



## Isothermal oxidation at high temperature of a nickel-chromium alloy in water vapor-rich air. Part 2: Metallographic characterization of the oxidized samples

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### ABSTRACT

The Ni-25Cr samples oxidized at high temperature with thermogravimetric measurements exploited on the mass gain kinetic field in the first part of this work, were here metallographically prepared and subjected to different investigations: X-ray diffraction and SEM observation of the outer scales, cross-section examination of the quality and thickness of the external oxides and chromium concentration in the subsurface. It appeared that, if sensible differences were found again between the present samples and samples of the same alloy but oxidized in dry air, the differences between oxidation with this higher water vapour content and oxidation with a less humidified air studied in a previous work, were not significant. This confirms the first feelings deduced from the kinetic results. In this range of water vapour concentration, the oxidation behaviour remains almost the same. Further investigations devoted to demonstrate an effect of water concentration in air must concern higher vapour concentrations associated to higher pressures. © 2014 Trade Science Inc. - INDIA

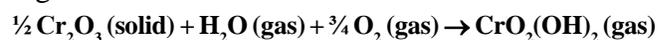
### KEYWORDS

Nickel alloy;  
Chromium;  
Water vapour;  
High temperature;  
Isothermal oxidation;  
Post-mortem metallographic  
characterization.

### INTRODUCTION

The presence of water vapour in hot air is known to possibly influence the progress of oxidation, on the kinetic field as well as on the mechanisms one<sup>[1]</sup>. Superalloys, which are among the most used metallic materials for service at high temperatures, are particularly concerned and their protective oxide scales, chromia, alumina and silica – developed over the piece surfaces thanks to high contents in Cr, Al and/or Si in these al-

loys<sup>[2]</sup> – are notably subjected to specific reactions and mass gain kinetic modifications. In the case of the chromia-forming superalloys, for example, the following reaction occurs<sup>[1,3]</sup>:



This new oxidation reaction affecting chromia<sup>III</sup>, which leads to new chromium containing specie – a volatile one – oxide-hydroxide of chromium<sup>VI</sup>, induces an overconsumption of chromium for a same thickness of the chromia scale, modifications of its structure (po-

rosities...) and thus its transport properties (with consequences of the anionic or cationic diffusion through this protective scale). This may influence the parabolic oxidation kinetic as it was often observed, and found again for a Ni-25Cr alloy<sup>[4]</sup>. Other possible effects which were noticed concern adherence of the chromia scale on the alloys, which was notably noticed to be better than in dry atmosphere<sup>[5-7]</sup>.

The high temperature oxidation behaviour is dependent not only on the presence or not of water vapour in air but also on the gaseous water concentration in this oxidant atmosphere. Differences were noticed again for the isothermal oxidation rate in the first part of this work<sup>[8]</sup>, but they were not very easy to interpret and it was expected that the metallographic characterization of the oxidized Ni-25Cr samples may help to understand why two water vapour contents may lead to different mass gain and chromia volatilization kinetics. This is the purpose of the present second part of the work to exploit the oxidized samples to allow clearing the effects of the water vapour concentration.

## EXPERIMENTAL

One can remind that the Ni-25Cr alloy, elaborated by foundry from pure nickel and chromium, was subjected to oxidation in industrial air (80% N<sub>2</sub>-20% O<sub>2</sub>) added with water vapour by targeting a relative humidity of 90% when the air was at 60°C (named “very wet air”) before being heated to the temperature wished for the isothermal stage. The considered isothermal stage temperatures were 1000, 1100, 1200 and 1300°C and their durations were all 48 hours (heating and cooling rates: 20°C min<sup>-1</sup> and 5°C min<sup>-1</sup>). The obtained thermogravimetric measurements were previously exploited to precise oxidation data concerning the heating phase<sup>[9]</sup>, the isothermal kinetic<sup>[8]</sup> and the cooling phase<sup>[7]</sup>.

The obtained oxidized samples were here studied, first by X-Ray diffraction (diffractometer Philips X'Pert Pro, wavelength of Ka transition of copper: 1.5406 Å). They were thereafter covered by electro-deposition of nickel for strengthening against possible oxide break during cutting. Cross-sections were prepared by cutting, embedding, polishing (SiC papers with grade from 240 to 1200, ultrasonic cleaning, 1 µm alumina on textile), then observed.

The observations of the oxidized surfaces before cutting were done using two Scanning Electron Microscopes (SEM): a Hitachi S4800 FEG SEM for the samples oxidized in very wet air, and a JEOL JSM7600F for older Ni-25Cr samples oxidized at the same temperatures and during the same times but in dry industrial air (80% N<sub>2</sub>-20% O<sub>2</sub>), for comparison. After cutting, embedding and polishing, the obtained cross-sections were examined using a third SEM (JEOL JSM6010LA). General and local chemical composition measurements were performed with the Energy Dispersion Spectrometry (EDS) devices equipping the SEM.

Wavelength Dispersion Spectrometry (WDS) concentration profiles, performed with a CAMECA SX100 microprobe, were acquired through the external oxide scale and the subsurfaces, perpendicularly to the extreme surface, to characterize the chromium depleted zone.

## RESULTS AND DISCUSSION

### Surface characterization

Before cutting the oxidized samples were observed in electron microscopy. Some micrographs taken in Back Scattered Electrons (BSE) mode (with “BSE” inserted) and the ones taken in Secondary Electrons (SE) mode, at different magnifications, are presented in Figure 1 to illustrate the oxide scale morphology. One can see that the scales do not entirely cover the surface, due to oxide detachment during cooling<sup>[7]</sup> (oxide spallation which did not occur – or at least much less frequently – for less humidified air<sup>[4]</sup>). They are also to be compared to the ones taken on a Ni-25Cr earlier oxidized in dry air at the same temperatures and for the same duration, presented in Figure 2 (for each oxide spallation also occurred). One can see that the rugosity of the outer parts of the chromia scales are similar, while there was a finer texture of the chromia scale formed on the Ni-25Cr alloys earlier oxidized in moderately humidified air<sup>[4]</sup>.

The XRD diffractograms performed on the surfaces of the oxidized samples before cutting all show that only chromia (Cr<sub>2</sub>O<sub>3</sub>) is present on the surface of the oxidized samples as shown by the two examples displayed in Figure 3 (Ni-25Cr oxidized 48h at 1100°C) and in

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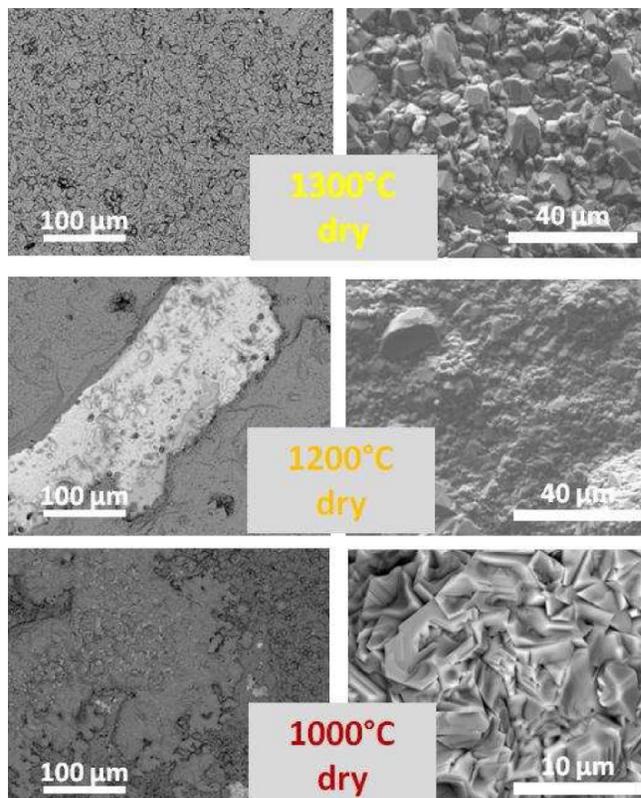
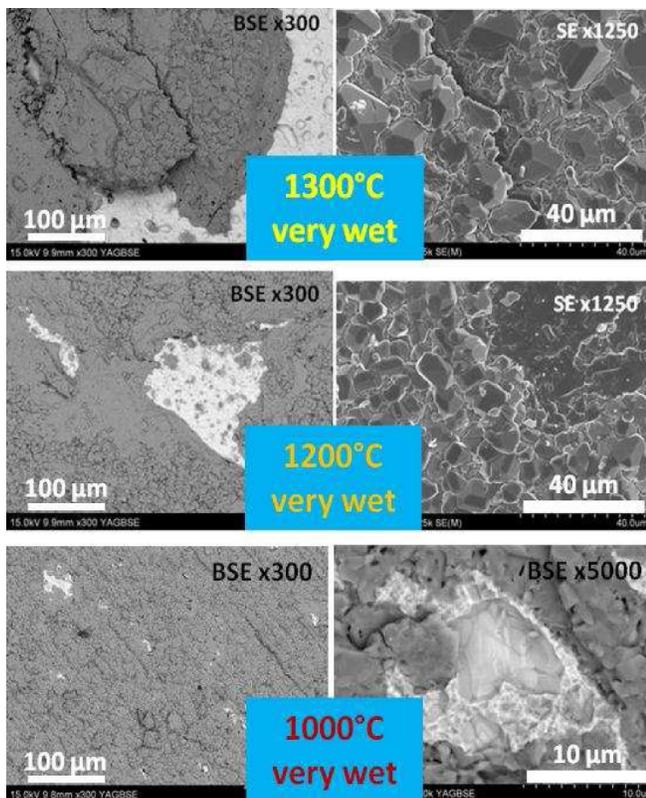


Figure 1 : The oxidized surface of three of the four samples observed with a SEM (Hitachi S4800)

Figure 2 : The oxidized surface of three of the four samples observed with a SEM (JEOL JSM7600F)

Figure 4 (Ni-25Cr oxidized 48h at 1200°C). The other peaks are to be attributed to the alloy itself (face centred

cubic crystalline network of nickel a little distorted by the presence of chromium in solid solution).

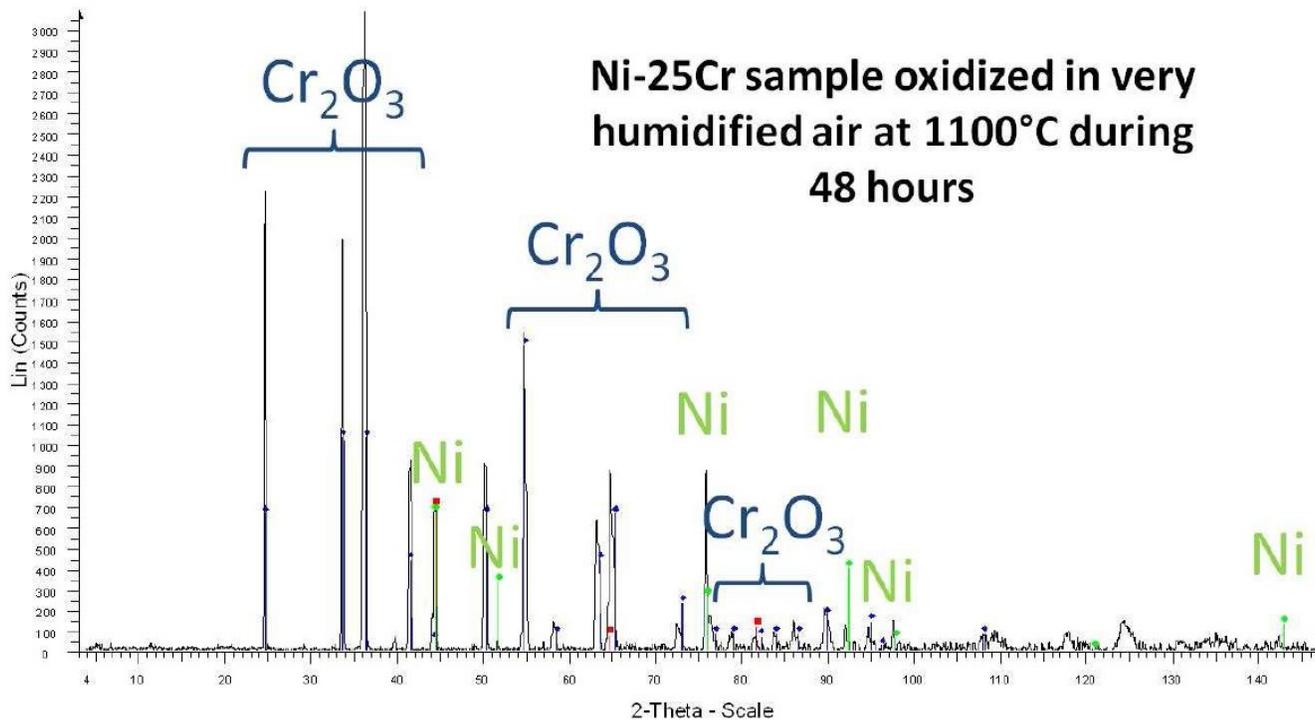
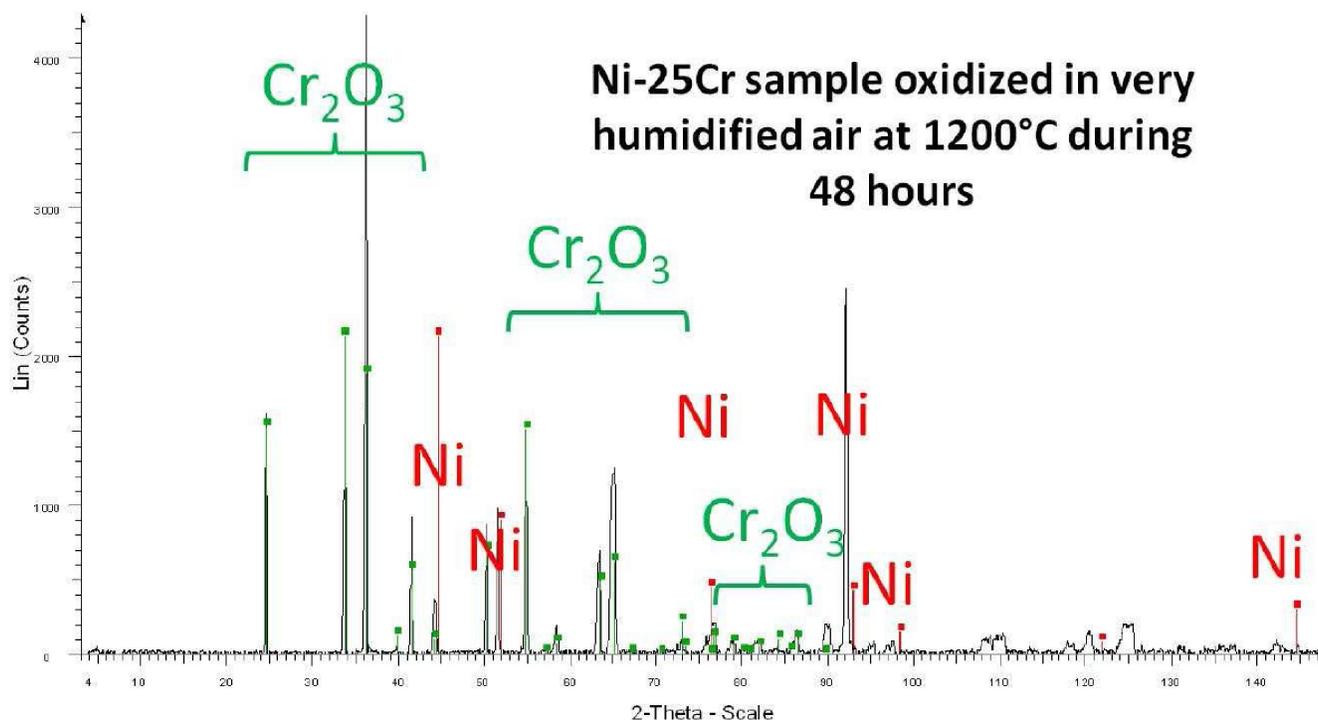


Figure 3 : XRD diffractogram acquired on the outer surface of the Ni-25Cr sample oxidized at 1100°C

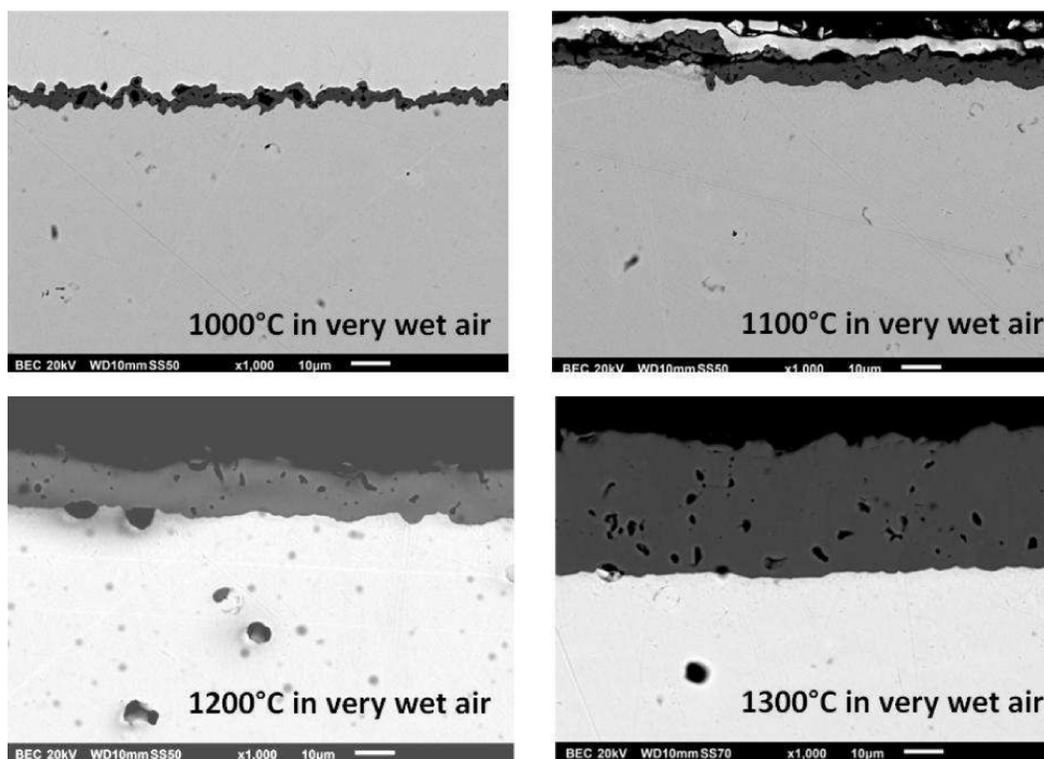


**Figure 4 : XRD diffractogram acquired on the outer surface of the Ni-25Cr sample oxidized at 1200°C**

### Cross-section characterization

After metallographic preparation achieved as described above the oxidized samples were examined in cross-section in electron microscopy again. The micro-

graphs given in Figure 5 show the oxides scales formed over the four samples. The oxide scale is obviously chromia in all cases, confirming the XRD results. The average thickness is logically higher for a higher tem-



**Figure 5 : SEM/BSE micrographs (JEOL JSM6010LA) illustrating the oxidized surfaces of the four samples**

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perature, as also graphically demonstrated in Figure 6. It varies from about 6 $\mu\text{m}$  for 48h at 1000 $^{\circ}\text{C}$  to 31 $\mu\text{m}$  for the same duration at 1300 $^{\circ}\text{C}$ . These values are lower than the corresponding ones earlier obtained for dry air<sup>[4]</sup> (from 5 at 1000 $^{\circ}\text{C}$  to 40 $\mu\text{m}$  at 1300 $^{\circ}\text{C}$ ) and even slightly lower than the ones earlier obtained for more moderately humidified air (80% of relative humidity in air at 40 $^{\circ}\text{C}$ )<sup>[4]</sup>.

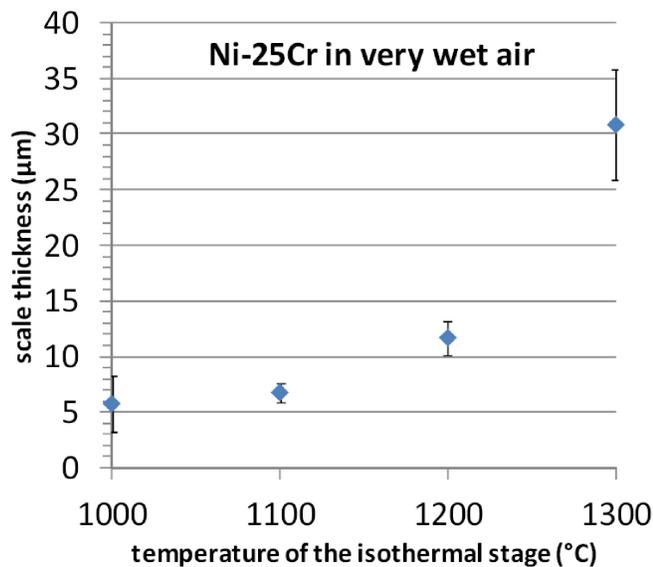


Figure 6 : Evolution of the oxide scale thickness with the temperature

Concentration profiles were performed in WDS with the microprobe through the external oxide scale and the subjacent alloy depleted zone. The results are presented in Figure 7, Figure 8, Figure 9 and Figure 10 for respectively 1000 $^{\circ}\text{C}$ , 1100 $^{\circ}\text{C}$ , 1200 $^{\circ}\text{C}$  and 1300 $^{\circ}\text{C}$ . First they confirm again that the external oxide is chromia. Second, several characteristic data were taken out these profiles: the chromium content in extreme surface (graphically represented in Figure 11), and the depth of the chromium-depleted zone (Figure 12).

One can see that the chromium content in extreme surface is lower than the initial Cr content in the alloy, but after 48 hours, even at 1300 $^{\circ}\text{C}$ , it remains high enough to allow the alloy displaying a chromia-forming behavior. It is at the same level as previously seen for the same alloy after oxidation for the same time and at the same temperatures in dry air and less humidified air<sup>[4]</sup>. The depth of the subsurface zone of alloy depleted in chromium logically increases with tempera-

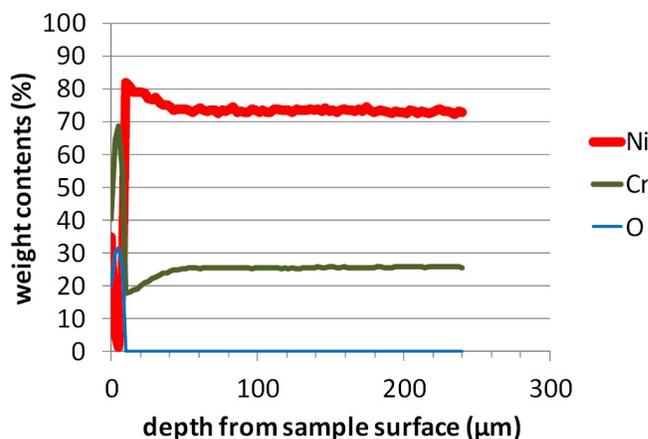


Figure 7 : WDS concentration profiles across the oxide scale and the subsurface of the Ni-25Cr oxidized at 1000 $^{\circ}\text{C}$  in very wet air

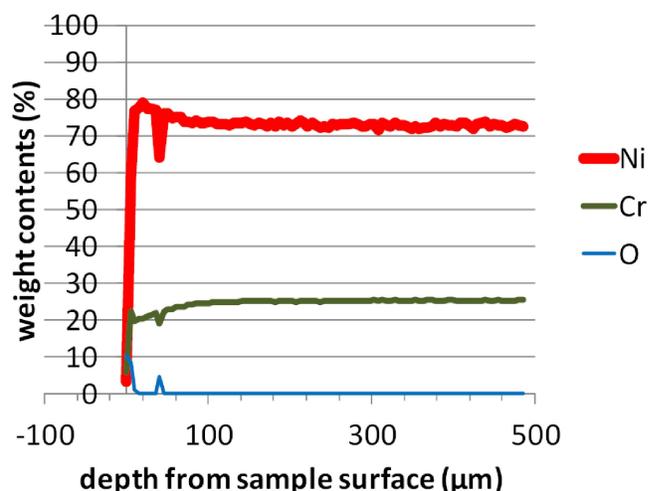


Figure 8 : WDS concentration profiles across the oxide scale and the subsurface of the Ni-25Cr oxidized at 1100 $^{\circ}\text{C}$  in very wet air

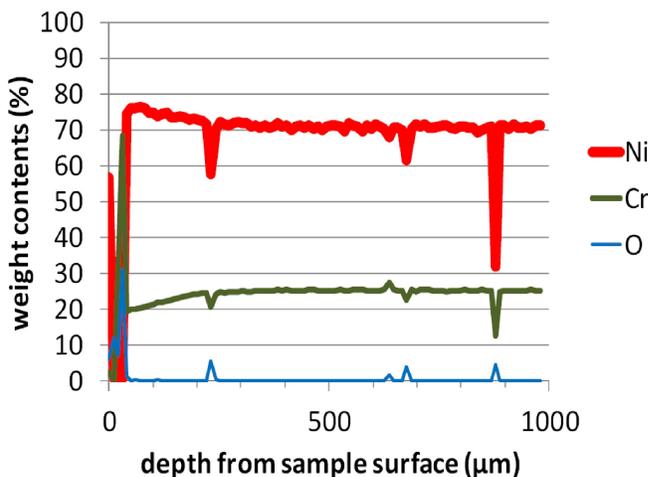


Figure 9 : WDS concentration profiles across the oxide scale and the subsurface of the Ni-25Cr oxidized at 1200 $^{\circ}\text{C}$  in very wet air

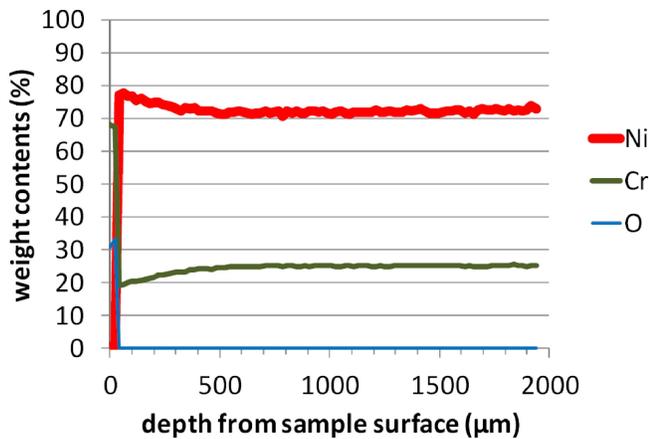


Figure 10 : WDS concentration profiles across the oxide scale and the subsurface of the Ni-25Cr oxidized at 1300°C in very wet air

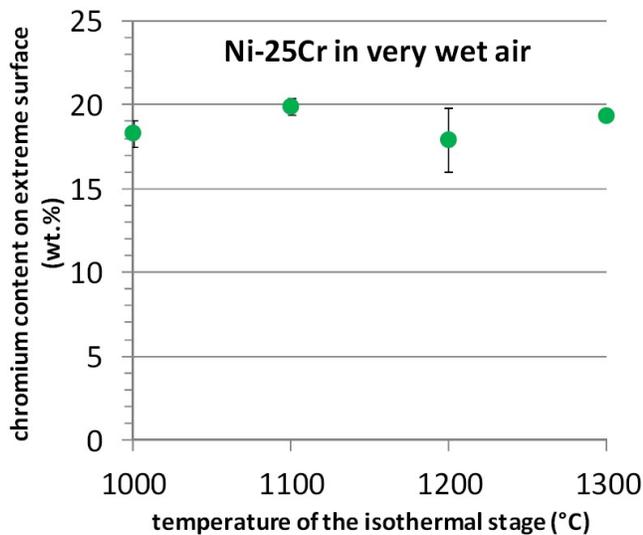


Figure 11 : Chromium content on extreme surface for the four temperatures (average and standard deviation calculated from two values taken from two concentration profiles)

ture. Here too the Cr-depleted depth are of the same level as previously observed for the same alloy after oxidation during the same time and at the same temperatures in dry air and less humidified air<sup>[4]</sup>.

### General commentaries

There were then no great differences between the Ni-25Cr samples oxidized here in very humidified air and the same alloy oxidized in less humidified air previously studied<sup>[4]</sup>. The external oxide scale are composed of only chromia in the two cases, the outer surface texture of these scales are similar, the chromium contents in extreme surface are globally the same and the same comment can be done for the chromium-depleted depth. The differences were more evident between oxidation

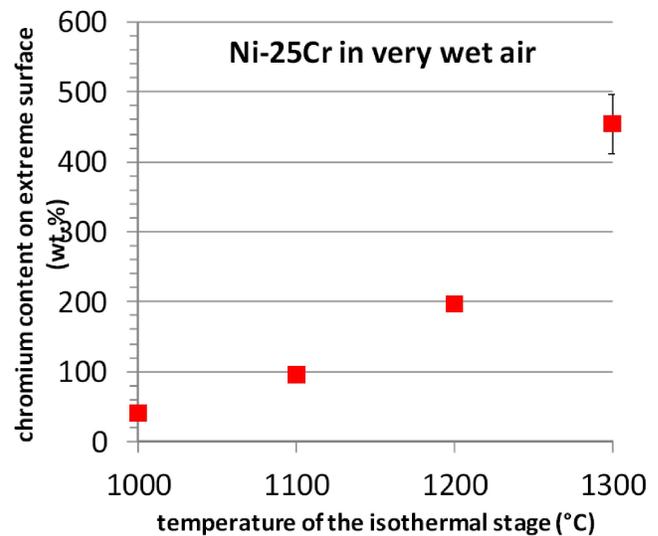


Figure 12 : Depth of the chromium-depleted zone in the subsurface for the four temperatures (average and standard deviation calculated from two values taken from two concentration profiles)

in dry air and oxidation in air moderately rich in water vapour. The single noticeable difference between the two water vapour concentrations is maybe the thickness of chromia scale which is here generally slightly lower than for less humidified air, this maybe evidencing a faster chromia volatilization for a higher water vapour concentration. The present metallographic results let think that the differences which seemed existing between the values of parabolic constant and of chromia volatilization constant are probably more due to measurement scattering than to a real effect of the vapour concentration. In contrast, it was however found again that hot oxidation in humidified air is different from hot oxidation in dry air.

## CONCLUSIONS

Thus, if the behavior in oxidation at high temperature of such a chromia-forming alloy as this Ni-25Cr alloy is strongly dependent on the fact that air is humidified or not, the influence of the content of air in water vapour content is not very important, at least in the range of vapour concentration tested in an earlier work<sup>[4]</sup> and in the present study. This was first suspected by considering the kinetic data in the first part, and here by exploiting the metallographic results. Deeper investigations will be done by increasing again the water concentration and by increasing the gas pressure at the same

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time, to come closer to the conditions encountered in steam turbine for example.

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