

THERMODYNAMIC MODELING OF THE SURFACE LAYER STRUCTURE ON INCONEL 600 OXIDIZED IN A CONTROLLED ATMOSPHERE

Abdallah Haouam^{1*}, Kamel Dawi², Bachir Merzoug¹

¹*Université Badji Mokhtar, Faculté des Sciences de l'Ingénieur,
Département de Génie Mécanique, Annaba 23000, Algérie*

²*Université de Technologie de Compiègne, Laboratoire Roberval
UMR 6253, 60205 Compiègne, France*

*Corresponding author: haouam_a@yahoo.fr

Received: February 15, 2011

Accepted: October 10, 2011

Abstract: Samples of Inconel 600 were isothermally oxidized in a controlled atmosphere with a special mounting at high-temperature oxidation. Along with this experimental study, a simulation of thermodynamic behavior of the material in the same oxidation conditions was carried out using the Thermo-Calc code. The thermodynamic modeling is able to predict the phase nature and its distribution in the structure of the surface layer resulting from the corrosion of the material in thermodynamic equilibrium in the absence of mechanical stress. The results of this simulation are supplemented to results obtained from the analysis by glow discharge spectrometry (GDS) which is performed on the samples tested.

Keywords: *oxidation, Inconel 600, GDS, modeling, Thermo-Calc.*

INTRODUCTION

Inconel 600 (Ni15Fe) is a nickel base alloy used in the chemical, food, oil and nuclear industries; especially in the steam generator tubes of nuclear power plants. It is sensitive to intergranular corrosion in primary and secondary cooling water under pressurized water reactor (PWR) operating conditions [1]. The mechanisms of oxidation of this alloy were investigated by several authors: Rousselet [2] studied the consequences of the defects generated by preliminary deformations under various atmospheres, Abadie [3] examined cracking by stress corrosion of the alloy 600, Gourgues [4] worked on the mechanic-oxidation interactions, Caron [5] was interested by the influence of hydrogen on the propagation of cracks under stress corrosion. Many published papers have focused on the properties of oxide layers grown on nickel alloys in complex atmospheres at high temperature. They report, in most cases, the oxide films formed in the primary circuit of nuclear reactors (PWR). This research aims at looking into the role of these films against corrosion problems. Almost all these papers describe the oxide layer as having a duplex structure formed by an inner Cr rich layer and an outer Ni rich layer [6-9]. The objective of this work was devoted to study the oxidation phenomena of Inconel 600 in the operating temperature interval of steam generators (SG) (350-550°C) in a corrosive environment (presence of oxygen and water vapor). In fact, the nature of the oxide layer and the modification of the underlying substrate are likely to play a major role in the mechanisms of stress corrosion cracking initiation. Their knowledge is essential for predicting the life and definition of safety margins of SG tubes. This experimental study is supplemented by a thermodynamic modeling of the generated oxidation layers using the Thermo-Calc code [10] that will enable us to predict the phase composition of the oxidation layers at thermodynamic equilibrium.

MATERIAL AND EXPERIMENTAL PROCEDURES

Material

The chemical composition of the material used in this study is given in Table 1. Inconel 600 is provided in the form of rolled sheets, which are then cut out in sheets of 2 mm thick. The samples obtained have a parallelepiped form of dimension: 18 × 12 × 2 mm. These samples undergo a mechanical polishing on only one side, using silicon abrasive carbide paper going up to 80-1200. This operation is followed by an annealing at 600°C during 1 hour to relax the residual stresses due to working on rough sheets, then polished to 4000 grade and finished with 3 µm alumina.

Table 1. Chemical composition of Inconel 600 (in weight percent) [11]

Ni	Cr	Fe	C	Si	Mn	S	Cu
Base	15.5	8	0.10	0.50	1.00	0.015	0.5

Oxidation procedure

The samples were oxidized in the temperature range 350-550°C according to the procedure shown in the Figure 1, using the oxidation installation used for the treatment as shown on Figure 2 and vapor generator shown on Figure 3.

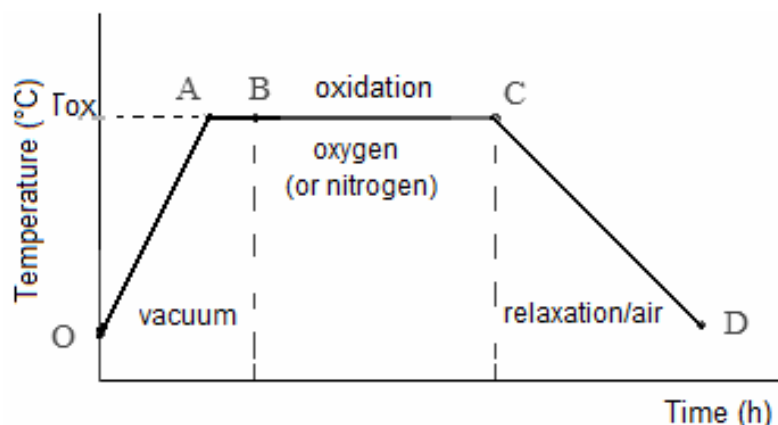


Figure 1. Experimental procedure of oxidation tests

The experimental procedure follows four steps:

OA: Sample heating phase under secondary vacuum until the desired temperature.

AB: Hold time under secondary vacuum at isothermal temperature (stabilization 20 min).

BC: Insulation of the vacuum pump and opening of the valve allowing the oxygen passage (or wet nitrogen) for 120 hours in laboratory conditions.

CD: Relaxation phase followed by cooling of the sample in air (approximately 6 hours).

“*Tox*” is the oxidation temperature (350, 450 and 550°C).

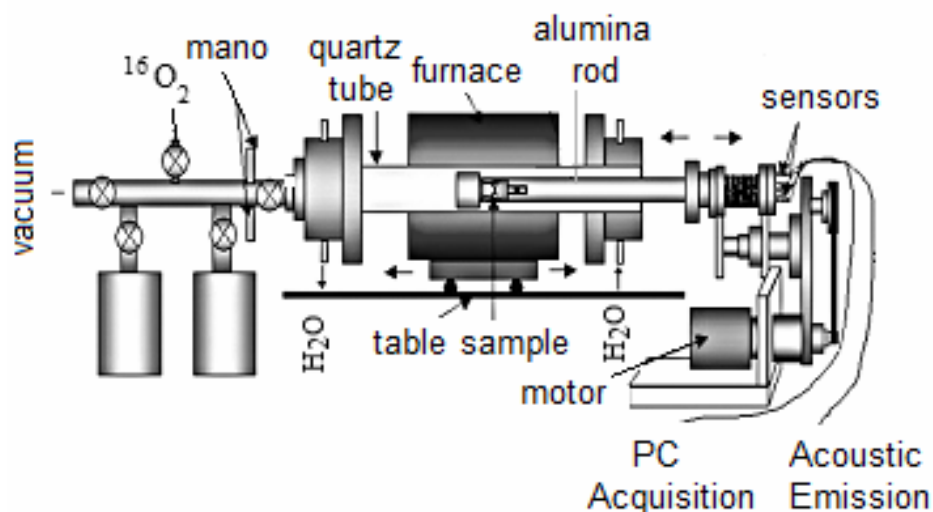


Figure 2. Oxidation installation

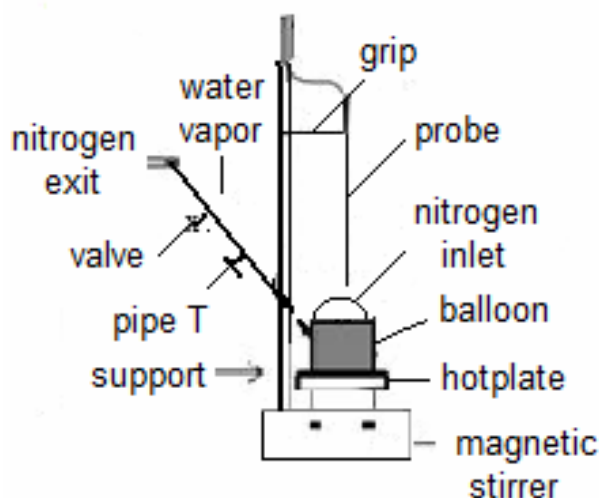


Figure 3. Vapor generator

This installation [12] makes it possible to follow simultaneously the oxidation of a sample and the evolution of the principal mechanical parameters (load and displacement) via two coupled sensors at the mobile jaw and are connected to a computer (control and acquisition) and to an acoustic emission chain allowing the follow-up of the damage of the samples at the time of the various thermo mechanical solicitation (creep, traction, bending). A sliding furnace allows the heating of the sample along the quartz tube to the desired temperatures. It should be noted that the samples presented in this article were not loaded mechanically during the oxidation and the "technique" of follow-up with the acoustic emission was also not used in our case.

The possible oxidation atmospheres are: oxidation under secondary vacuum, oxidation under oxygen and/or water vapor. The vacuum evolution of the quality of the oxidized surface is used as a test of reference. The difference between the tests carried out in vacuum and those carried out under other atmospheres (oxygen or water vapor) makes it possible to analyze the influence of an oxidized surface layer on the behavior of the system and to go up with the intrinsic physicochemical properties of the oxidized layers. The vacuum is obtained by two pumps, one primary and the other secondary allowing a reduction of the pressure down to approximately 2.10^{-6} mbar. Oxygen is introduced into the enclosure by a micrometric valve from an oxygen bottle connected to the assembly. Whereas the water vapor is generated by the passage of nitrogen from a balloon with three collars connected to the assembly (Figure 3), and is also introduced to the assembly by a micrometric valve; the nitrogen comes from an external bottle. Two environments were studied: a dry atmosphere with ~100% oxygen and a humid atmosphere with ~20% by volume of water vapor balanced with nitrogen.

Thereafter, the oxidized samples are analyzed by glow discharge spectrometry (GDS) [13].

Technique of analysis GDS

This technique was used to measure the corrosion layer thickness. The rugosimeter used is of type Surtronic 3+ (Taylor Hobson) with contact. The acquisition software is Talyprofile. The principle of measurement is simple, it consists in making two analyses GDS, thus to make two holes on the sample surface. The first analysis relates to the totality of the corrosion layer as well as the base metal. It makes it possible to specify the erosion time necessary to erode the corrosion layer alone. By applying this time during the second analysis, one can make a hole of depth equal to the thickness of the corrosion layer.

THERMODYNAMIC MODELING

This experimental work is followed by a thermodynamic simulation using Thermo-Calc code, allowing a thorough knowledge of the oxidation layers susceptible to be formed during the oxidation tests.

Thermo-Calc developed in 1981 is a flexible code for all kinds of thermodynamic computation and establishment of phase diagrams. It allows, using adapted thermo chemical data bases, to determine the state of balance of a system using a minimization algorithm of the total Gibbs energy G (free enthalpy). It is accompanied by several data bases generated by Scientific Group Thermo data Europe (SGTE), an international organization of collaboration for the thermodynamic data bases. The base used in this study is the SSUB3 containing 4000 stoichiometric condensed compounds and gaseous species [14].

Simulation procedure

This numerical simulation is able to predict the nature and the composition of the phases resulting from the oxidation of the material tested in the absence of mechanical solicitation. To deepen this thermodynamic analysis, we sought to describe the different layers of oxidation formed using Thermo-Calc code. For this, we vary the atmosphere composition in contact with the alloy from 0% (% of the oxidizing atmosphere supposed at the scale/substrate interface) to 100% (% of the oxidizing atmosphere at the scale/gas interface); thus, the code calculates the equilibrium state of the system for various proportions of the atmosphere in contact with the alloy and gives us the successive phases which could be formed at thermodynamic equilibrium from the scale/substrate interface (small fraction of the atmosphere), upper part of the layer which is in direct contact with the atmosphere (high fraction of the atmosphere). To facilitate and simplify calculations, only the composition of the three principal elements Ni, Cr and Fe were taken into account in the calculations.

RESULTS AND DISCUSSION

The technique of analysis by spectrometry with glow discharge allowed the layout of the profiles of concentrations of oxides in the temperature interval considered for all the tests carried out. GDS technique is not quantitative, the profiles of concentrations are obtained in depth and the axis of the concentrations is graduated in arbitrary units (au). One distinguishes on each graph (Figures 4, 5, 6, 9 and 10) corresponding to a given temperature two well defined zones: a curved zone corresponding to the oxide layers formed and a linear zone corresponding to the matrix of the material on which the principal components appear: Ni, Cr and Fe.

The presentation of the results is divided into two parts: a first part relates to the tests carried out under oxygen and a second part concerning the results obtained in the presence of water vapor.

Oxidation under oxygen

Concentration profiles of the chemical elements depending on the oxide thickness are shown in Figures 4, 5 and 6.

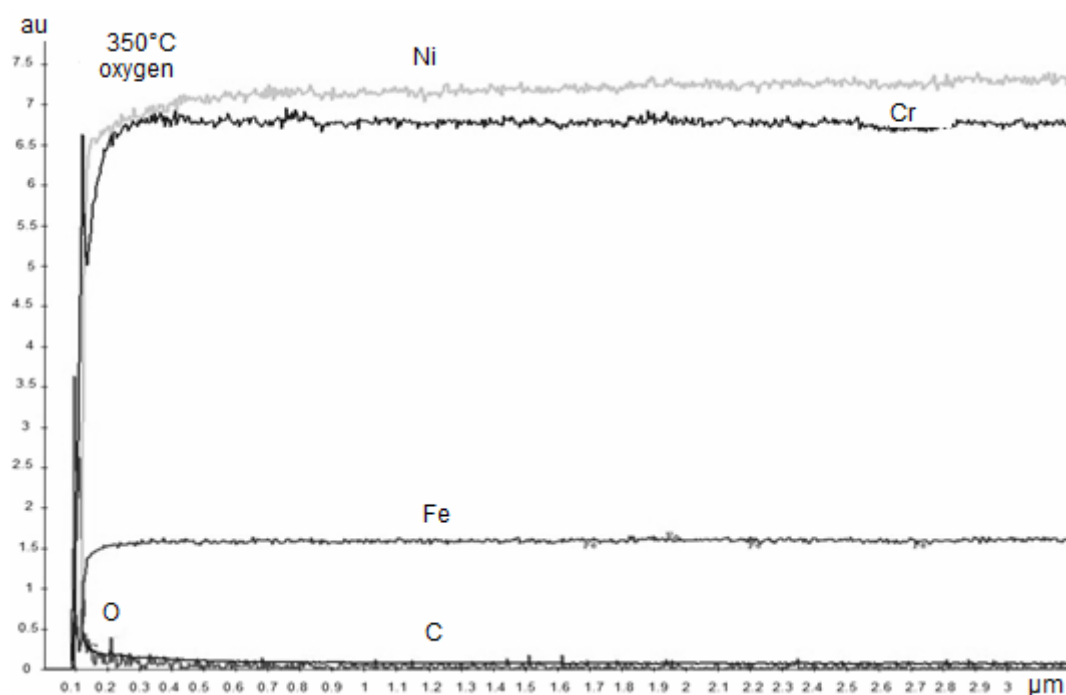


Figure 4. Concentration profiles of the elements versus oxide thickness following oxidation by O_2 at 350°C (120 h)

The recorded oxide film thickness (Cr_2O_3) obtained is approximately $0.3 \mu\text{m}$; it shows the very low Inconel 600 reactivity at 350°C (Figure 4).

GDS analysis shows the presence of an oxide coating rich in Cr, Fe at 450°C (Figure 5). The resolution of this analysis does not enable us to distinguish the various layers of oxide likely to be present. The same was noticed at 550°C (Figure 6).

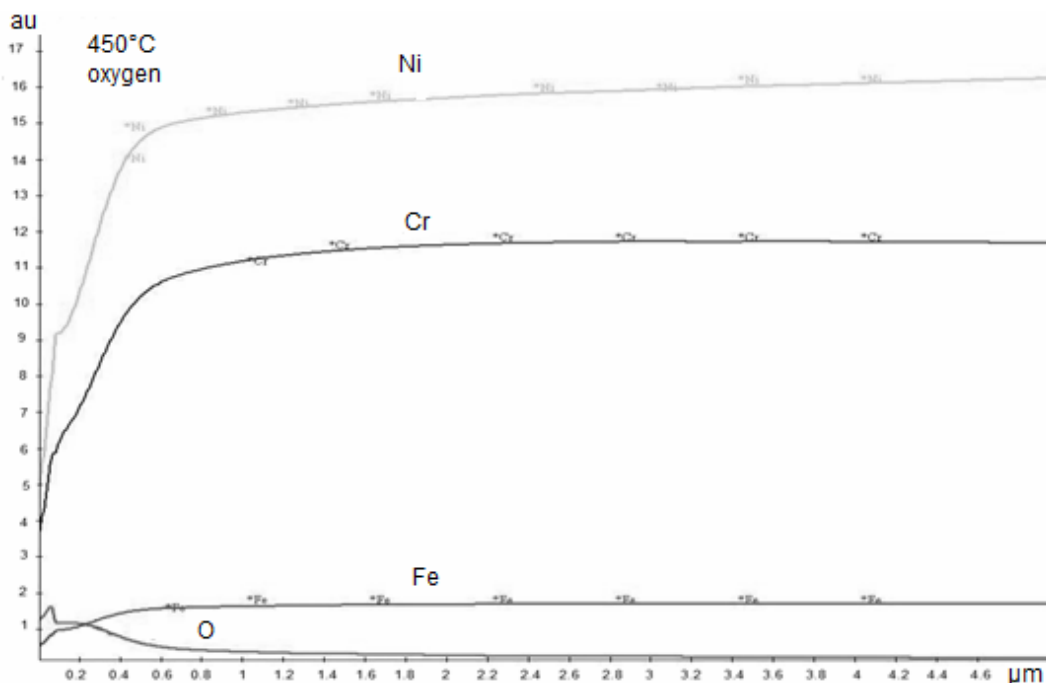


Figure 5. Concentration profiles of the elements versus oxide thickness following oxidation by O₂ at 450°C (120 h)

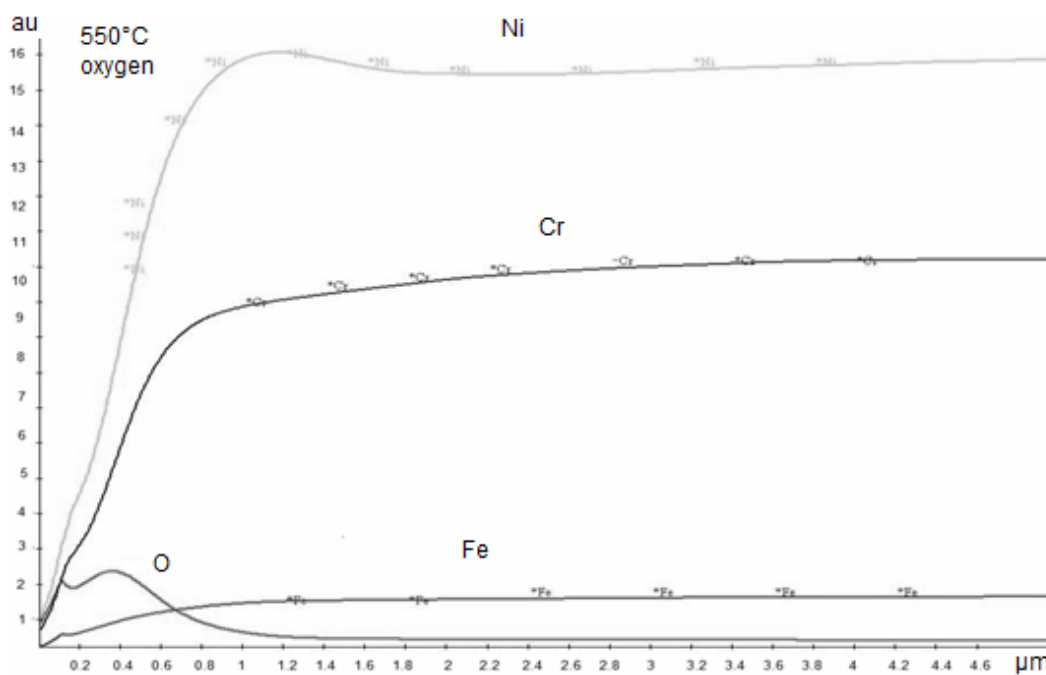


Figure 6. Concentration profiles of the elements versus oxide thickness following oxidation by O₂ at 550°C (120 h)

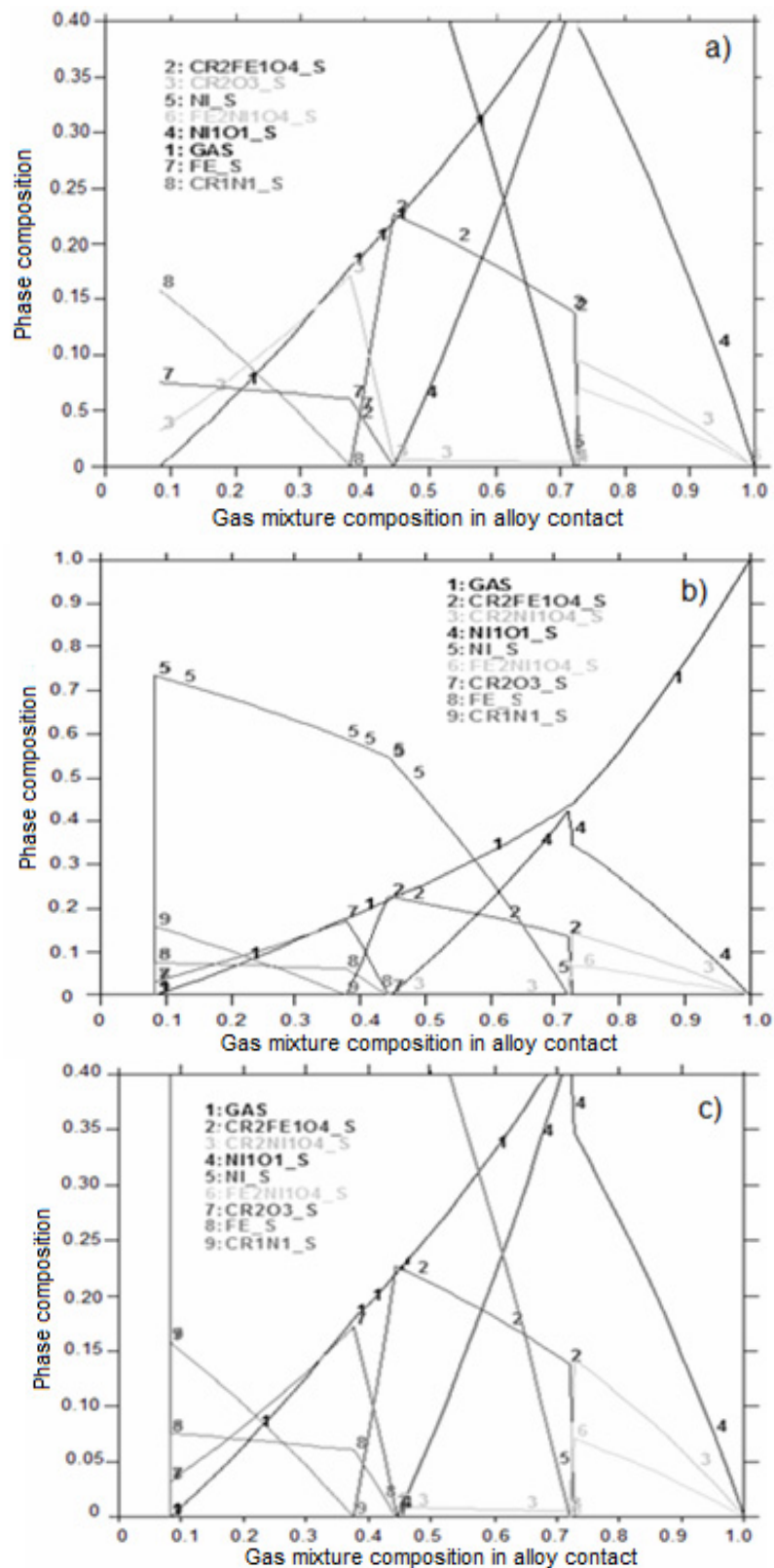


Figure 7. Results of the numerical simulation of the phase composition under synthetic air at : a) 350°C, b) 450°C and c) 550°C

The thickness of the oxide film is approximately $0.8\ \mu\text{m}$ at 450°C and is approximately $1.2\ \mu\text{m}$ at 550°C , it is relatively more significant at 550°C than at 450°C because of the oxygen activity more spread out in time and in temperature.

The diagrams of the phase composition obtained by simulation using the Thermo-calc code are shown in Figure 7.

Figure 8 is a schematic representation of the results obtained after the thermodynamic simulations were carried out using the Thermo-Calc code for different temperatures: 350 , 450 and 550°C in an atmosphere enriched in oxygen.

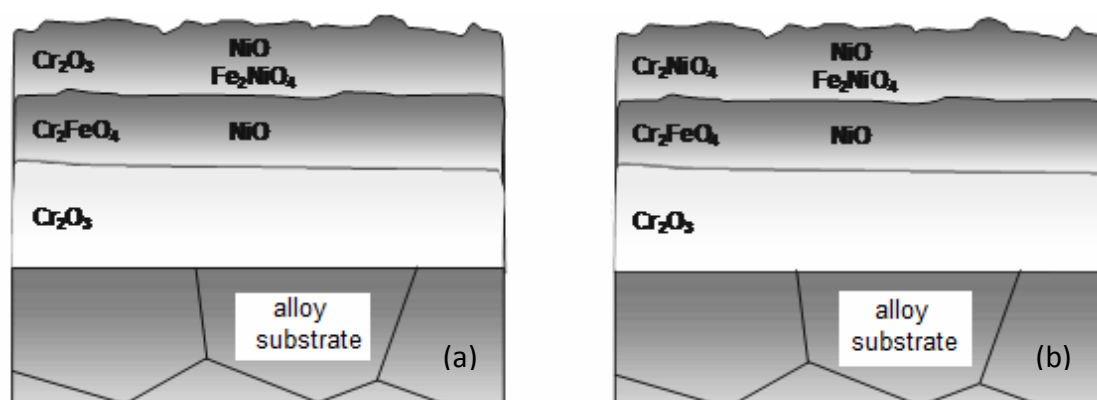


Figure 8. Model of the layers structure obtained under synthetic air at $P = 10^5\ \text{Pa}$ at: a) 350°C , b) 450°C or 550°C

Let us take the case of 350°C , thermodynamic modeling shows that Cr can oxidize to give the formation of chromine Cr_2O_3 at the interface metal-layer, Cr_2FeO_4 in the intermediate zone and finally again Cr_2O_3 on the surface. Ni also oxidizes to give the formation of NiO in the intermediate and external zone and Fe_2NiO_4 in the external zone. By increasing the temperature to 450 or 550°C , we notice, compared to the case 350°C , the disappearance of the Cr_2O_3 phase from the surface and its replacement by the Cr_2NiO_4 . This modeling shows well the transverse distribution of the various phases which are formed at thermodynamic equilibrium. Thus, we notice that the passage from 350 to 450°C or 550°C does not considerably change the nature of the formed products; this allows us to note a weak influence of the temperature under these experimental conditions. The strong chance to find a protective Cr_2O_3 coating at the interface metal-layer could explain the very low thickness of the oxidation layer formed.

Oxidation in the presence of water vapor

The test with 350°C was not carried out because of the low reactivity of the alloy at this temperature. Figures 9 and 10 present two GDS analyses carried out on two corroded samples of Inconel 600, in an atmosphere enriched in water vapor, respectively, at 450°C and 550°C during 120 hours. These analyses show the formation in both cases of a layer of corrosion made up of, at least, two oxide layers: a layer on the surface rich in Cr and Fe: (Cr_2FeO_4) and a deeper layer rich in Cr: (Cr_2O_3). The only principal difference between the two temperatures appears in the thickness of the corrosion layer formed. Indeed, this layer increases appreciably with the temperature; it goes from $1\ \mu\text{m}$

at 450°C to 1.4 μm at 550°C. The thickness of the oxide layers formed in water vapor is greater than those formed under oxygen. This reveals the most harmful effect of the water vapor on the material as a consequence of the additional effect of hydrogen embrittlement. Water vapor facilitates oxidation by internal growth (anionic mechanism) insofar as the oxidizing element associated with water vapor, OH^- ion, diffuses more readily than the O^{2-} ion responsible of the internal growth under oxygen, because it is smaller and less charged [15].

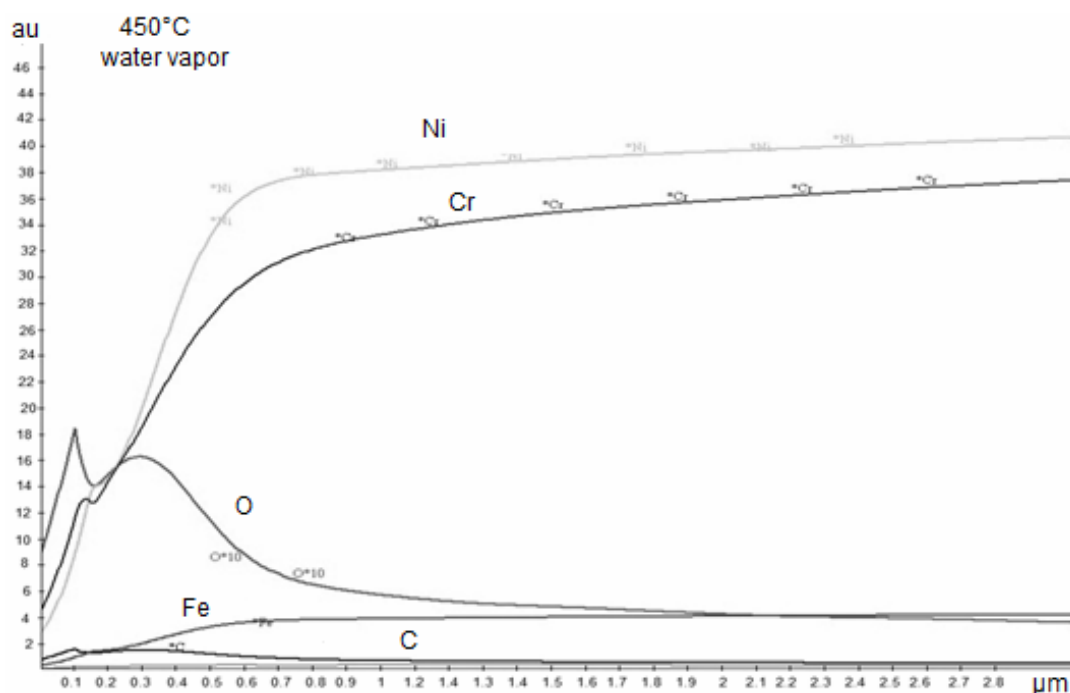


Figure 9. Concentration profiles of the elements versus oxide thickness following oxidation by water vapor at 450°C (120 h)

This experimental study was followed by a thermodynamic modeling. The phase composition diagrams are represented in Figure 11.

Figure 12 is a schematic representation of the results obtained after the thermodynamic simulations carried out using the Thermo-Calc code for different temperatures: 350, 450 and 550°C in an atmosphere enriched in water vapor.

These results show in all the cases, for the temperatures 350, 450 and 550°C, the formation of two oxide layers: Cr_2O_3 in the immediate vicinity of the substrate and Cr_2FeO_4 on the surface. This comes from the decomposition of carbides $(\text{CFe})_{23}\text{C}_6$ present in alloy leading to the oxide formation rich in Cr and Fe [2].

These thermodynamic simulations corroborate the results obtained with GDS analysis from the enrichment point of view in Fe and Cr on the surface and in Cr at a deeper zone.

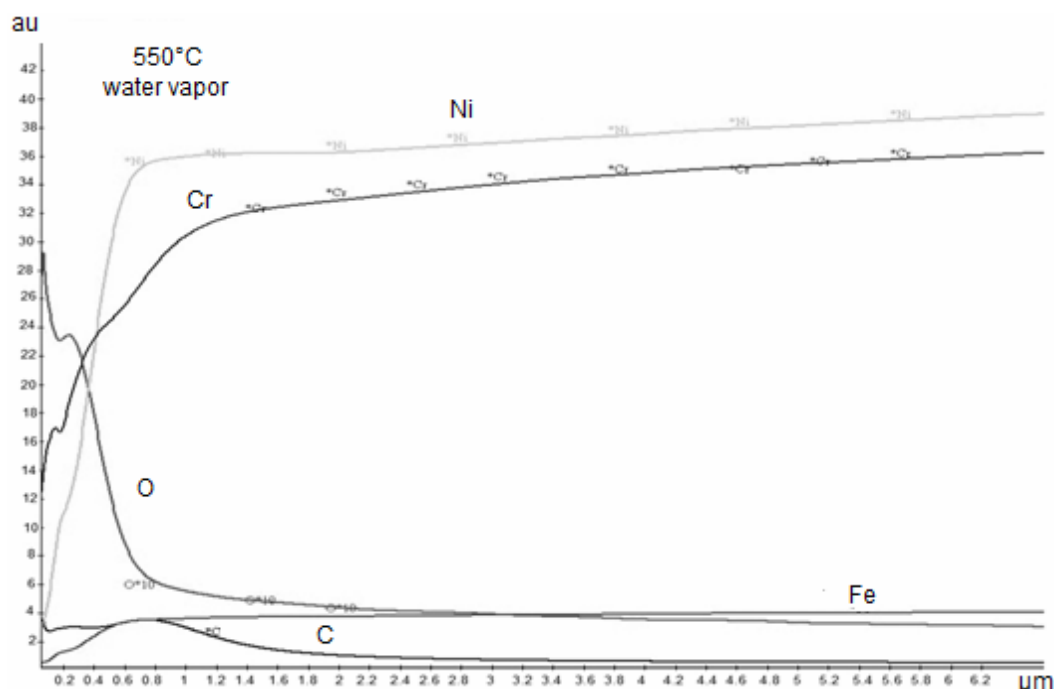


Figure 10. Concentration profiles of the elements versus oxide thickness following oxidation by water vapor at 550°C (120 h)

CONCLUSION

Having a good grasp of the oxidation mechanisms of nickel base alloys under a controlled atmosphere in temperature is important for their use in high stress applications in the nuclear industry. It is essential for the prediction of the lifespan and the definition of the safety margins of steam generator tubes in Pressurized Water Reactor power plants.

Thus, for the tests of isothermal oxidation carried out under oxygen and those under water vapor, a very thin corrosion layer is formed. Under these two atmospheres and in the considered interval of temperature (350-550°C), the protective Cr_2O_3 layer at the interface metal-layer is formed.

GDS analysis shows that the oxide layers formed under water vapor are thicker than those formed under oxygen as expected because of the previously mentioned arguments. Thermodynamic modeling was applied to determine the surface layer structure on Inconel 600 oxidized under various atmospheres. According to the simulation, it appears indeed a stratification of different oxide layers. The oxide layers formed are identified. An inner Cr rich layer (Cr_2O_3) is obtained for the two atmospheres. The external layers are different: under oxygen, an external Ni rich layer (NiO , Fe_2NiO_4 , Cr_2NiO_4) is obtained whereas under water vapor, this one is mainly made of Cr_2FeO_4 , independently of the temperature.

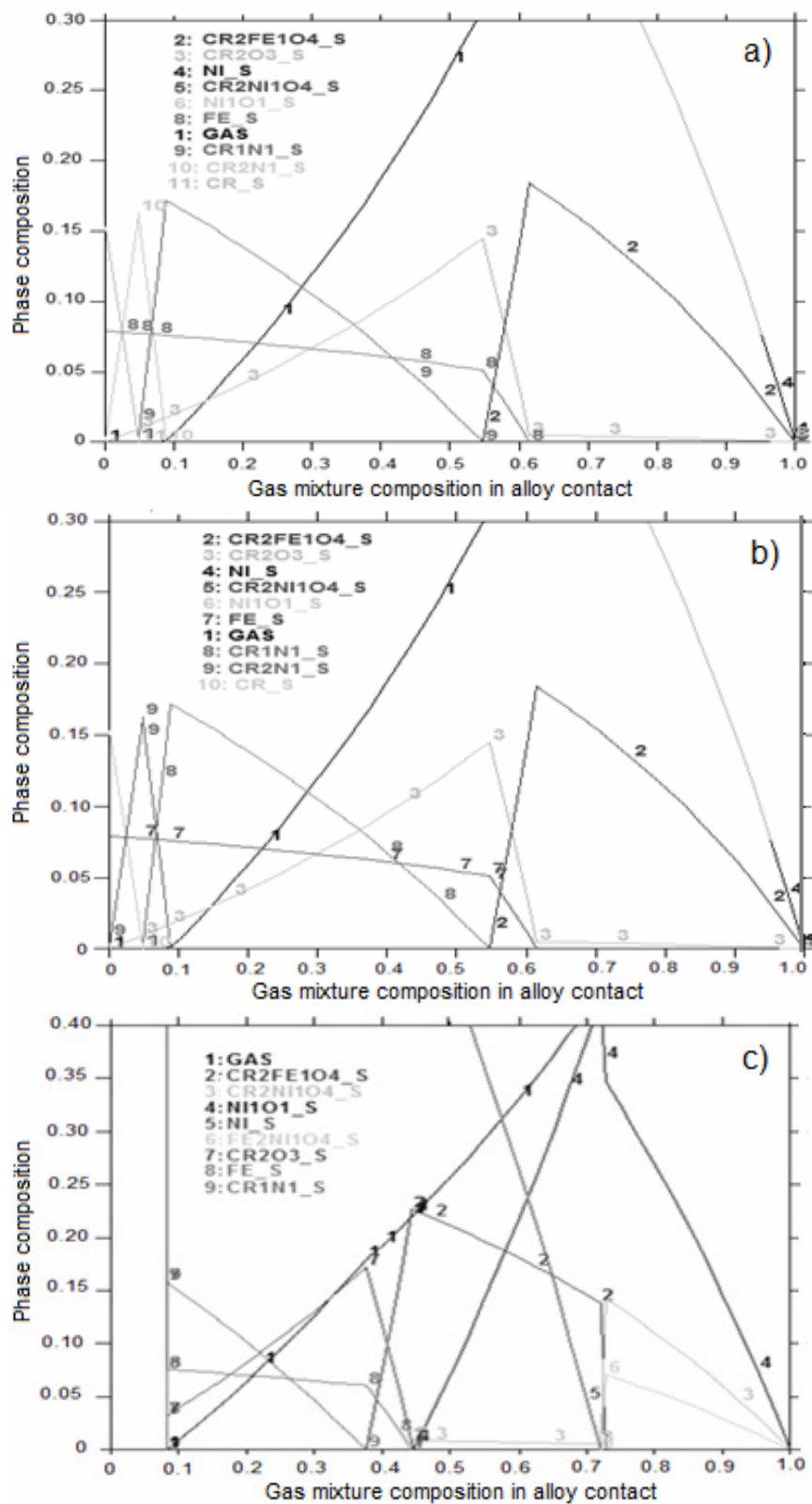


Figure 11. Results of the numerical simulation of the phase composition under water vapor at: a) 350°C, b) 450°C and c) 550°C

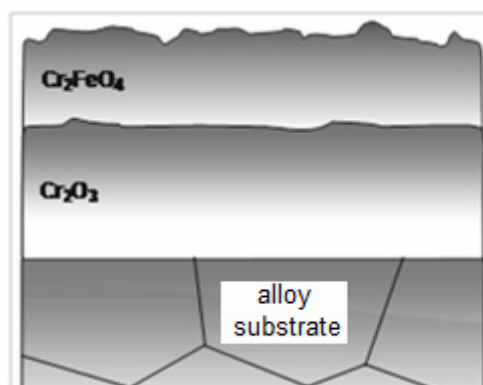


Figure 12. Model of layers structure obtained under water vapor at $P = 10^5$ Pa at 350, 450 or 550°C

The model is consistent with literature. The phases' nature and their distribution in the structure of the oxidized surface layer determined by Thermo-Calc code constitute an essential complement to the glow discharge spectrometry analysis.

This study must be supplemented again by various analyses of characterization using Scanning Electron Microscopy (SEM), Energy Dispersive X-rays spectroscopy (EDX) and surface techniques analysis such as X-rays Photoelectron Spectroscopy (XPS) to confirm the results obtained by GDS and thermodynamic simulation.

REFERENCES

1. Martson, T.U., Jones, R.L.: *Proceedings of the Fifth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors*, American Nuclear Society, La Grange Park, IL, **1999**, 3-9;
2. Rousselet, J.M., Moulin G., Huntz A.M.: Rôle des défauts créés par une déformation préalable et des impuretés (C.S) sur les mécanismes d'oxydation d'un alliage Inconel 600, *Traitement mécanique et thermique des surfaces*, Vol. **2**, "Technologie, Applications industrielles, Contrôles et Essais", Editions Traitements de surface, **1984**, Paris, p.137-155;
3. Abadie, P.: Fissuration par corrosion sous contrainte de l'alliage 600 à haute température: contribution d'une approche phénoménologique à la compréhension des mécanismes, *Thèse de Doctorat*, ENSM de Saint-Etienne et ENSM de Paris, **1998**;
4. Gourgues, A.F.: Interactions mécanique-oxydation à haute température dans l'alliage 600: Application à la fissuration dans le milieu primaire des réacteurs nucléaires à eau sous pression, *Thèse de Doctorat*, Ecole Normale Supérieure des Mines de Paris, Paris, **1997**;
5. Caron, D.: Influence de l'hydrogène sur la vitesse de propagation des fissures de corrosion sous contrainte dans l'alliage 600 en milieu primaire des réacteurs nucléaires à eau sous pression, *Thèse de Doctorat*, INSA de Lyon, **2000**;
6. Zahs, A., Spiegel, M., Grabke, H.R.: Chloridation and oxidation of iron, chromium, nickel and their alloys in chloridizing and oxidizing atmospheres at 400-700°C, *Corrosion Science*, **2000**, **42**, 1093-1122;
7. Gourgues, A.F., Andrieu, E.: High-temperature, oxidation-assisted inter granular cracking resistance of a solid-solution-strengthened nickel base alloy, *Materials Science and Engineering A*, **2003**, **351**, 39-55;
8. Ziemniak, S.E., Hanson, M.: Corrosion behavior of Ni Cr Fe Alloy 600 in high temperature, hydrogenated water, *Corrosion Science*, **2006**, **48**, 498-521;

9. Machet, A., Galtayries, A., Zanna, S., Klein, L., Maurice, V., Jolivet, P., Foucault, M., Combrade, P., Scott, P., Marcus, P.: XPS and STM study of the growth and structure of passive films in high temperature water on a nickel-base alloy, *Electrochimica Acta*, **2004**, 49, 3957-3964;
10. www.thermocalc.com;
11. <http://goodfellow.com>, Informations sur matériaux Inconel, **2004**;
12. Haouam, A.: Comportement en flexion 4 points à température moyenne (350-550°C) d'alliage base nickel. Etude de la fissuration et du rôle de la vapeur, *Thèse de Doctorat*, Université Technique de Compiègne, **2009**;
13. Charbonnier, J.C., Hocquaux, H., Loison, D.: Application de la spectrométrie à décharge lumineuse, *Techniques de l'Ingénieur*, **1993**, volume **P4**, P 2715;
14. Saunders, N.S., Miodownik, A.P. (editors): *CALPHAD (Calculations of Phases Diagrams): A comprehensive guide*, Pergamon Press, **1998**;
15. Galerie, A., Wouters, Y., Caillet, M.: The kinetic behaviour of metals in water vapor at high temperatures: can general rules be proposed?, *Materials Science Forum*, **2001**, volumes **369-372**, 231-238.