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# ON THE ROLE OF OXYGEN PARTIAL PRESSURE ON THE COMPOSITION OF THE OXIDE LAYER FORMED ON ALLOY 690 AT 700°C

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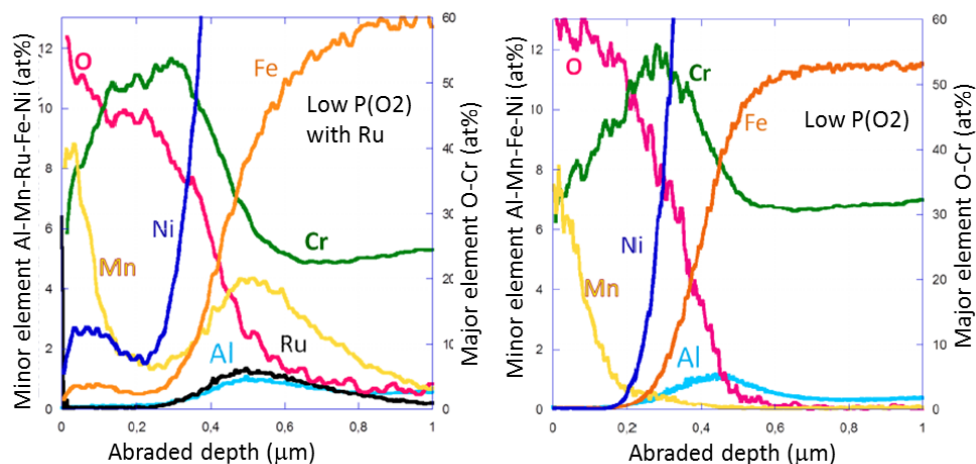
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**Extended Abstract** : Steam generator tubes in pressurized water reactors (PWR) are made of nickel based alloy such as alloy 600 or alloy 690. During oxidation process of this alloy in water at high temperature, nickel cations are released in the primary media. After neutron flux exposure in the reactor core, these cations can turn into radioactive products, such as <sup>58</sup>Co. If carried through the primary circuit, these radioactive products precipitate and contaminate the loop, making maintenance more difficult.

In order to limit nickel cation release, the aim of this work is to form a very protective scale (continuous, rich in chromium and nickel free) at the Alloy 690 surface by a pre-oxidation treatment performed at 700°C under different oxygen partial pressures (low  $P(O_2) \approx 10^{-6}$  bar and high  $P(O_2) \approx 0.2$  bar). So oxidation kinetic study of alloy 690 has been performed by thermogravimetry which has shown no effect of  $P(O_2)$  on the variations of oxidation rate over time. The morphology of the oxide scale formed during the test was observed using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The results are very similar for both  $P(O_2)$  : the scale is made of a continuous layer and preferential oxidation along the alloy grain boundaries (GB). Just beneath the oxidized zone in alloy GB, the formation of cavities is also observed. Moreover glow discharge optical emission spectrometry (GDOES) and X-ray Diffraction analyses have highlighted in

both cases an oxide layer rich in chromium ( $\text{Cr}_2\text{O}_3$ ). Nevertheless for low  $P(\text{O}_2)$ , a Mn and Cr spinel is observed near the outer surface of the scale whereas for higher  $P(\text{O}_2)$ , a similar spinel layer is made of Ni, Fe, Mn and Cr. So the oxygen partial pressure modifies the oxide composition although it has no effect on the oxidation kinetics. In order to better understand the influence of  $P(\text{O}_2)$  on oxide composition and on its evolution over time, two kind of experiments have been performed. The first one used a catalyst or an inhibitor in order to increase or decrease the dissociation rate of oxygen. Thus, ruthenium has been deposited on the alloy surface before oxidation in low  $P(\text{O}_2)$  in order to enhance the  $\text{O}_2$  dissociation rate. As show in figure 1, the better dissociation of oxygen at the surface entails the formation of an oxide layer containing nickel and iron at the external interface which was not the case for a sample without ruthenium. On the contrary, gold has been used as a  $\text{O}_2$  dissociation inhibitor for experiment with high  $P(\text{O}_2)$ . The gold deposit also modify the composition of the oxide layer. When gold is deposited prior to oxidation test, the oxide layer formed under high  $P(\text{O}_2)$  is free of nickel and iron contrary to what is observed without gold. These experiments show that oxygen dissociation rate play a role on the oxide composition formed on nickel base alloys at  $700^\circ\text{C}$ .



**Figure 1.** GD-OES profiles performed on oxide scale formed on Alloy 690, with and without deposit of ruthenium prior to oxidation test, after about 300h of oxidation at  $700^\circ\text{C}$  under low  $P(\text{O}_2)$ .

The second kind of experiment corresponds to oxidation tests with change of  $P(\text{O}_2)$  at the start of isothermal stage at  $700^\circ\text{C}$ . These experiments with a change of atmosphere have underlined the importance of the  $P(\text{O}_2)$  during the transient heating stage on the final composition of the oxide layer.

These experiments enable to better understand the link between the dissociation of oxygen at the external interface and the composition of the oxide layer formed on alloy 690 at  $700^\circ\text{C}$ .