ABSTRACT

Metallic materials for high temperature applications in a VHTR must meet high level criteria in terms of thermal stability, mechanical properties especially creep strength, formability as well as weldability; compatibility with the specific reactor environment is a further challenge. Nickel base alloys 617 and 230 containing 22 wt. % chromium and strengthened by molybdenum, cobalt and/or tungsten are promising candidates for the Intermediate Heat exchanger (IHX). Corrosion resistance is a key point to select between candidate materials. The ability to maintain an oxide layer as an efficient barrier versus internal corrosion under mechanical loading is investigated. Few differences could be observed between these two alloys when pre oxidized in air.

INTRODUCTION

The ANTARES program of Areva NP aims at developing a Very High Temperature Reactor to produce electricity and hydrogen or to supply any other industrial plant requiring high temperature process heat. The concept is based on a modular Gas-Cooled Reactor (GCR) operating at high temperature (maximum 850°C to 950°C) in indirect cycle. The thermal power produced in the reactor core is transferred from the primary coolant, namely helium, to a secondary circuit via a heat exchanger, the Intermediate Heat exchanger (IHX). The current option considers a mixture of nitrogen and helium as secondary coolant.

In this way, all the expected kind of degradations, such like corrosion, are intensively studied [1] [2].

The corrosion resistance of many materials is achieved by the formation of a dense and protective oxide scale which preserves the metal from rapid degradation as long as the scale keeps its integrity. However, these oxides are brittle and their failure destroys the barrier function giving a direct access for corrosive species to the metal substrate which results in increasing the oxidation rates. For that reason, one can easily imagine the point in studying and understanding how surface scales crack when the substrate is mechanically stressed.

Evans [3] put forward a process of cracking for oxide layers under tensile stress. He showed that the first cracks appeared at defects in the oxide scales (hollows, inclusions) and then quickly spread, thus showing that thick oxide scales crack more quickly than thin ones (the number and the length of the defects being higher in the thick oxide scales). Many mechanical models developed in order to calculate the critical stress for oxide failure [3–10] were put forward, but there are very few experimental investigations to validate them. Nagl et al. [4,5] evidenced the cracking of NiO and Fe3O4 scales during in situ four-point bend tests by associating observations through optical microscope, scanning electron microscope (SEM) and recordings of acoustic emissions aiming to detect the formation of cracks. During those investigations, the authors pointed out that failure in NiO started with through scale cracks which developed quickly into a network of equidistant cracks. They showed that the inter-cracks distance decreases linearly with the stress in the oxide according to mechanical models [4]. Nagl et al. evidenced a lower limit for the inter-cracks distance which corresponds to the onset of spallation. These concepts were recently published by Perusin [11] and have orientated our work.

Using nitrogen as coolant for the secondary side could lead possibly to nitrides formation in alloys’ extreme surface [12]. A preoxidation in air could act as an efficient barrier against nitridation, if its integrity is maintained in service conditions [13]. The IHX is designed for a 20 year lifetime. During this long period, several oxide rupture are possible due to oxide growth stresses, thermal cycling, vibrations, erosion etc… It is the aim of the present paper to report some recent developments concerning the understanding of scale failure due to mechanical stresses for IHX candidate alloys. Oxidation in air environment was chosen first to demonstrate the validity of the method, and due to its potential application in plant as pre-treatment for the component. Other results concerning oxide layers formed in primary side atmosphere will be published later.
The study is based on results obtained thanks to a specific apparatus developed for SEM in situ tensile tests. The evolution of cracks in the oxide scale was recorded along the deformation (up to the rupture of the specimen) and results were analysed in terms of inter-cracks spacing.

**EXPERIMENTAL PROCEDURE**

**Tensile Machine**

The investigations were conducted on samples (0.7mm thick) with the chemical composition given in table 1. Their shape is adapted to the micro tensile machine described Figure°1 placed in a JEOL 440 SEM chamber. Thus, high magnification and high resolution images could be realised during all the tensile tests.

![Figure 1 Schematic of the tensile machine. The dimensions of the specimen are shown on the upper left corner](image)

The tensile machine is developed by CIRIMAT research team [11]. The elongation velocity, obtained with this system, is of 4.74\(\mu\)m/s, resulting to \(\frac{d\varepsilon}{dt} = 6 \times 10^{-4} \ \text{s}^{-1}\) for the samples used. Both force and displacement are recorded. In this work, tensile tests were performed at room temperature.

**Materials**

The tensile test samples were cut out through electrodischarge machining, then ground down to 1200-grit emery paper by grade 1200 paper before being cleaned through ultrasonic waves first in acetone then in ethanol.

<table>
<thead>
<tr>
<th></th>
<th>Inconel 617</th>
<th>Haynes 230</th>
</tr>
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<tbody>
<tr>
<td>Ni</td>
<td>base</td>
<td>base</td>
</tr>
<tr>
<td>Cr</td>
<td>21.6</td>
<td>22.0</td>
</tr>
<tr>
<td>W</td>
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<td></td>
</tr>
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<tr>
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<td>9.2</td>
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<tr>
<td>Cu</td>
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<td></td>
</tr>
<tr>
<td>C</td>
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<td>0.105</td>
</tr>
<tr>
<td>B</td>
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<td>0.002</td>
</tr>
</tbody>
</table>

Table 2 Chemical composition of the alloys (in wt. %)

The specimen were oxidised for 100 h at 900°C in an electric furnace refreshed with synthetic air (1 ml/s).

**RESULTS**

Oxide layers aspect before tensile test is illustrated by Figure 2. We can observe slight difference between the two compositions. Some kinds of crystal are observed on Inconel 617 and nodule on Haynes 230. In both cases, the nature of the oxide is the same \(\text{Cr}_2\text{O}_3\).

![Figure 2 Oxide formed in air at 900°C during 100 hours on (a) Inconel 617 and (b) Haynes 230, before tensile tests](image)

The stress–strain curve obtained at room temperature with the apparatus presented before is shown in Fig. 3. Tensile tests were stopped at several strain levels to take high resolution images of the cracking of the oxide scale (that is
the reason why some small hooks due to stress relaxation can be seen on the curve).

![Figure 3 Stress–strain curve of Inc.617 and H.230 oxidised 100 h at 900°C in air—(Tests performed at room temperature).](image)

The images displayed in Fig. 4 and 5 were all taken at a magnification 500×, and each one was submitted to further statistical studies. It should be noted presently that everything possible was done so that the photos could be taken in the same sample area, whatever the deformation ratio. Below 1.5% of deformation, no cracking could be observed for Haynes 230 and 1.28% for Inconel 617. The first cracks appeared at the early beginning of the plastic zone of the materials (Fig. 3). Those first cracks, perpendicular to the strain axis, run across the entire width of the sample. Then the higher the deformation gets, the more the cracking network increases and new cracks appear between older ones (Fig 4 and 5). The spreading of those new cracks was followed and showed that they too eventually ran through the width of the sample.

A statistical study of the inter-cracks spaces was then carried out; this study was done using images taken at 500× magnification and a constant total number of inter-cracks spaces. The number chosen was 10. Some of the results are presented in Fig. 6. The analysis showed that the more the deformation increases, the smaller the inter-cracks spaces get, which agrees with the formation of new cracks. The evolution of this average spacing versus strain obeys a power law of the strain as shown in Fig. 6. This law can be written as

\[ d = D (\varepsilon - \varepsilon_0)^{-n} \]

where \( d \) is the mean inter-cracks spacing in \( \text{Cr}_2\text{O}_3 \), \( D \) a constant expressed in \( \mu\text{m} \), \( \varepsilon \) the tensile strain of the sample and \( \varepsilon_0 \) a constant which is set equal to the strain of the material at the yield point (0.003 in that case). Least square fitting of the experimental points leads to the values of parameters:

- \( D = 0.14\mu\text{m} \) and \( n = 0.70 \) for Inc.617.
- \( D = 0.07\mu\text{m} \) and \( n = 0.58 \) for H.230.

The study was carried out until the specimen broke and it is worth noticing that the inter-cracks distance still diminishes with strain up to the failure of the specimen (close to 30% total strain). Moreover the average inter-cracks spacing varies with the plastic strain according to a power law.

![Figure 4 Cracking of the Cr2O3 scale during a tensile test on a H.230 sample oxidised for 100 h at 900°C in air. The same area is imaged at increasing strain showing the densification of crack network.](image)
Figure 5 Cracking of the Cr$_2$O$_3$ scale during a tensile test on a Inc. 617 sample oxidised for 100 h at 900°C in air. The same area is imaged at increasing strain showing the densification of crack network.

Figure 6 Evolution of the distance between cracks versus the strain percentage.

The lower limit for the average inter-cracks distance was related by Nagl et al. [3] to the spallation of the oxide scale. In the present study, the oxide some spallation could be observed, for both alloys, a threshold is reached nearly for the same strain (Fig 6).

DISCUSSION CONCLUSION
The full study of the cracking of a thin Cr$_2$O$_3$ scales carried out in situ in the SEM allowed to provide new data for the understanding of an oxide scale behaviour on a substrate under tensile stress. Haynes 230 and Inconel 617 pre oxidized in air at 900°C were analyzed and the same kind of behaviour is observed.

The scales are brittle, and multiple cracks are observed parallel to the straining direction. Detachment and other delamination have been observed, corresponding to a threshold in the inter cracks distance evolution.

The statistical study of that cracking thus allowed to show that new cracks keep forming until the material breaks. As a consequence the average inter-cracks distance still decreases with increasing tensile deformation according to a power law of plastic strain. The mechanical properties of the Cr$_2$O$_3$ layer could help for the design of the component in term of stability and acceptable in service deformation induced by thermal cycling or vibration.

Next step of this work will concern thermal cycling tests and tensile tests performed on primary side like IKX Helium.

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