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## **Some examples of thermodynamical modelisation use for a better understanding of sub-surface microstructural phenomena after high temperature oxidation of superalloys**

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## INTRODUCTION

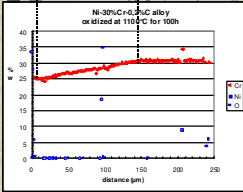
When superalloys are being oxidized at high temperature, oxide scales grow on their surface, involving some of their constitutive elements. Among them are aluminum and chromium - added to the alloy to form a protective stoichiometric oxide scale - and other reactive elements such as titanium or tantalum. Then, these elements diffuse from an increasing depth in the bulk towards the oxidation front. When temperature and/or time exposition are high enough, concentration gradients appear and a progressive disappearance of phases, dispersed in the matrix and containing some oxidizing elements, can occur. If we know where metallic elements from disappearing phases are going to, it is much more difficult for other constitutive elements. For instance, chromium carbides get dissociated into Cr - involved in the oxide scale growing - and carbon. The latter element can diffuse towards the oxidation front to be oxidized by air into CO<sub>2</sub>, or can go back into the matrix. Carbon, light element which is moreover present in small quantity in most superalloys (less than 2%w), is difficult to analyse by microprobe. Fortunately, the association of metallographic examinations, microprobe analysis of heavier elements and thermodynamical modelisation can help to know where light elements are going, to better specified the oxidation phenomena or its microstructural consequences.

## FIRST EXAMPLE : CASE OF TWO SIMPLE NICKEL BASE ALLOYS

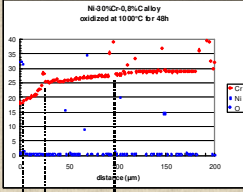
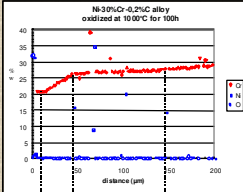
Chromia scale Carbideless zone Unaffected zone



Two simple refractory alloys Ni-30Cr-0.2C and Ni-30Cr-0.8C (%w) were elaborated by HF induction melting. Oxidation tests at 1000°C and 1100°C were performed on especially prepared samples. Metallographic preparations and examinations, followed by both pinpoint and linear profile microprobe analysis, were done on oxidized samples. New precipitates (Cr<sub>3</sub>C<sub>2</sub>) obtained by solid state transformation were identified, and chromium content gradient were clarified.



Cr content profiles obtained by microprobe analysis through the zone affected by oxidation



Comparing %Cr profiles to the different microstructural zones allows to associate both carbideless zone and zone with new carbides to chromium content intervals.

Carbon cannot be easily analyzed, because of its very low content and atomic number. Nevertheless, the phases metallographically revealed, give some indications on local carbon contents, so on the new form of this element after carbides dissociation.

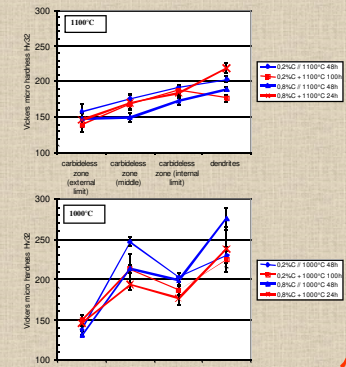
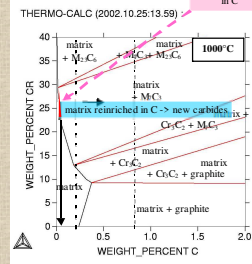
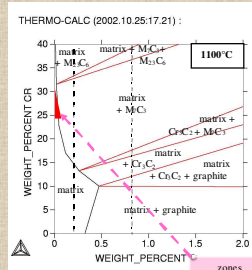
More precisely, after oxidation at 1100°C, carbon has probably followed chromium towards the oxidation front where it is converted into CO<sub>2</sub>, helped by the high temperature. At 1000°C it seems that the initial microstructure, containing Cr<sub>7</sub>C<sub>3</sub> carbides, has been substituted by both :

➤ on the external side : a carbideless zone strongly impoverished in C,

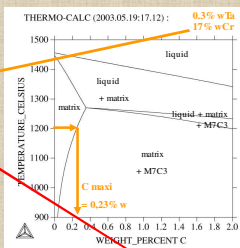
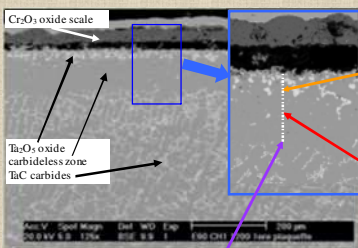
➤ on the internal side : a zone having lost its intergranular Cr<sub>7</sub>C<sub>3</sub> carbides and got new Cr carbides, precipitated inside grains with an acicular shape.

This latter observation suggests that C liberated from the disappearing carbides, came back into the matrix where they form these new carbides with Cr initially present in solid solution. Here they are less exposed to oxidation than in grain boundaries.

The occurrence of these new microstructure could have consequences on mechanical properties : softening in the carbideless zone and hardening where new acicular carbides appeared.



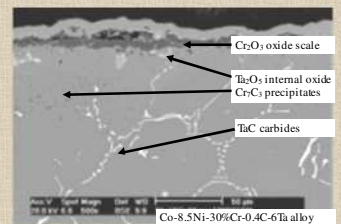
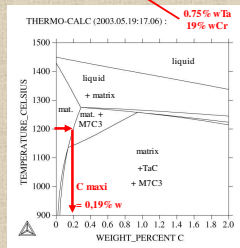
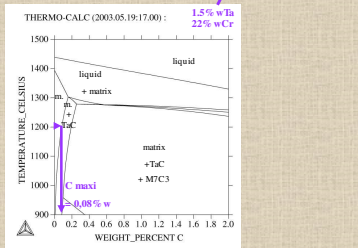
## SECOND EXAMPLE : CASE OF A COBALT BASE SUPERALLOY



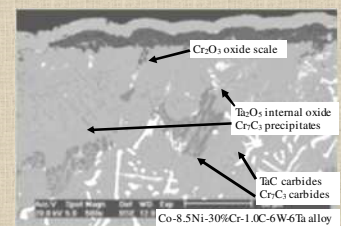
For the same exposition time, the higher the temperature is, the deeper the carbideless zone is (ex. on left: a cobalt base superalloy oxidized at 1200°C). Three points were analyzed by microprobe on the two zone limits and in the middle. ThermoCalc calculations were realised on the (Co-Ni-Cr-Ta) local compositions and the corresponding %C-T diagrams were drawn.

For the three points, the absence of other phase except the matrix indicates that the carbon content becomes smaller when the point is closer to the bulk-external oxide interface. Moreover, carbon content in this zone is smaller than the bulk's one (which is equal to 0.38%w). So, as for the nickel alloys at 1100°C, this high temperature seems to have promoted a diffusion of Cr, Ta and overall C too, towards the oxidation front.

On the contrary, at lower temperatures, it is possible, like for nickel alloys, to observe new carbides precipitated in solid state near the oxidation front. On the right, two examples of cobalt base superalloys, with one or two types of carbides, respectively TaC for the upper alloy and TaC and M7C3 for the lower one, can be seen. Here, the precipitation of new carbides could be related to the rarefaction of TaC (Ta diffusing to the oxidation front) and the capture of free C by chromium present in matrix solid solution. But, to better know the carbon content, quantitative image analysis must be done.



Scanning Electron Microscope pictures obtained on the oxidation front of two cobalt-base superalloys after 100 hours at 1000°C in air



Scanning Electron Microscope pictures and Microprobe analysis obtained on the oxidation front of a cobalt-base Co-8.5Ni-30Cr-0.4C-6Ta superalloy after 100 hours at 1200°C in air (during oxidation Ni remained at 8.5%) ; Thermocalc calculations made on these three analysis, C remaining free

## CONCLUSIONS

In the high temperature oxidation field as well, thermodynamical modelisation is able to give useful indications for a better understanding of both the occurrence of new phases and the destination of light elements. The examples of results given here are overall qualitative, but quantifications are possible by the mean of image analysis. This technique allows the determination of surface - then volume, weight and finally molar - fractions of each phases metallographically observed. Indeed, knowing all the heavy elements contents and quantities of the different phases, then comparing these data to modelisation predictions, this method would identify the content of the last and light element such as carbon. The classical equation between chemical composition and the following microstructure is then inverted, the new unknown quantity being %C.