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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In-situ analysis of internal strain evolution during heat treatment in sol-gel thermal barrier coatings	**Experiment number**: MA1491
Beamline: ID15B	**Date of experiment**: from: 06/06/2012 to: 09/06/2012	**Date of report**: 23/08/2012
Shifts: 10	**Local contact(s)**: Veijo Honkimaki (+Thomas Buslap)	*Received at ESRF:*

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Report:

Aims of this project are, to investigate, in «Sol-Gel» Thermal Barrier Coatings (TBCs) deposited on NiPtAl bond coated superalloy substrates using the dip coating technique, (i) first, the origin of crack network formation while a standard heat treatment is carried out during the last step of their processing (sintering) (ii) secondly, the development of cracks and spalls during cyclic oxidation representative of service conditions.
These TBCs consist of Yttria-stabilised zirconia (YSZ) characterized by the tetragonal phase t'-ZrO_2.
By using the high energy X-Rays of ID15B, which allow very fast measurement speeds, the in-situ continuous monitoring of multiple Bragg peak shifts (link to elastic macro-strain) and broadening (sintering and micro strains) was successfully carried out during heat treatment.
A resistive heater with a sandwich geometry and with openings for the X-ray beams was mounted and diffraction signals were recorded simultaneously (in transmission) on the two-dimensional (2D) PIXIUM detector placed at 746,35 mm from the specimen. The energy was set at 87.1 keV. Due to very intense diffraction peaks from the substrate (which is a single crystal), we decide to focus our attention only on the TBC, by using a "grazing incident" geometry (the beam, with an appropriate size, is going, by transmission only through the TBC). The experimental set-up is shown on figure 1.

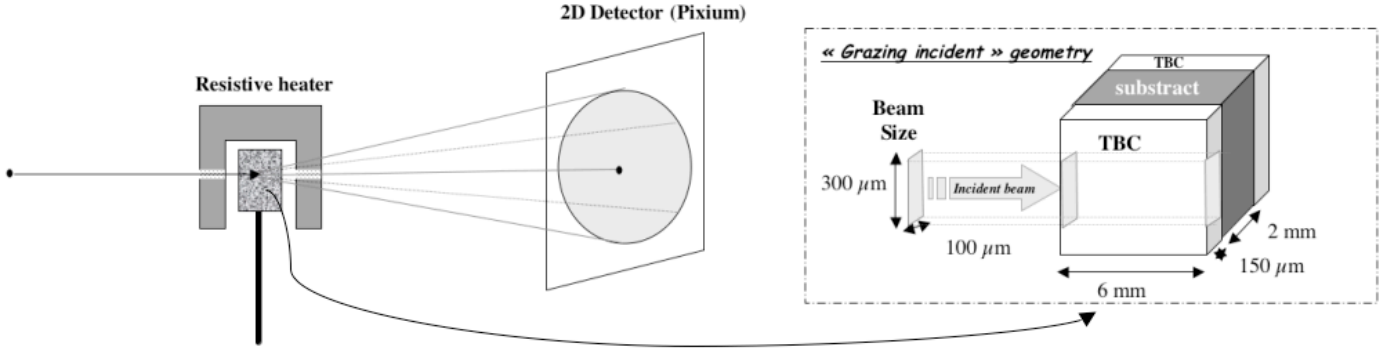

Figure 1 : Schematic of the high-energy X-Ray transmission set-up illustrating the sample geometry and X-ray beam size.

Different kind of experiments were carried out:
1. In-situ thermal treatment representative of the process (from room temperature till 1100°C with heating and cooling rate of 100°C/h). Diffraction patterns were recorded every 30 minutes (acquisition time was 40 sec).
2. In-situ cyclic oxidation at 1100°C (five 1-hour cycles with high heating and cooling rate). Diffraction patterns were recorded every 10 sec with an acquisition time of 4 sec during the fasts heating and cooling, and every 5 minutes (Acquision time of 40 sec) during the holding at 1100°C for 1hour. Unfortunately we only performed this measurement on 1 sample.

3. Measurement on “static” samples.
So a large amount of nice quality diffraction data was recorded and are currently being analysed.
For example, the in-situ thermal heat treatment experiment allows a precise investigation of elastic strain evolution in the TBC during its sintering by studying the diffraction peak position shift as illustrates by figure 2a for the tetragonal (440) YSZ reflection. The corresponding Bragg positions were obtained by fitting the (440) reflection using Split Pseudo-Voigt functions. Note that due to this fitting procedure (that we are going to use for all the data set), the relative error on the peak position (Δd/d) is about $1x10^{-3}$. Figure 2b shows the strain (ε_T^{440}) evolution with temperature T of the $(440)_{YSZ}$ reflection. The strain ε_T can be expressed as : $\varepsilon_T^{hkl} = \frac{d_T^{hkl} - d_0^{hkl}}{d_0^{hkl}}$ where d_T^{hkl} is the interplanar spacing of (hkl) planes at a given temperature T and d_0^{hkl} is the corresponding “stress-free” interplanar spacing (here the reference state for d_0^{hkl} is considered at the initial temperature which is at RT as we are interested in the relative Bragg peak shift). The orange and pink straight lines belong to the theoretical “thermal” elastic strain ($\varepsilon_{Thermal} = \alpha_l \Delta T$) occurring during temperature changes (ΔT), i.e. respectively during heating and cooling. It was assumed that the linear coefficient of thermal expansion (α_l) of the YSZ was not the same as its value is strongly dependant to the porosity. So during heating (before sintering – porous YSZ) and cooling (after sintering – dense YSZ), a α_l of, respectively $8.5x10^{-6}$ °C^{-1} and $11x10^{-6}$ °C^{-1} for the YSZ were used.
During heating, the elastic strain ε_T^{440} is clearly not linear and revealed different features: i) from RT to around 450°C the strain fluctuations could be related to the calcination of residuals organics compounds that are known to decomposed between 100°C and 400°C) ; ii) between 450°C and 700°C, even if some data are missing due to a loss of the beam, it seems that the strain is mainly linked to the thermal expansion ; iii) above 700°C, a high increase of the elastic strain/stress is observed (deviation from the linear thermal expansion). It can be explained by the sintering of the YSZ add to the growing of an Alumina Al_2O_3 layer (between the subtract and the TBC). Indeed, during the sintering, the metallic substrate is opposed to the large shrinkage of the YSZ coating, thus leading to the development of this tensile-stress state.
During cooling and particularly between 1100°C and 700°C, the elastic strain shows some fluctuation that could be explained by the cracks network formation leading to a substantial relaxation of the stresses in the YSZ. Indeed, due to the mismatch in the thermal expansions of the YSZ ceramic coating and the metallic substrate, on cooling the metal tends to contract more than the ceramic, leading to the development of stresses into the YSZ layer. Thus, it seems that these stresses are relaxed into the coating by microcraking (mainly above 600°C), which further develop into a crack network (as observed after the thermal treatment - inset of figure 2b).
Concerning the FWHM evolution (clearly revealed on figure 2a), its study is under progress but we believe that the sharpening and intensity increase of Bragg peaks should be linked to the increase of the crystallite size and the decrease of the porosity during the sintering.

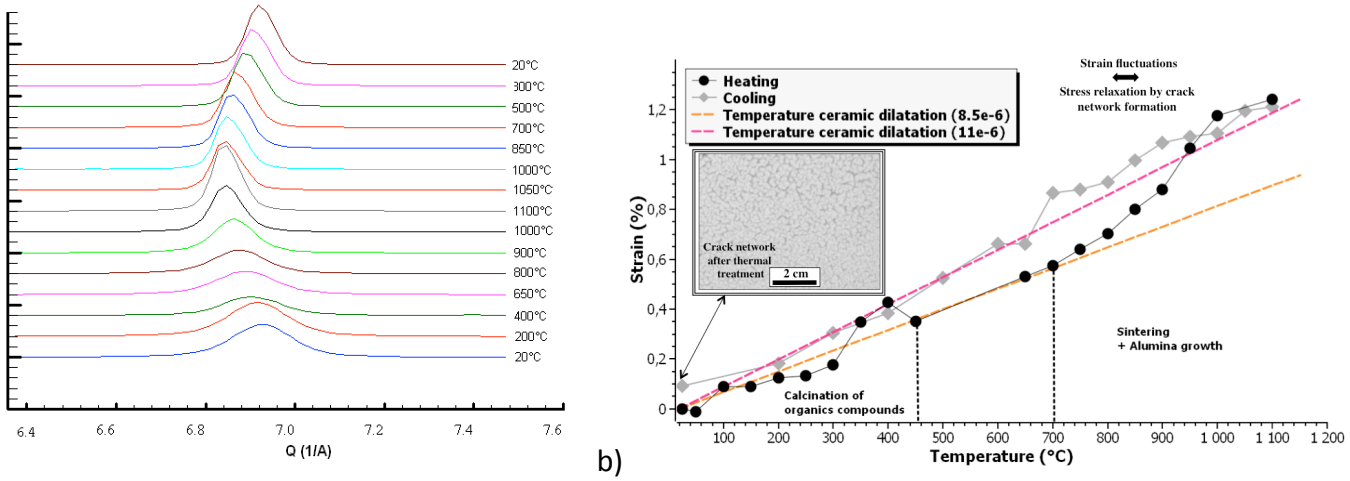

Figure 2 : (a) Series of 1D diffraction patterns (I=f(Q)) of the (440) peaks of the YSZ on heating and cooling. (after integral)
(b) Stain evolution of (440) planes on heating and cooling (Lattice strain is compared with expected evolution due only to thermal expansion)

In summary, this experiment was succesfull and the first analysis of the data are giving nice and interesting results. Even if data anlysis (evolution of FWHM and peak positions for all the data) is still on going, these preliminary results show that this type of experiment and technique are very promising for the characterization of «Sol-Gel» Thermal Barrier Coatings (TBCs).

Note that we are currently preparing a paper to be submitted for publication in international journals and we also plan to submit an other proposal at ESRF to correlate these first analyses with ultra-fast micro-tomography for in-situ imaging study (porosity evolution and cracks formation and development).