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# On the Understanding of TGO Growth and Spallation in Nickel Aluminides

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**Abstract.** This paper describes various parameters influencing oxidation kinetics, oxide's morphology and spallation phenomena encountered while studying nickel aluminides in high temperature oxidation. Questions are raised about the possibility of making precise lifetime or failure predictions of coatings and TBCs systems. Changes in growth mechanism due to the presence of elements other than Ni and Al in nickel-aluminide base coatings, the effect of atmosphere, particularly water vapor, and the effect of surface preparation and of crystallographic orientation are the main parameters discussed in this work.

## Introduction

Because of their high temperature resistance, nickel or iron aluminide intermetallics are used or tested for high temperature aeronautic and energy production applications. The oxidation resistance of those materials is due to the formation of a protective compact alpha-alumina layer, playing the role of diffusion barrier. The material's lifetime depends also on the ability of this layer to stay adherent in high temperature applications, particularly under thermal cycling. During high temperature service in oxidizing environment, the thermally grown oxide may lose its mechanical integrity [1]. Many reasons exist to explain the failure of the oxide scale such as thermal expansion mismatch [2], interfacial cavity formation and interface degradation [1, 3-6], underlying alloy composition change, oxide and alloy phase [7, 8], and oxide growth mechanism. Predicting materials lifetime would require prediction of the occurrence of these phenomena, and this is at the moment impossible to do. The question which is presently addressed is the definition of the conditions for which simplified models are representative of complex system evolution.

In this paper, we report a non exhaustive list of examples of various parameters which affect the oxide morphology and growth kinetics, and also the interfacial cavities growth encountered during nickel base alloy oxidation in the 900°C - 1200°C temperature range.

## Alloys composition effect on the growing direction

Depending on the alloy composition, the oxide growth mechanism can vary from mainly anionic to mainly cationic. Examples of change in the growth mechanism and oxide scale morphology for four nickel base alloys with different compositions are given in Fig.1. A palladium modified beta-NiAl, with 600 grit paper polished surface, and after 306 hours isothermal oxidation at 950°C (Fig.1-a) shows large outward growth of whiskers assumed to be transient alumina. The oxide layer is partially spalled. Reversed oxide spalls (see arrows in fig 1a) show the alloy initial surface image in the oxide inner face, indicating that oxide grows only by outward diffusion. Inner surface morphology is a memory of polished alloy surface. In the (Fig.1-b) is presented a beta-NiAl single crystal, with a mirror polished surface, after 6 hours, oxidized at 900°C. Roughness in the oxide inner face (R) and isolated alpha alumina crystallites indicate small amount of inward oxygen diffusion. In the case of AM3™ single crystal superalloy oxidized at 1200°C for 19 hours (Fig.1 c), oxidation leads to complex oxide structure and composition with an inwardly growing alpha alumina columnar structure and with an outward growing spinel type oxide (c, top image). Metallic particles are detected inside the oxide layer (bright spots in the BSE micrograph indicated by M). Imprints after oxide scale spalling (c, bottom image) is due to inward oxide growth. With similar oxidation conditions, the grit blasted platinum modified NiAl shows no spalling. The surface morphology is similar to that of the surface before oxidation, indicating the absence of outward growing oxide (Fig.1 d).

Transmission electron microscopy image of a NiAl (100) single crystal oxidized at 1050°C for one hour is reported in figure 2. The white arrows show oxidation of former cavities by inward oxygen diffusion. The black arrow shows irregular oxide inner surface due to inward oxide growth.

For these relatively short time oxidation treatments, whereas NiAl forms an oxide scale grown by outward aluminum and slightly inward oxygen diffusion, oxidation mechanism for palladium modified alloy is mainly cationic and it is mainly anionic for platinum modified alloys. For the AM3™ single crystal superalloy with a complex composition, oxidation leads to a very complex oxide structure as explained before.

When oxide grows by outward diffusion of aluminum, at temperatures below 1000°C, transient alumina forms with a high growth rate before it transforms to the thermodynamically more stable alpha alumina which acts as a diffusion barrier [7, 9]. The oxide growth rate controlled by diffusion depends of the alpha alumina layer thickness. This thickness depends on direct slow growing alpha alumina and of the transient to alpha alumina transformation. This transformation makes difficult the kinetics constant calculation from TGA mass gain curves, and one should be cautious when using  $k_p$  values for long term predictions. It may also be noted that during long term oxidation of alumina forming coatings, the composition of the alloy below the oxide scale changes because of aluminum consumption and elemental diffusion from the superalloys substrate. Then, changes in oxide growth mechanisms, kinetics and scale adherence are expected.

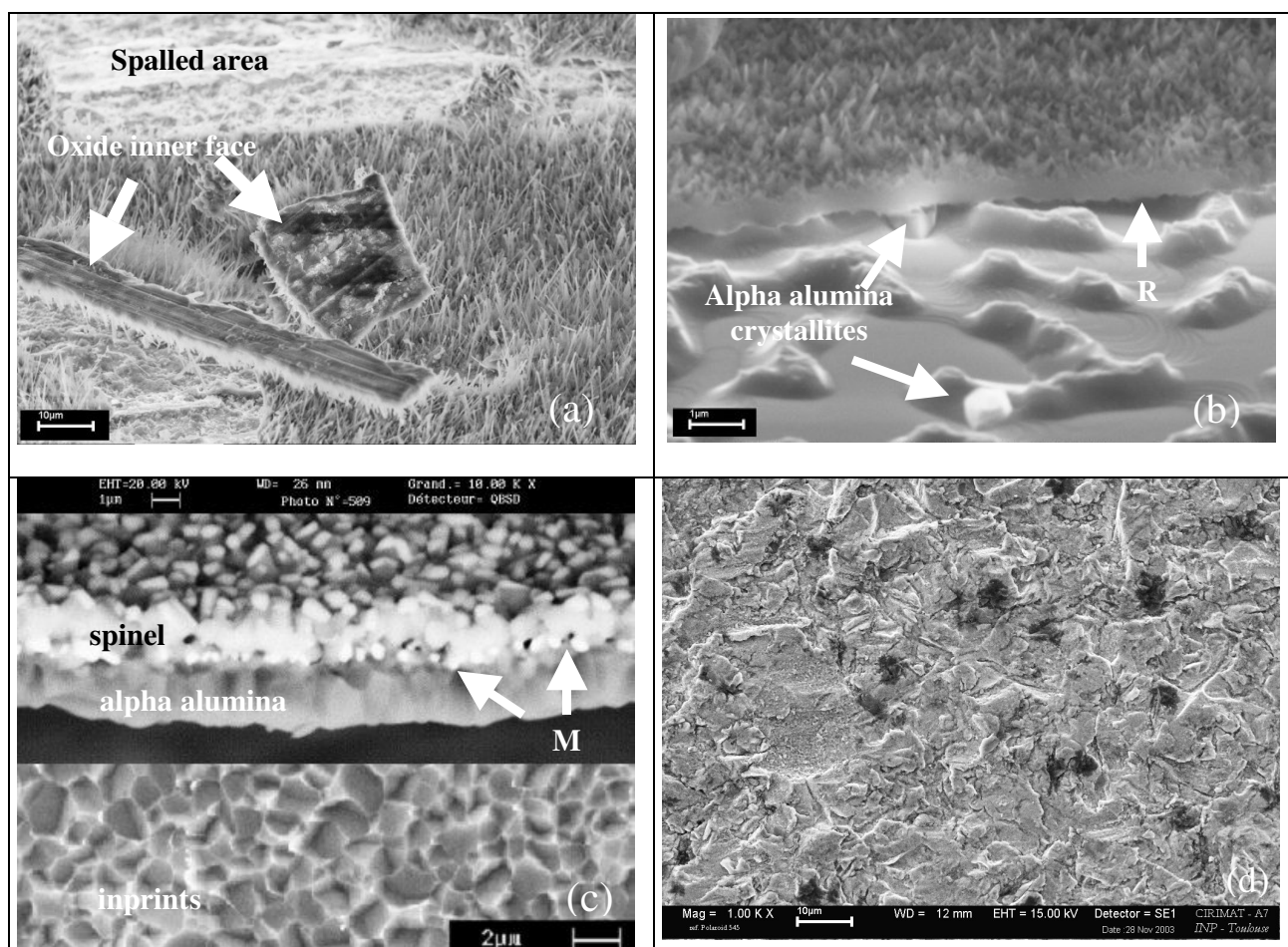


Fig. 1. Oxide scale morphology for four different nickel base alloys. a) palladium modified NiAl. (600 grit paper polishing, 950°C, 306 hours isothermal oxidation), b) beta-NiAl B2 structure (100) oriented single crystal, oxidized for 6 hours under oxygen, at 900°C, c) AM3 single crystal superalloy oxidation at 1200°C for 19 hours, under oxygen (c, top image) and footprint after oxide scale spalling (c, bottom image). d) surface morphology of a grit blasted platinum modified NiAl sample oxidized at 1100°C for 20 hours. No spallation was observed.

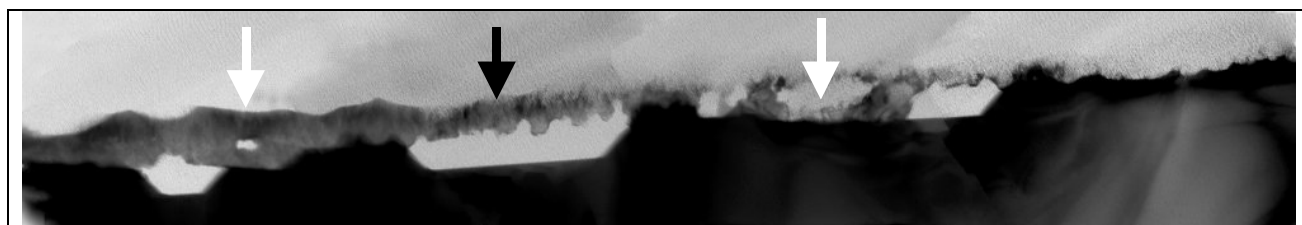


Fig. 2. TEM micrograph of NiAl (100) single crystal oxidized 1 hour at 1050°C under oxygen. The white arrows show oxidation of former cavities by inward oxygen diffusion. The black arrow shows irregular oxide inner surface due to inward oxide growth.

### Atmosphere control and oxide morphology change

Needle like oxide morphology is commonly observed in nickel aluminides and identified as transient alumina growth before its transformation to thermodynamically more stable alpha alumina.

Ni-base superalloy IN-100 coated with (Ni,Pd)Al has been oxidized at 900°C and 950°C, respectively in laboratory air and an dry air, for 6 hours. At 950°C in dry air, (Fig 3b), the oxide scale thickness is uniform and both interfaces are smooth. At 900°C (fig 3-a), as well as at 950°C (not shown here) in laboratory air, whiskers with length up to 5µm are observed. Nevertheless, in both cases, dry and laboratory air, oxide growth proceeds by cationic diffusion. Moreover, interfacial cavities are also observed both in dry and in laboratory air. The drastic changes in morphologies observed comparing fig 3a and 3b are probably due to the presence of water vapor in lab air.

Another important difference between dry air and lab air oxidation is the extent of spallation which is much more pronounced for the first case. Because of the manufacturing process, as received (Ni,Pd)Al coating presents large grains of about 50µm average diameter and grain boundary roughness of up to 20 µm height. When the sample is oxidized under laboratory atmosphere, decohesion proceeds in small areas, corresponding to parts or entire grains and limited by coating grain boundaries. When oxidized under dry air, spallation occurs on large surfaces, including several grains. Recent work on long term cyclic oxidation of some alumina forming alloys in wet and dry air indicates a greater amount of transient oxide formation in wet air. Also more profuse scale spallation is reported for wet air [10, 11], which is different than the result presented here for short term isothermal oxidation.

These examples emphasize the necessity of a careful control of the atmosphere because oxide scale adherence has a strong impact on materials durability. Many cyclic oxidation tests are conducted in laboratory air with a non constant and non reproducible water content from one laboratory to another, and this may influence the reproducibility of experimental cyclic oxidation kinetics results.

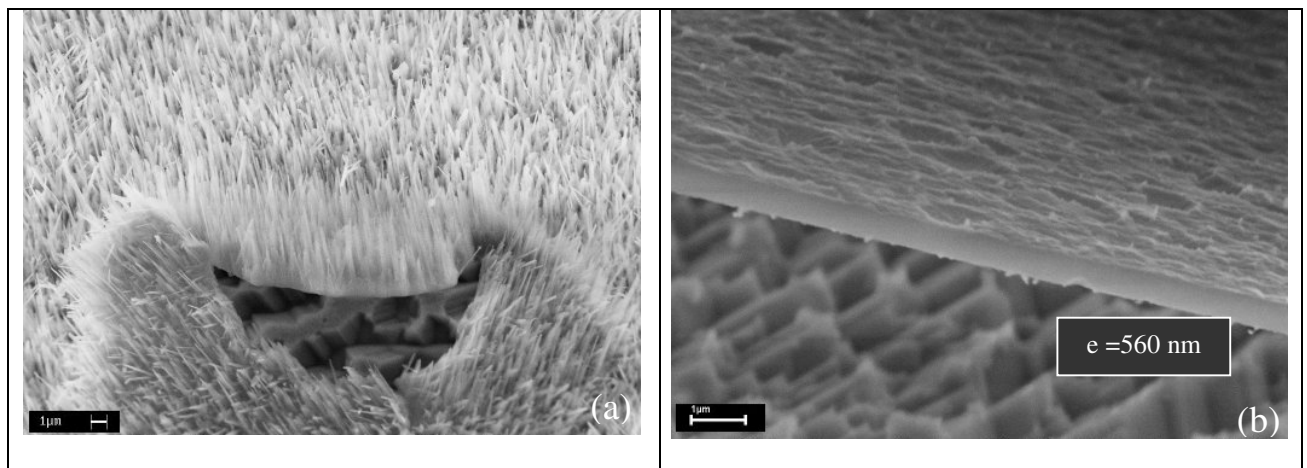


Fig. 3. (NiPd)Al coated IN100 sample oxidized (a) for 6h at 900°C under laboratory air and (b) at 950°C under synthetic dry air.

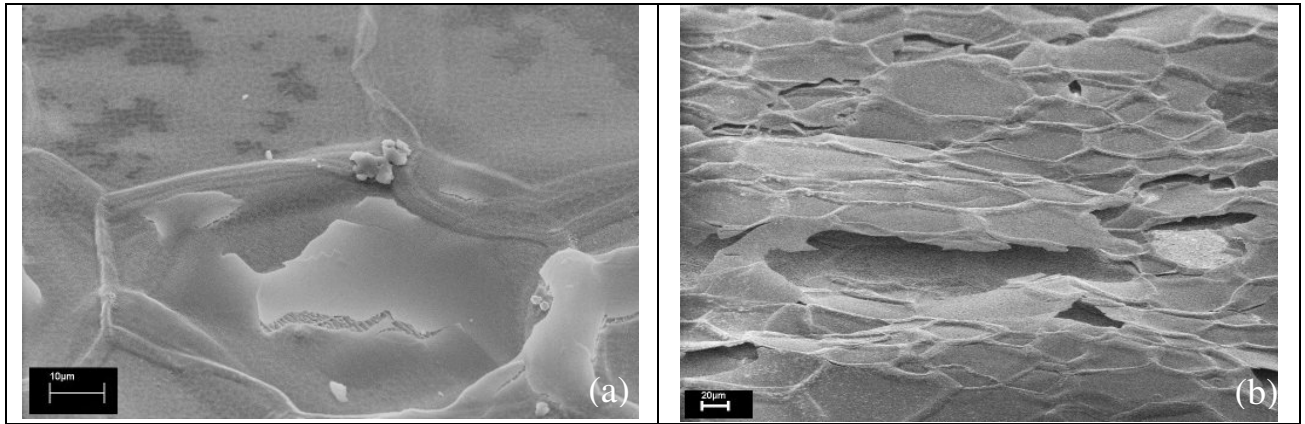


Fig. 4. (NiPd)Al coated IN100 sample oxidized for (a) 6h at 900°C under laboratory air showing local spallation and (b) 6h at 950°C, under synthetic dry air showing large area of spalled oxide scale.

### Surface preparation effect

In previous works, the effect of grit blasting on (Ni,Pd)Al coating oxidation was reported, leading to some improvement of the adherence and limitation of the transient oxide formation when combined with low oxygen pressure [12, 13]. The reason for this improvement is not well understood, however, examples presented on fig. 5 suggest that mechanical deformation of the alloy seems to be responsible of this effect. Indeed, Fig 5 shows the surface modification effect on the cavities growth (Fig 5a and 5b) at the early stage of oxidation at 950°C and 1020°C where one can notice the absence of cavity formation on scratched areas. The locally deformed scratched area can be compared to polished or grit blasted samples.

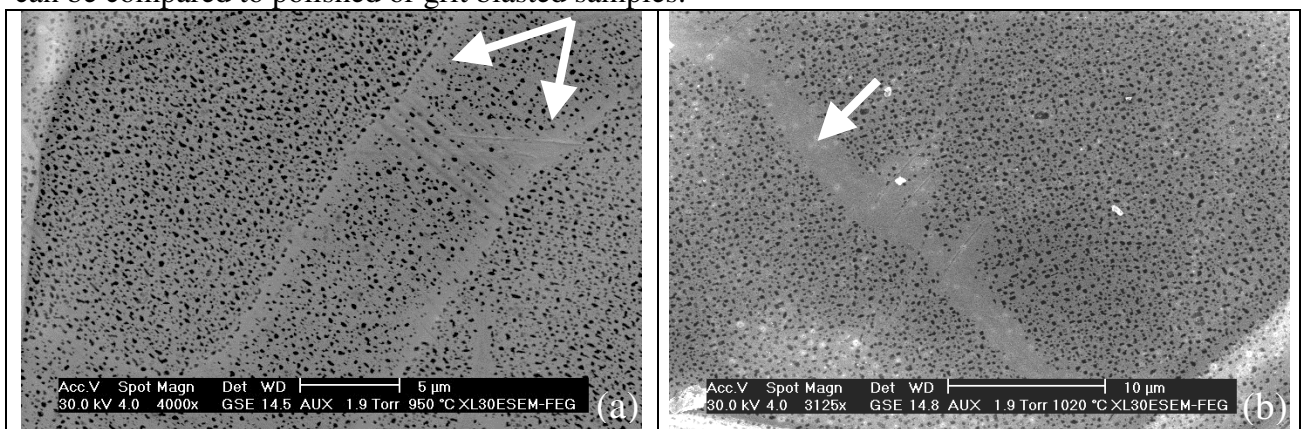


Fig. 5. (Ni,Pd)Al coating on IN100 : Surface preparation effect on the cavity growth and oxide scale morphology : in-situ ESEM observation of early stage of oxidation at (a) 950°C and (b) 1020°C showing the absence of cavity formation on scratched areas indicated by white arrows. Dark points represent cavities.

While the as received coating develops inwardly growing particular oxide morphologies with platelet formation on the palladium modified NiAl grains boundaries, the polished sample develops an oxide with a uniform morphology, independent of the location or crystallographic orientation of coating grains. Figure 6 shows the oxide scale morphology of as-received (Fig 6a) and 600 grit SiC polished (Fig 6b) surface of (Ni,Pd)Al, oxidized at 950°C for 196 hours. In terms of oxide scale adherence and morphology, these two examples are comparable to the large scale mechanically deformed surface when samples are grit blasted. The improvement of the adherence may then be attributed to the substrate modification induced by the deformation.



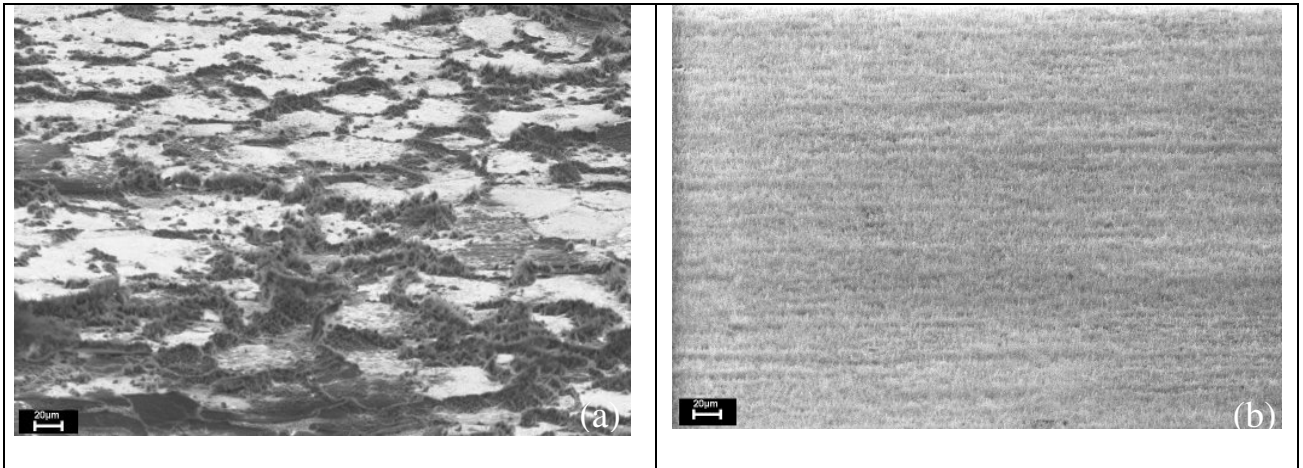


Fig. 6. a) as-received and b) 600 grit SiC polished surface of (Ni,Pd)Al coating on IN100, oxidized at 950°C for 196 hours. Large scale platelets are developed on grain boundaries of as-received sample while no platelets are observed on polished sample.

### Crystallographic orientation effect

Crystallographic orientation is one of the most important parameter affecting the oxide growth rate and oxide adherence [5, 14-16]. Particularly, in the case of cationic oxide growth mechanism, interfacial cavities form during high temperature oxidation, oxide can spall locally because of large cavity formation or because of higher oxide growth rate due to unfavorable crystallographic orientation of some grains. Coating grains boundaries or twin boundaries constitute diffusion short-circuit, which may explain the locally higher growth rate shown in Fig. 7 (white arrow) if aluminum diffusion in the coating is rate controlling.

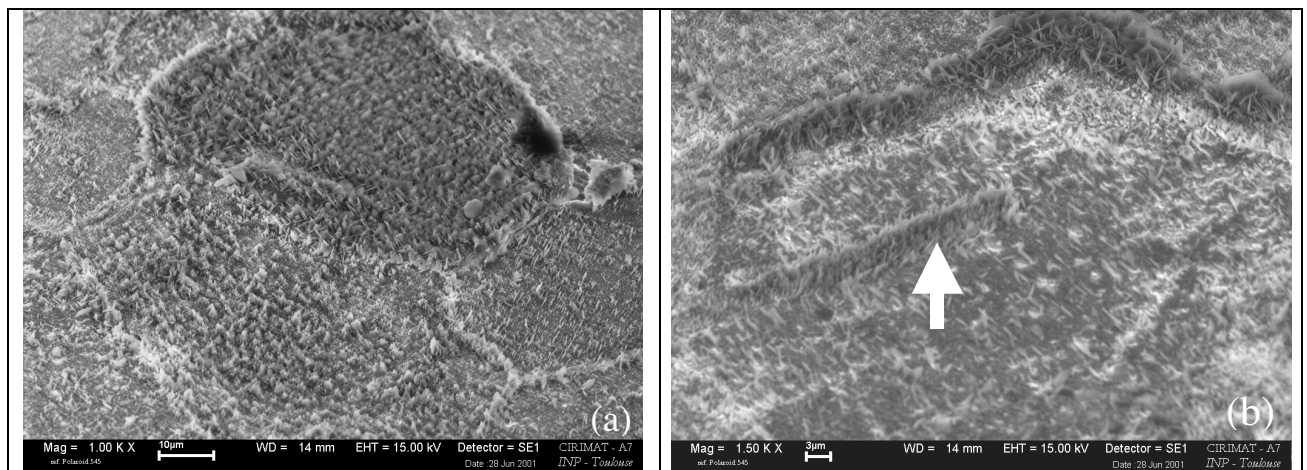


Fig. 7. Crystallographic orientation affecting a (Ni,Pd)Al coating, oxidized at 950°C for about 200h. a) SEM observation showing differences of morphology and growth rate for grains of different crystallographic orientations, b) a twin boundary with platelets formation (arrow).

### Chemical pollution

Chemical pollution is an important factor influencing the oxidation kinetics and the TGO adherence to the substrate. Sulfur effect on the oxide scale adherence is abundantly discussed in the literature. Other chemical impurities can modify oxide scale structure, morphology and scale adherence in TGO and TBCs [17-22]. Fig. 8 shows a NiAl single crystal containing few cracks and porosity, where segregated Mg was detected, initially present in the alloy composition (119 wppm). When



oxidized in cyclic conditions, Mg rich areas lead to a particular morphology: oxide layer seems to be thicker and no ridges are observed in polluted areas. This observation shows once again the influence of impurities affecting the oxide growth mechanism.

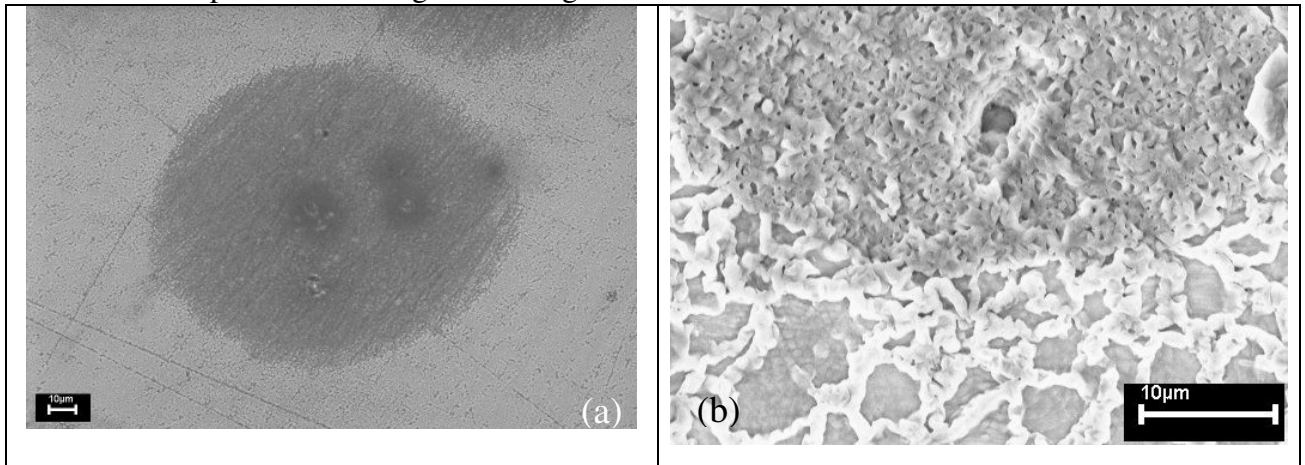


Fig. 8. a) Local Mg contamination effect on the oxidation behavior of a NiAl single crystal . b) zoom in Mg rich area leading to particular morphology : oxide layer seems to be thicker and no ridges are observed in polluted areas.

### Concluding remarks

The above examples show the direct or indirect influences of various parameters on the oxidation behavior of nickel aluminides.

- Compact alumina scale constitutes a diffusion barrier for oxygen or oxidizing species. Oxide growth can proceed by anionic or cationic mechanisms, depending on the alloy or coating composition which modify the nature and quantity of impurities in alumina,
- Chemical pollution may act to modify oxidation and diffusion mechanism, affect oxide growth kinetics and oxide / alloy interface mechanical properties.
- Water vapor in the oxidizing atmosphere can be sufficient to greatly influence oxide scale microstructure, favoring transient alumina whiskers growth and modifying the extent of spallation.

Improvements of the oxide scale protective character necessitates the control of many materials and oxidizing condition parameters. Models have been presented in the literature which take in account some of them, but experimental results show their interdependence, with the consequence of limiting the universal character of lifetime prediction models, especially if a mechanism change occurs during the test.

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