(3) formation of a compound oxide intermediate layer between scale and substrate which acts as diffusion barrier or modifies the binding energy;

(4) provision of alternative sites for vacancy sinks preventing vacancies condensing to generate interfacial voids or porosity;

(5) mechanical keying or pegging of the scale to the alloy by protrusions - "pegs" - produced by the selective oxidation of the active element addition at the oxide scale/alloy interface.

Although a number of investigations have proven that pegging and reduction of interfacial void formation are responsible for improvement of the oxide scale adhesion in a great

number of alloys containing reactive elements, it appeared that a unique mechanism cannot be applied to all alloy systems and an interaction between several mechanisms has been proposed [11]. More recently it has been proposed that the role of the reactive element is to prevent the segregation of impurities such as sulphur to the scale/substrate interface, preventing the weakening of what is postulated to be an inherent strong metal/oxide interface [12,13].

In this work the effect of the following elements: Hf, Ti, Ta, Mo on the oxidation behaviour of aluminide coatings, has been investigated. The results might be summarised as follows.

Hafnium: brings an improvement in oxide scale adhesion by the formation of oxide pegs which may extend through almost the whole coating in case of HTLA coating which are thinner than the LTHA coatings. These oxide pegs have been found to be HfO_2 sheaths encapsulated with alumina. The morphology of these pegs may account for the improvement of adhesion of the oxide scale, since oxide pegging alone is not sufficient to improve adhesion.

Tantalum: brings a decrease in oxidation rate and a significant scale adhesion improvement. EDAX analysis and X-ray diffraction have shown that tantalum is concentrated in an under-layer composed of alumina, spinel and mixed AlTaO_4 oxide. This spinel layer develops quite uniformly at the interface of the oxide scale and the Ni_3Al layer resulting from β -NiAl aluminium depletion by oxidation. It may act as a barrier towards oxygen, hence the decrease of the oxidation rate. It is currently postulated that yttrium R.E. effect may be ascribed to the formation of a spinel oxide barrier [14]. In this way, tantalum, obviously, acts as a reactive element.

Molybdenum: the situation with molybdenum is not as clear as with tantalum. A small decrease in the oxidation rate is observed. In addition a slight improvement in oxide adhesion may be the cause of the longer pre-parabolic stage. However, because EDAX analysis does not permit to clearly separate an oxide from a spinel it was not possible to identify, either a mixed oxide or a substituted molybdenum spinel. Further investigations are needed to establish the type of mixed oxide formed with Mo and its actual location in the scale.

Titanium: shows in all case a deleterious effect on the oxidation of aluminide or chromaluminide coatings. Owing to the rapid diffusion of titanium through the aluminide, TiO_2 nodules forms at the surface of the oxide scale in the beginning of the oxidation, concurrently with alumina growth. These nodules develop into pegs throughout the whole oxide scale and may reach the coating. These pegs may then favour the oxygen diffusion through the oxide and therefore accelerate the oxidation. These are harmful pegs. Titanium, definitely, does not behave like a reactive element.

5. Conclusions.

In the light of these observations we propose to class the reactive elements into two classes.

1) **Sheath formers:** elements, like hafnium which develop a pegging oxide scale with oxide sheaths (good pegs) which may provide an improvement of the scale adhesion by a keying effect;

2) **Spinel formers:** elements which develop at the oxide/substrate interface either a continuous layer of a mixed oxide (like a spinel) or segregation of a mixed oxide (like yttrium garnet) which may result in a decrease of the oxidation rate by hindering the oxygen diffusion. Tantalum or yttrium are good candidates for this class of reactive elements.

Besides, this work has confirmed that an improvement of the oxidation resistance of aluminide coatings may be obtained by hafnium addition in the substrate alloy, and that this

improvement is due to an improved oxide scale adhesion by the formation of hafnium oxide pegs. This is an avenue for future research for an economic improvement of aluminide coating oxidation resistance.

Acknowledgements.

The authors wish to thank Turbine Components Corporation (Dr. G.W. Govard) and HEUR-CHROME Company (Dr. P. Mazars) for having provided the samples, respectively of aluminide coatings, and of chromaluminide coatings, used in this study.

References

- [1] HINDAM H., SMELTZER W.W., *J. Electrochem. Soc.* **127** (1980) 1630.
- [2] GOWARD G.W., BOONE D.H., *Oxid. Met.* **3** (1971) 475-495.
- [3] STREIFF R., BOONE D.H., Reactivity of Solids, P. Barret, L-C. Dufour Eds. (Elsevier Publ. Amsterdam (NL), 1985) pp. 195-197.
- [4] N'GANDU MUAMBA J.M., STREIFF R., BOONE D.H., High Temp. Corrosion, R. Streiff, J. Stringer, R.C. Krutenat and M. Caillet Eds. (Elsevier Sequoia Pub. Lausanne, 1987) pp. 111-121; *Mater. Sci. Eng.* **88** (1987) 111-121.
- [5] N'GANDU MUAMBA J.M., STREIFF R., High Temp. Corrosion 2, R. Streiff, J. Stringer, R.C. Krutenat and M. Caillet Eds. (Elsevier Science Pub. Barking (U.K.), 1989) pp. 391-405; *Mater. Sci. Eng.* **A121** (1989) 391-405.
- [6] DUPRÉ B., STEINMETZ P., ROQUES B., PICOIR R., *La recherche Aérospatiale* **4** (1977) 213.
- [7] ALLAM I.M., WHITTLE D.P., STRINGER J., *Oxid. Met.* **1** (1978) 35; *ibid.* **13** (1979) 381.
- [8] STRINGER J., ALLAM I.M., WHITTLE D.P., *Thin Solid Films* **4** (1977) 377.
- [9] SMEGGIL J.G., BORNSTEIN N.S., High Temperature Protective Coatings, S.C. Singhal Ed. (AIME Publ., 1983) pp. 61-74; High Temperature Corrosion in Energy Systems, M.F. Rothman Ed. (AIME Publ., 1985) pp. 681-695.
- [10] WHITTLE D.P., STRINGER J., *Philos. Trans. R. Soc. Lond.* **A28** (1980) 309.
- [11] HUNTZ A.M., The role of active elements in the oxidation behavior of high temperature metals and alloys, E. Lang Ed. (Elsevier Science Pub. Barking (U.K.), 1989) pp. 81-109.
- [12] FUNKENBUSCH A.W., SMEGILL J.G., BORNSTEIN N.S., *Metall. Trans.* **A16** (1985) 1164-1166.
- [13] SMIALEK J.L., *Metall. Trans.* **A18** (1987) 164-167.
- [14] CHOQUET P., MEVREL R., High Temp. Corrosion 2, R. Streiff, J. Stringer, R.C. Krutenat and M. Caillet Eds. (Elsevier Science Pub. Barking (U.K.), 1989) pp. 153-159; *Mater. Sci. Engin.* **A121** (1989) 153-159.