Standard Project

Experimental Report template

Proposal title: **Viscoplastic characteristics of chromia thermally grown ceramic films under the influence of reactive elements**		**Proposal number:** 02-02- 839
Beamline: BM02 CRG-D2AM	**Date(s) of experiment:** from: 02 to: 08 November 2016	**Date of report:** 2017
Shifts: 18	**Local contact(s):** Nathalie Boudet	*Date of submission:* *February 2016*

Objective & expected results (less than 10 lines):

This proposal takes place in the 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, but also in the case of doped materials. Indeed, it is well known that the addition of reactive elements (RE) can greatly improve the degradation resistance of these materials.
Thus, it was planned to undertake X-ray diffraction measurements in situ during oxidation of the metallic alloys. The oxidation experiments were undertaken with Ni28Cr model alloys with or without Y or Zr as RE.
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).
Finally, the main part of the planned experiments was undertaken and the determination of the thermomechanical parameters was possible. The elementary mechanisms involved in the creep behaviour of the ceramic films were also determined.

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 low-temperature jumps imposed both to the doped NiCr materials and the reference material. In complement, the oxide microstructure development during the course of oxidation was 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 (FRELON Camera) capture peaks in reflection mode of the Cr2O3 ceramic film (Fig. 1). 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.

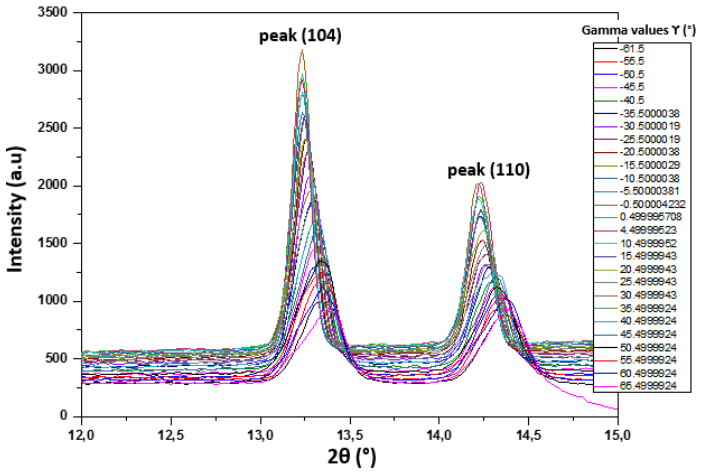

Fig. 1 : chromia (104) and (110) diffraction lines as a function of the gamma angle, after the caking procedure

The selected approach consisted, in a first step, in developing chromia thin films with a fixed grain size, by oxidizing the substrate at different high temperatures, for three hours. Then, in a second step, several temperature jumps of 50°C, 100°C or 150°C were applied towards lower values, down to the inferior limit temperature for creep thermal activation (700°C), in order to impose mechanical loadings. The oxide creep response was then investigated along each subsequent isothermal plateau. The aim was here to fix the initial chromia grain size in order to study the only influence of the thermal activation on the diffusion-creep mechanism.

The analysis of XRD peaks obtained from Debye-Scherrer rings allowed to get the following main results:

- The diffracting volume of chromia thin films continuously developed during the initial 3h oxidizing period and the crystalline growth of chromia grains occurred only during this period, for 20 min to 3 h depending on oxidation temperature.
- For subsequent isothermal plateaus, coming after temperature jumps, neither the quantity of chromia nor a growth of chromia grains could be evidenced.
- The addition of compressive thermal stresses resulting from temperature jumps provoked the start of creep stress release mechanisms, as well during the cooling as during subsequent isothermal periods.
- The comparison of experimental results to a first theoretical approach implying diffusion-creep (Norton exponent equal to 1) was in favour of this stress release mode (Fig. 2).
- The creep coefficients could be estimated for the first time for chromia under the thin film form and the influence of chromia grain size could also be confirmed.
- All the acquired data allowed to calculate the activation energy of diffusion elementary mechanisms affecting creep strain ($Q = 130 \pm 5$ kJ.mol^{-1}). The comparison with data from literature led to propose that, for TGO chromia thin films, the stress release by diffusion creep is very likely governed by a mechanism involving diffusion of oxygen ions at the chromia grain boundaries (Fig. 3).

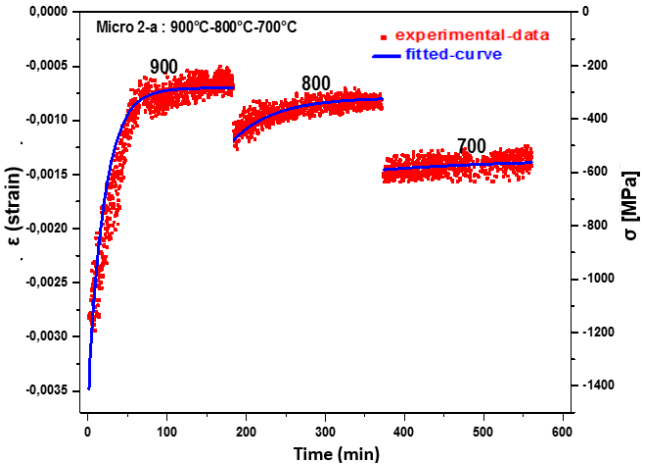

Fig. 2 : strain/stress evolution. For the microstructure 2a build at 900°C, with the subsequent low-temperature jumps of 100°C and isothermal stress release (raw data and fitting)

In particular for the doped materials (the two studies systems (Ni28Cr + Y_2O_3)/Cr_2O_3 and (Ni28Cr + Zr)/Cr_2O_3)) :

- The chromia microstructure has been built by an initial oxidation at 1000°C, then low temperature jumps of 100 °C have been applied up to 800°C.
- Concerning the strain/stress evolution with the oxidation time, it has been observed as for the reference material that a stress jump corresponds to an imposed thermal jump, then stress release periods appear during the isothermal plateau.
- Compared to the reference material, a shift is observed in the inflexion time which corresponds to the maximum magnitude stress value, and that shift increases with the dose of reactive element.
- The maximum magnitude stress values are always inferior to the ones for the reference material. Consequently, the stress release amplitudes are also inferior. And the dose of reactive element has no effect on this behaviour.
- Finally, the creep coefficients for the chomia films have also been determined, and it decrease for the doped materials. And the thermal activation of these coefficients is still clearly observed.
- The corresponding grain boundaries diffusion coefficients and activation energies have been deduced (Fig. 3).
- It appears an inversion of the elementary mechanism that governs the diffusion-creep behaviour of the TGO.
- In addition, the evolution observed with the dose of reactive element (either for Y or Zr) suggests the existence of a critical limit to obtain such an inversion.
- Below such a limit the mechanism which governs the diffusion-creep behaviour seems to be the same (inward oxygen transport) that for the reference material, but with a clear diminution of the oxygen transport rates.

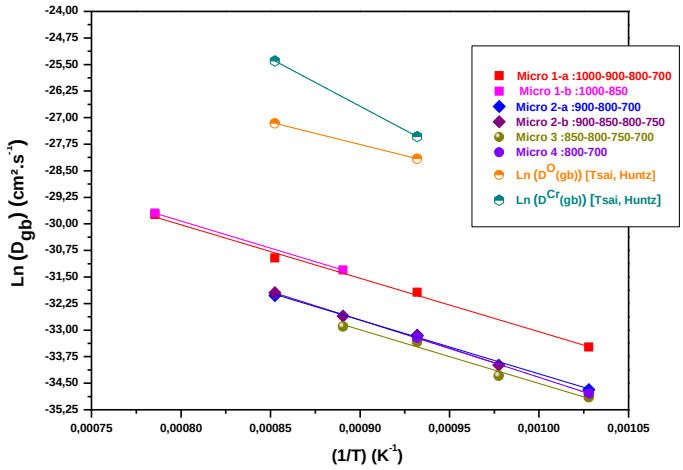

Fig. 3 : D_{gb} grain boundary diffusion coefficients evolution as a function of temperature for the 4 microstructures, and comparison with literature data

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 8. 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 02-02-825, different presentations and publications have already been done (see below). This work was a significant part of the PhD thesis of Felaniaina Rakotovao (defended at the end of 2016) and Zaojun Tao (defense at the end of 2017) :

[1] Z. Tao, F. Rakotovao, JL. Grosseau-Poussard, B. Panicaud, G. Geandier, PO Renault, P. Goudeau, N. Boudet, N. Blanc, *Oxidation of Metals*, **2017**, 88 :15-27, référencé Scopus
[2] B.Panicaud, JL. Grosseau-Poussard, Z. Tao, F. Rakotovao, G. Geandier, PO. Renault, P. Goudeau, N. Boudet, N. Blanc, *Acta Mechanica*, sous presse en **2017**, référencé Scopus
[3] 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, *Materials Science Forum*, sous presse en **2017**
[4] F. Rakotovao, Thèse de l'Université de La Rochelle, **2016**

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