Standard Project

Experimental Report template

Proposal title: **In-situ investigation at high temperature of residual stresses in chromia formers. A way to obtain the viscoplastic characteristics of thermally grown ceramic films**		**Proposal number:** 02-02-825
Beamline: BM02 CRG-D2AM	**Date(s) of experiment:** from: 10 to: 16 November 2015	**Date of report:** 2016
Shifts: 18	**Local contact(s):** Nathalie Boudet	*Date of submission:* *February 2015*

Objective & expected results (less than 10 lines):

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 stress release mechanisms for thermally grown chromia thin films on NiCr 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 low temperature jumps (supposed to impose an additional thermal strain).
Compared to the previous Proposal (02-02-821) a new 2D camera has been used (FRELON camera providing from the Detector Pool), thus it has been now possible to get the images all along the course of oxidation. Also, concerning the induction furnace providing from the Sample Environment Laboratory, it was optimised thus thermal cycling experiments (regular subsequent high and low temperature jumps) were also possible. Finally, the main part of the planned experiments was undertaken. However, it was decided to focus on the behaviour of only one chromia forming alloy (NiCr).

Results and the conclusions of the study (main part):

The main results obtained from these experiments were 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 * 1500 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 800-1000°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 conditions. However, given the chosen configuration for the experimental setup, Cr_2O_3 lines rapidly appear in addition to the NiCr. From the intensity and the integral width (Fig. 1) an accurate description of the microstructure was done. In particular, it was clearly shown that the ceramic grains mainly growth during the very initial oxidation period, while the development of the chromia film is continuous during all the first oxidation plateau of 3 hours. The later corresponds to the building of the film microstructure.

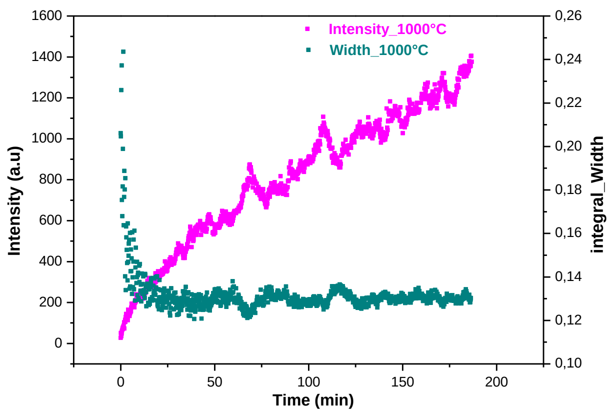

Fig. 1 : Intensity and integral width evolution for a chromia microstructure built at 1000°C on NiCr during a first plateau of 3 hours.

Finally, four chromia ceramic film microstructures have been built at respectively 800, 850, 900 and 1000°C, with corresponding increasing grain sizes (0.2 to 0.8 µm) and film thicknesses (500 nm to 3 µm). The eventual presence of texture from the first moments of oxidation has also be appreciated (not shown). 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.

After building the microstructures, low temperature jumps were applied, and the internal stress determination was also undertaken from the analyses of the images providing from the 2D detector. It was done both for the initial building period (first plateau), and also just after the low-temperature jumps (subsequent plateaus). An example of the later experiment is shown in Fig.2 for the microstructure initially built at 1000°C.

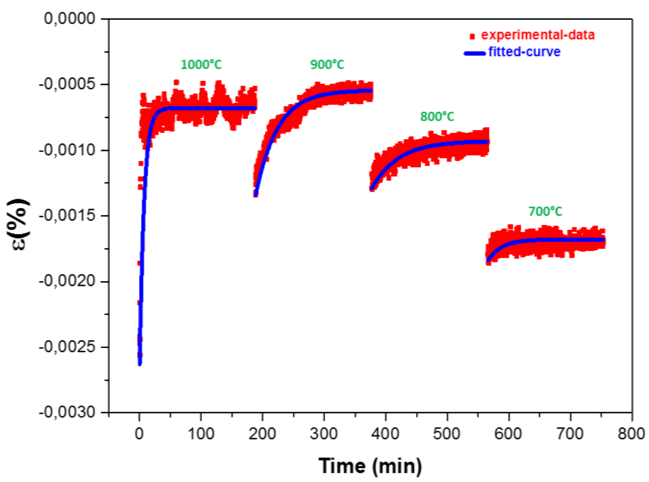

Fig. 2 : Internal strain evolution as a function of the oxidation time, for four subsequent plateaus of 3 hours, at respectively 1000, 900, 800 and 700 °C. The three later are observed after low-temperature jumps of 100°C. The microstructure has been built initially at 1000°C during the first plateau (no more significant evolution of the intensity or the width during the subsequent plateaus at lower temperatures)

During the first step observed at 1000°C 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 is possible.

This methodology has been reproduced for the 4 initial microstructures built at 1000, 900, 850 and 800°C. And from a confrontation with our modelling (fitted curve in Fig. 2), the creep mechanism has been identified. Indeed, with a Norton exponent value < 2, the fitted curves well describe the experimental evolution which is consistent with diffusion-creep. The corresponding creep coefficients J_{ox} have been deduced (Fig. 3) for the first time in chromia thermally grown oxides films.

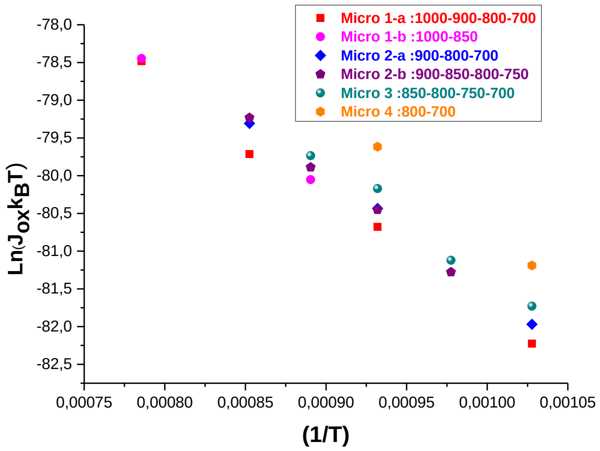

Fig. 3 : Creep coefficients J_{ox} as a function of the oxidation temperature, for the four initially built microstructures at respectively 1000, 900, 850 and 800°C. Both the initial building temperatures and the ones corresponding to the subsequent plateaus after the jumps are reported.

The variation of the J_{ox} diffusion-creep coefficients with the temperature has also been reported in Fig. 3 for the 4 initial microstructures, but also with different applied values (100 or 50°C) of the low temperature jumps.
At first, it appears a good reproducibility for the creep coefficients providing from an identical initial microstructure. Then, considering the thermal activation for one initial microstructure, it is clear that intermediaries low temperature jumps induce as expected well intercalated creep coefficient values.
Also, for one initial microstructure the variation of the creep coefficients with the temperature are coherent with an Arrhenius law. And the slope is about the same for the 4 initial microstructures. Thus, a corresponding activation energy of about 130 KJ/mol has been deduced. This value is not directly comparable with literature because no such data are available for diffusion-creep in chromia in particular as a thermally grown oxide. However, a tentative can be done to compare with the parabolic kinetic constants obtained from the diffusion limited growth of such chromia films. If we plot the evolution of such kinetic constants with the temperature a value of about 128 KJ/mol is also obtained which seems definitely to confirm the occurrence of diffusion-creep as the main stress release mechanism.
Finally, from Fig. 3 the size effect associated to the well-known diffusion-creep equation seems also to be satisfied. Indeed and as expected for a fixed temperature, the creep coefficients increase as the grain sizes decrease (visible through the initial building temperatures which induce an increasing grain size when such building temperatures also increase). Such a behaviour is in total agreement with e.g. the Coble equation.

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, in particular now for the specimens which have been tested under thermal cycling conditions. Also from the J_{ox} values for chromia thermally grown oxides films, the associated diffusion coefficients will be obtained in order to determine the elementary mechanisms involved. 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.

Justification and comments about the use of beam time (5 lines max.):

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, the total number of analysed samples was about 10. 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):

From the present Proposal which was a continuation of the previous one number 02-02-821, different presentations and publications have already been done or will be in 2016 (see below). However, data analysis is obviously still now continuing. This work is part of the PhD thesis of Felaniaina Rakotovao (defense at the end of 2016) and Zaojun Tao (defense at the end of 2017) :

- MECA-SENS8th, 8th International Conference on Mechanical Stress Evaluation by Neutron and Synchrotron Radiation, 28 Sep-02 Oct 2015, Grenoble :
communication orale et publication à paraître en 2016 dans Material Science Forum "Strains in thermally growing Cr_2O_3 films measured in-situ using Synchrotron X-Rays"
Rakotovao F., Tao Z., Panicaud B., Grosseau-Poussard J.L., Geandier G., Renault P.O., Goudeau P., Boudet N., Blanc N., Vitoux H., Gorges B
communication orale et publication à paraître en 2016 dans Material Science Forum "« Identification of thermomechanical parameters in a thermally grown chromia, thanks to synchrotron radiation facilities"
Z. Tao, F. Rakotovao, JL. Grosseau-Poussard, B. Panicaud, G. Geandier, PO. Renault, N. Boudet, N. Blanc

-XI Colloque Rayons X et Matière, 01-04 December 2015, Grenoble
communication par affiche : "Utilisation du Rayonnement Synchrotron pour déterminer les caractéristiques viscoplastiques de films d'oxydes thermiques de chromine »
F. Rakotovao, Z. Tao, B. Panicaud, JL. Grosseau-Poussard, P. Girault, G. Bonnet, G. Geandier, PO. Renault, P. Goudeau, N. Boudet, N. Blanc, H. Vitoux, B. Gorges

-HTPCM 2016 9th International Symposium on High-Temperature Corrosion and Protection of Material Les Embiez 15-20 May 2016
communication par affiche et publication à paraître en 2017 dans Oxidation of Metals : « Stress build-up and relaxation in chromia scales during high temperature oxidation"
F. Rakotovao, Z. Tao, B. Panicaud, P. Girault, G. Bonnet, JL. Grosseau-Poussard, G. Geandier, PO. Renault, P. Goudeau, N. Boudet, N. Blanc, H. Vitoux, B. Gorges
communication par affiche et publication à paraître en 2017 dans Oxidation of Metals : « Modeling of the mechanical behaviour of a chromia forming alloy under different thermal loadings"
Z. Tao, F. Rakotovao, JL. Grosseau-Poussard, B. Panicaud, G. Geandier, PO. Renault, N. Boudet, N. Blanc

-Colloque "La Métallurgie, quel avenir ?" Ecole des Mines, Saint Etienne, 27 Juin-01 Juillet 2016
communication orale : « Comportement viscoplastique de films d'oxydes thermiques caractérisé par diffraction sur Rayonnement Synchrotron » F. Rakotovao, Z. Tao, B. Panicaud, JL. Grosseau-Poussard, P. Girault, G. Bonnet, G. Geandier, PO. Renault, P. Goudeau, N. Boudet, N. Blanc, H. Vitoux, B. Gorges