ESRF	**Experiment title:** In-situ investigation at high temperature of growth stresses in chromia formers. Influence of microstructure on stress release mechanisms	**Experiment number**: 02-02-821
Beamline: D2AM GM CRG	**Date of experiment**: from: 5/11/2014 to: 11/11/2014	**Date of report**: 26 01 2015
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Report:

This proposal takes place in the general context of a better understanding of materials degradation mechanisms in extreme environments. In particular, the aim of the present study was to correlate microstructural elements to growth stress magnitude evolution and stress release mechanisms for thermally grown chromia thin films on Ni-30Cr alloys. Thus, it was planned to undertake X-ray diffraction measurements in situ during oxidation of the metallic alloys. To this end, a High Temperature induction furnace providing from the ESRF Sample Environment Laboratory was used. In addition, it was decided to use a 2D detector large enough to get sufficient Psi values, to extract the stresses evolution in the chromia films during the course of isothermal oxidation, and also during short plateau just after temperature jumps.
Finally, only a part of the initially planned experiments has been possible for two main reasons :

- At first, the camera 2D (MAR CCD providing from the Detector Pool) was not stabilised during the experiment despite the efforts of the colleagues from the Detector Pool. It finally gave rise to numerous acquisition problems, meaning that a significant part of the obtained images were not usable, and some of the planned experiments had to be dropped.
- Secondly, it was not possible to use the induction furnace in all the expected configurations, initially planned with the Sample Environment Laboratory. In particular, the thermal cycling experiments (regular subsequent high and low temperature jumps) were not available, probably due to a non-correct assignment of the PID parameters. Only experiments with temperature jumps to lower temperature were finally possible. Anyway, we have also to underline the quality of the induction

furnace which both allows to attain high given temperature with a very good convergence and high speed, and to stabilize the temperature with a good precision.

Because of the two problems presented above, it was necessary to reorganise a little bit the content of the project, and finally the number of experiments and corresponding specimens was reduced. However, the main results expected from these experiments are the same, i.e. the kinetic of the growth stress from the isothermal measurements (isothermal plateau), and the study of the stress release mechanism after the low-temperature jumps. In complement, the oxide microstructure development during the course of oxidation is also investigated from both the peaks intensity and width evolution.

Studies of in situ XRD were carried out in Synchrotron at the ESRF D2AM line, with an energy of 20 KeV. The dimensions of the X-Ray beam (300 µm * 300 µm) allows to maximise the diffracted intensity from the earlier oxidation steps. To observe their oxidation and to form the oxide Cr2O3, the samples have been heated in the temperature range 700-1000°C under atmospheric air, with the induction heating stage from ESRF Sample Environment Laboratory. Relatively high heating and cooling rates have been used (150°C/min) to reduce direct oxidation and thus stress build up and stress release during these heating and cooling steps, and in order to highlight the study only during the subsequent plateau.

A two-dimensional detector capture peaks in reflection mode of the Cr2O3 ceramic film and the NiCr metallic substrate. The kinetic of formation of such phases naturally depends on the oxidation condition. However, given the chosen configuration for the experimental setup, Cr2O3 lines rapidly appear in addition to the NiCr (Fig. 1).

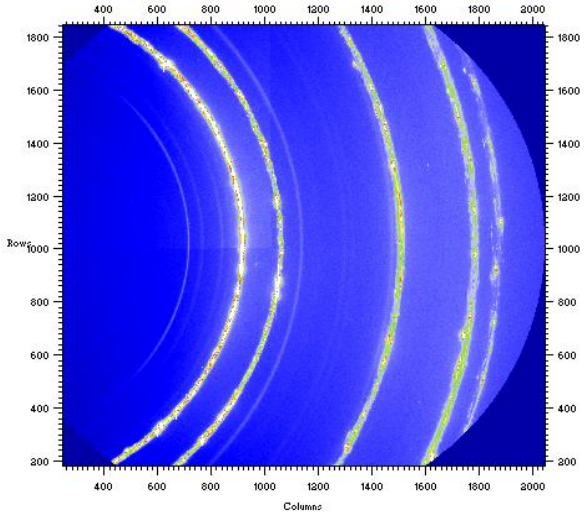

Fig. 1 : 2D image obtained in-situ at high temperature (700-1000°C), showing the Cr2O3 ceramic film and substrate NiCr diffraction lines. NB: The strongest and spotty diffraction pattern correspond to the NiCr substrate.

The complete analysis of the data will allow to obtain for each oxidation temperature the intensity and width of the diffraction peaks in the direction of the azimuth, and also the evolution with the oxidation time. It will give both the phase formation kinetic and an accurate description of the microstructure. The first results clearly show the impact of the oxidation condition, in particular the oxidation temperature which influences the chromia film thickness and the ceramic grain size. The eventual presence of texture from the first moments of oxidation may also be appreciated. Finally and as expected, the X-ray Synchrotron source allows us to perform good quality measurements with a rather high dynamic, in a quite short recording time.

From these experiments the internal stress determination is also undertaken from the analyses of the images providing from the 2D detector. It is done both for the isothermal oxidation, and also during the plateau just after the low-temperature jumps. An example of the later experiment is shown in Fig.2. While the quality of the analysis of the data has still to be ameliorated some first conclusions can be clearly drawn.

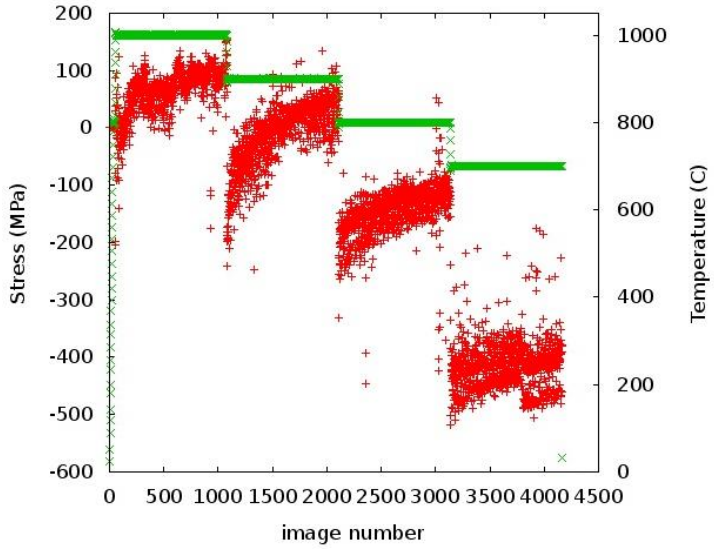

Fig. 2 : internal stress/strain evolution as a function of the image number (oxidation time), for four subsequent plateaus of 3 hours, at respectively 1000, 900, 800 and 700 °C. The three later are observed after low-temperature jumps of 100°C.

The first step observed at 1000°C corresponds to the initial oxide growth with its corresponding microstructure development. It is evidenced by an increase of the integrated intensity (not shown here) only observed during this first plateau at 1000°C. In addition, during the very first oxidation times on this plateau, the strain/stress seems to increase in absolute value which may correspond to the stress build-up step. Subsequently, even if some strange variations are observed, the mean stress/strain value rapidly drops as a sign of isothermal relaxation.
After that, three low-temperature jumps have been imposed, and it is clearly visible from Fig.2 that a stress/strain jump is clearly associated to these temperature jumps at respectively 900, 800 and 700°C. The low-temperature jump induces as expected an additional compressive strain/stress to the oxide film. Then, the creep-relaxation of the thermally grown ceramic is also clearly visible on each plateau. In particular, it appears that the strain rate varies with the temperature as a proof of the thermal activation of the creep mechanism. Thus, from this example, it is evidenced, that for an initial microstructure of the ceramic film initially developed in that case at 1000°C, the subsequent study of the creep behaviour will be possible. In particular, from a confrontation with our modelling the creep mechanism will be identified, e.g. from the Norton exponent value, and the creep coefficient will be obtained. From the variation of the later with the temperature, the activation energy and diffusion coefficient will also be determined.

Data processing is now continuing with the diffraction studies in order to obtain a meaningful description of the microstructure evolution in relation with the oxidation kinetic successive steps, and also to get the stress/strain development and relaxation for all the different specimens and oxidation conditions that have been studied in the present Proposal. These kinds of combined experiments represent a first for these high temperature working materials, e.g. chromia formers. In particular, it is a first attempt to obtain the specific viscoplastic characteristics for such thermally grown thin films of ceramic materials.

At the beginning of the project, almost three shifts have been necessary to setup and to calibrate the experimental device, i.e. alignment of the beamline at the desired energy, furnace installation and calibration for the detector. Finally, taking into account the problems with the furnace and the detector during the course of the proposal, the total number of analysed samples was reduced, and also the duration of the oxidation

steps. Reference bulk and powder specimens were also analysed at high temperature. It was necessary to take into account the dilatation effect of both the studied material and the sample holder. Finally, the use of Synchrotron Radiation was mandatory to perform such XRD experiments because the diffracting volumes are quite small, high photon flux is required. Furthermore, since the samples under investigations are composed of a stacking of the ceramic film and the metallic substrate (Cr2O3/NiCr) tunable wavelength was required to avoid peaks overlapping.

Publication(s):

As explained above, data analysis is obviously still now continuing. This work is part of the PhD thesis of Felaniaina Rakotovao (defense at the end of 2016). Two presentations are already planned in 2015 from the results obtained in this proposal :

- MECA-SENS8th, 8th International Conference on Mechanical Stress Evaluation by Neutron and Synchrotron Radiation, 28 Sep-02 Oct 2015, Grenoble

-XI Colloque Rayons X et Matière, 01-04 December 2015, Grenoble