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Live observation of the oxidation of coated interconnects with environmental electron microscopy

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Abstract

Coatings on SOFC interconnect steels are complex and challenging to investigate due to the high number of chemical elements which are present and interact with each other. In this work, advanced electron microscopy techniques are used to study the steel oxidation in its initial stage (first days), where scale is built up and first elemental diffusions and interactions may be clearly seen. First the surface of a coated steel piece is observed in an environmental scanning electron microscope (E-SEM) at high temperature (880°C) under a pressure of pure oxygen (40Pa) allowing a direct observation of its morphological evolution during oxidation for 48h (Fig.1 (a)-(c)). For post data treatment, images were segmented using a machine-learning plug-in available in ImageJ (Fig.1 (d)), and the size of the grains on the surface quantified as a function of time. After the oxidation experiment in the E-SEM, a focused ion beam (FIB) was used to extract a TEM lamella from the exact same zone as that observed during the in situ exposure (rectangle in Fig.1 (a)-(d)), targeting specific grains where a two-stage growth could be observed. This post-mortem TEM cross section observation (Fig. 1 (e)-(f)) allows correlations of the sub-surface microstructure and grains with the surface structures seen during the in situ oxidation process. The system studied so far concerns Ce-Co coated SSHT steel (Sandvik).

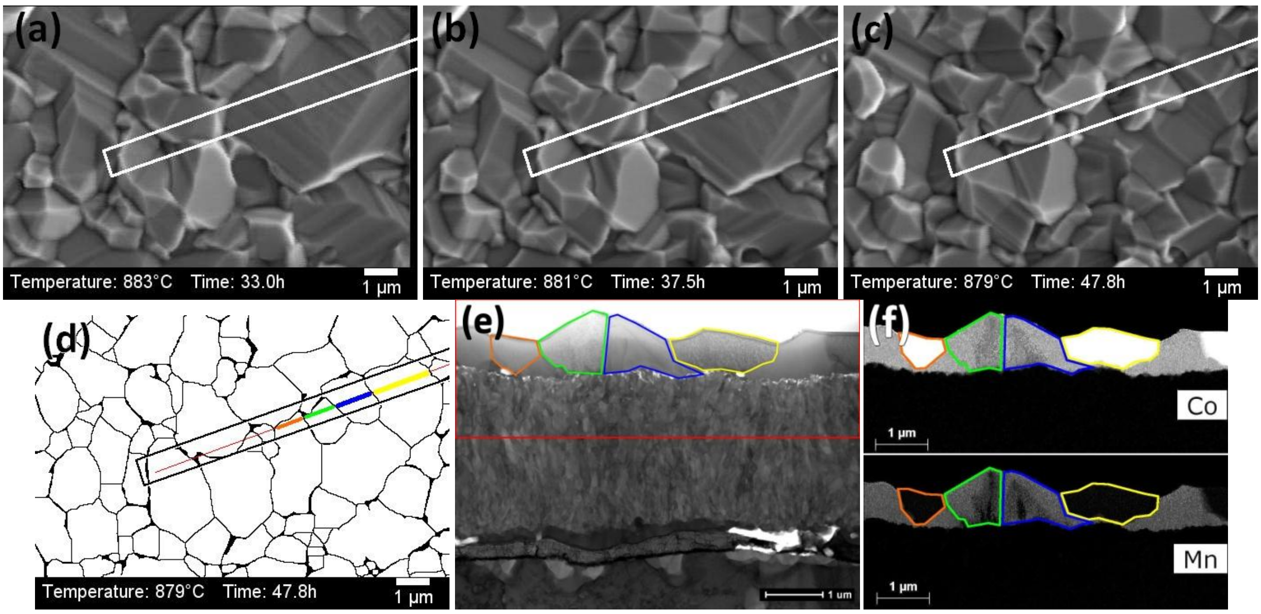

Fig.1: (a-c) Observation with ESEM, (d) segmentation, (e) TEM analysis and (f) EDX analysis of the Ce-Co coating oxidation with color identification for 4 grains.

Introduction

Solid Oxide Fuel Cell degradations are sometimes difficult to understand because of the lack of direct observations. Extensive post-test analyses on aged stacks or components generally imply a complete dismantling, which means that periodic observations of comparable samples are usually not possible. Hence, in this study, a complete method to better understand surface chemistry of components of a stack by observing them in-situ is demonstrated. This method is a combination of electron microscopy techniques and includes live observation of the surface under exposure to various atmospheres at high temperature, analysis of the images and the post-test analyses of the observed area's sub-surface.

It is known that avoiding chromium evaporation remains one of the challenges for the development of interconnects as it contaminates electrodes and degrades their performance. Various solutions try to mitigate the problem. An established measure is the use of coating. In this paper, we investigate the case of a cobalt-cerium-coated steel which was demonstrated to be efficient. A better understanding of the oxidation of such coated steels should help in improving its intended functions.

1. Scientific Approach

Environmental Scanning Electron Microscopy allows to observe samples under various atmospheres at high temperature, such as SOFC parts exposed to temperatures comparable to real conditions (up to 900°C) and their in-situ surface reactions. FIB-SEM allows precise cross section preparation of TEM lamellae at interesting sites of the sample. TEM observations and analyses of such lamellae reveal chemistry and microstructure of the first microns below the surface which correspond to the oxidized coating and its interface with the bulk steel.

The aim of this study is to demonstrate the potential of the combination of electron microscopy techniques to understand SOFC materials degradations. Part of this technique was previously shown [1]. The focus of this paper is:

- the new post processing of the ESEM images (using a Weka machine learning plugin in combination with watershed/distance map processing).
- the demonstration of the correlation that can be established between live observation and the post-test sub-surface analysis.

2. Experiments/Calculations/Simulations

A 5 by 5 mm and 0.2mm thick piece of coated steel was used. This was a commercial Sandvik Sanergy steel with its coating made of 10 nm of Ce covered by 600nm of Co. The layers are deposited at Sandvik by a PVD process on their steel (SSHT, Sandvik Sanergy High Temperature steel).

A modified FEI quanta 200 was used for the live observation. The performed modifications to the instrument are described elsewhere [2,3].
The sample was heated to 880°C under 40 Pa of Pure Oxygen. The observation of the same site lasted for 48 hours under these conditions. The images were aligned during the

post processing treatment with an ImageJ plugin called “Template Matching”. The resulting stack of images was cropped to keep the largest possible field of view without having black pixels and produced a final square observation area of around 20 by 20 microns. This area corresponds to 75% of the original area.

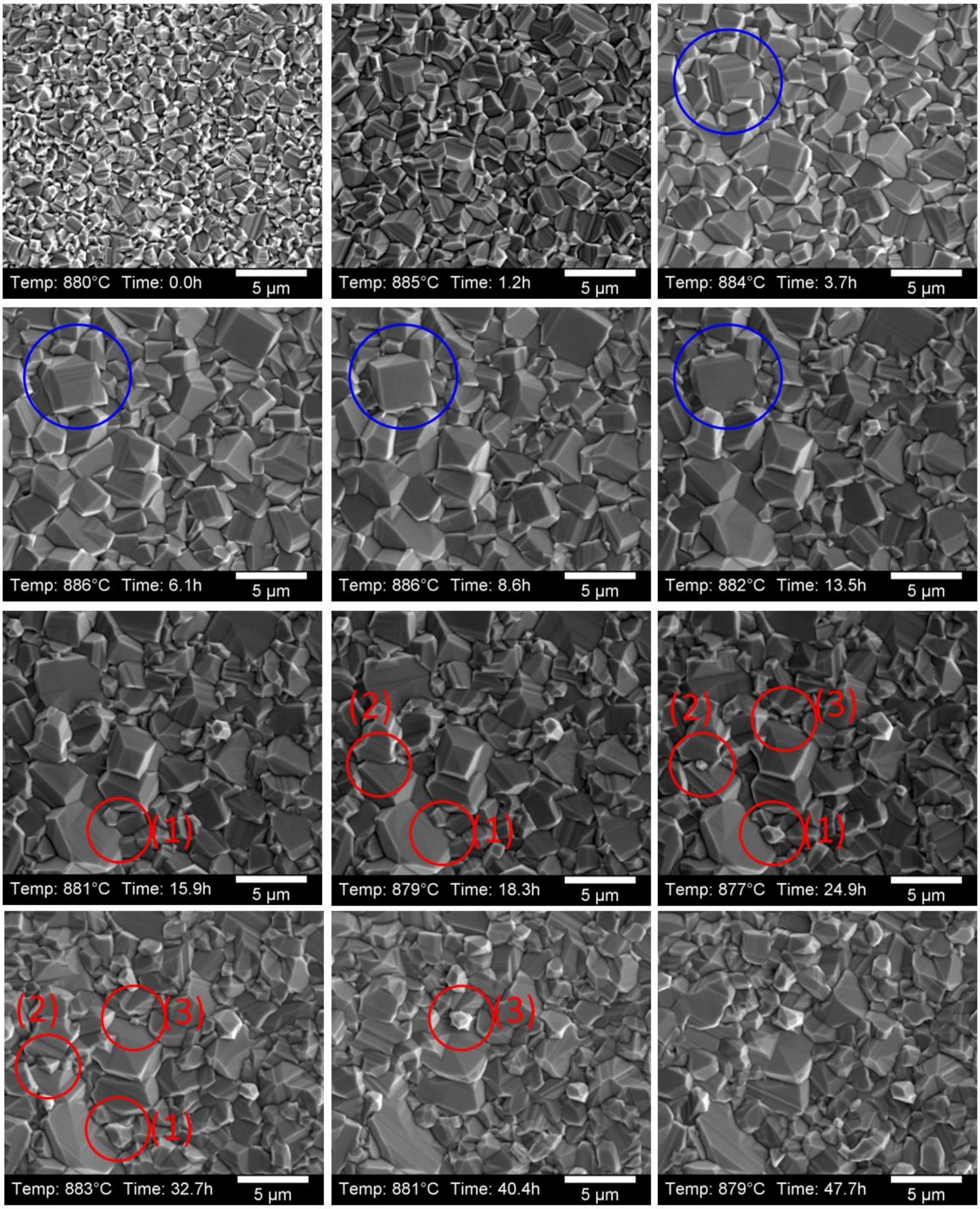

Figure 2: ESEM observation of the oxidation of the surface of the cobalt coating from the start to 48h. (Online video: https://goo.gl/rMRXyB). In blue, a grain with the initial cubic shape is highlighted. In red, the appearance of three new grains is highlighted.

Weka machine learning was used to process the segmentation. As presented in Fig. 3, the segmentation consists in 4 steps:
- Teaching/learning process by the machine.
- Machine segmentation, fig 3(b).
- Watershed distance map process, fig 3(c).
- Grain size characterisation, fig 3(d).

Several 2-dimensional training features were tested for the segmentation. The most accurate and time-saving reveal to be the "Gabor", "Hessian" and "difference of Gaussian" features. The type of distance calculations used for the distance map was Borgefors (3,4). For the watershed process, the parameters were 2 for dynamic and 4 for connectivity. For more details about the plug-in and their options, one can refer to the plug-in description sheet [4,5,6].

Carefully locating the observed area during ESEM oxidation, it has been possible to extract a cross section lamella from that exact area with a FIB/SEM. After thinning, the 100nm-thin lamella was transferred and observed with a Tecnai Osiris TEM. EDX analyses were also conducted on the lamella. We chose to observe a region where a grain with different shape emerged from a cubic one.

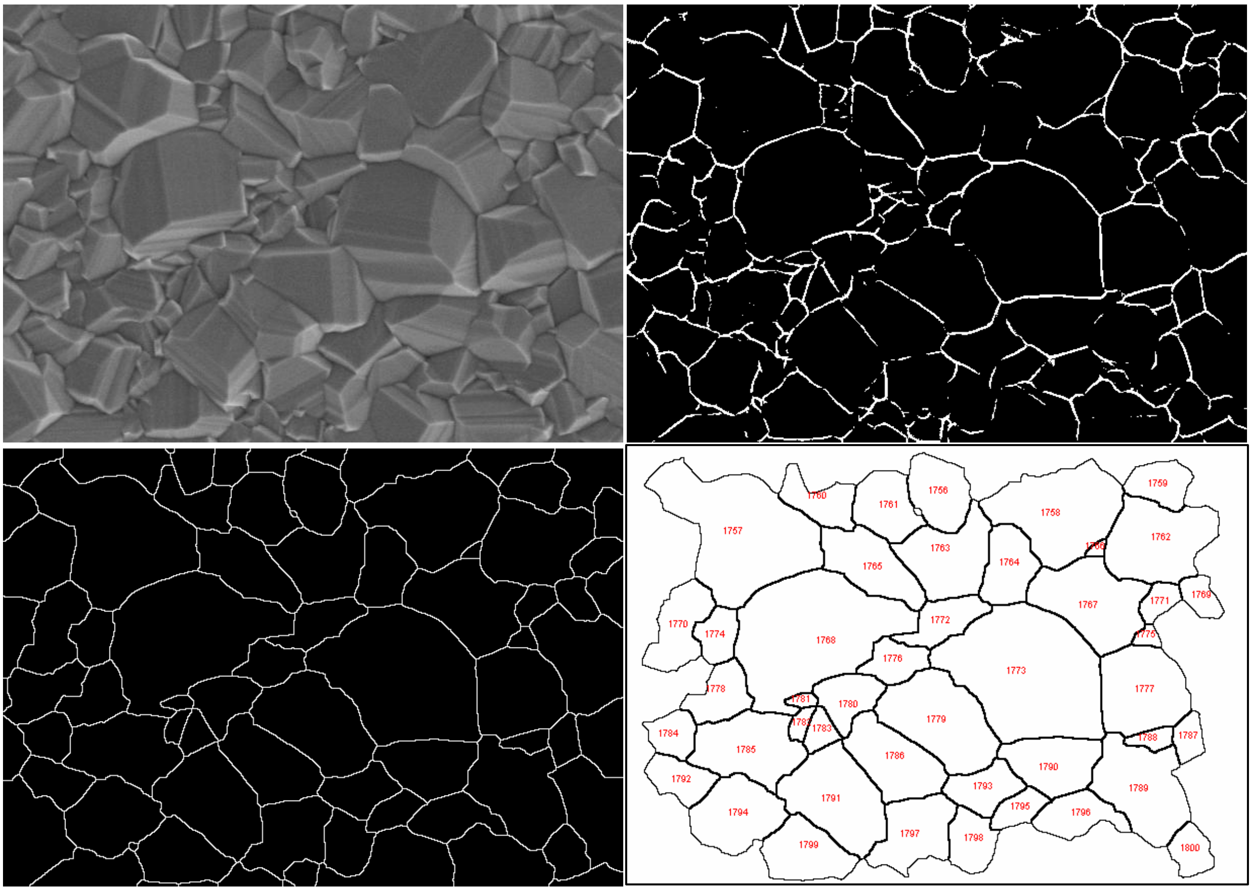

Figure 3: the segmentation process: (a) original image, (b) segmentation by the Weka machine learning process, (c) final segmentation after application of the distance transform watershed process, (d) grains taken into account for the grain size quantification.

3. Results

The first part of the investigation consists in the in-situ observation of the oxidation of the surface of the coated steel. Images from in-situ observation are shown in Fig.2. One can monitor the growth of the grains as highlighted in red. This is observed from the start of the oxidation. Then, starting after 15 hours, new grains begin to appear as highlighted in blue. The first grains present a cubic shape while the new grains show a more irregular shape.

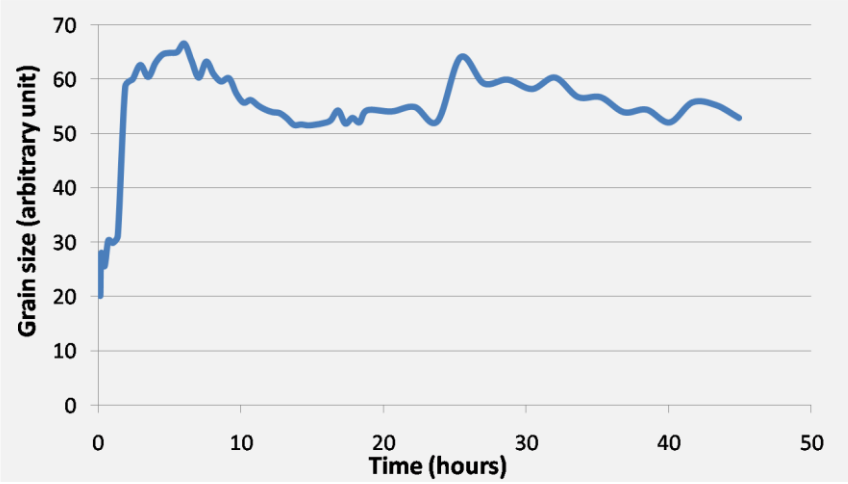

Figure 4: Graphic showing the increase in size of the surface grain. The size is in arbitrary units as it is not possible to know the size of the grain from 2D surface observation only.

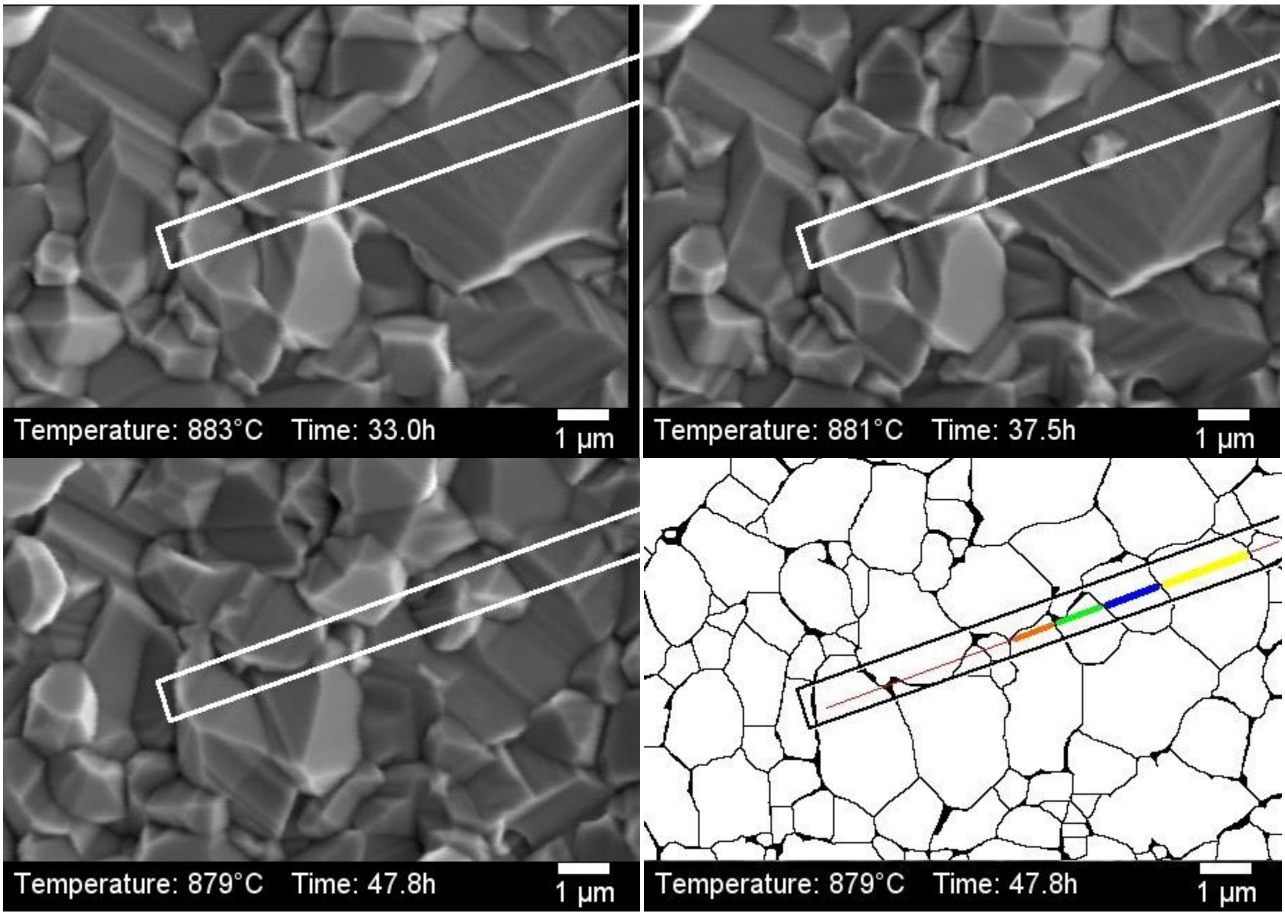

Figure 5: Image from the ESEM observation of the area of interest with position of the extracted lamella. On the segmented version of the last image, the grains of interest are identified with colours (online video: https://goo.gl/VBXYDh).

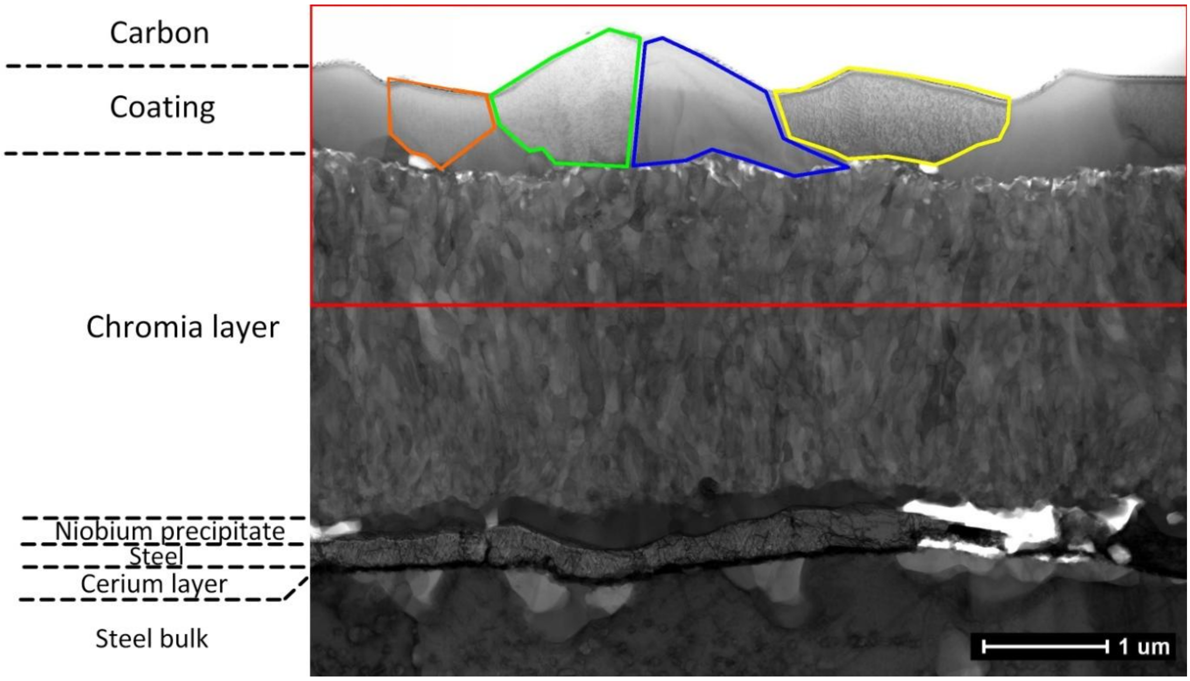

Figure 6: TEM bright field image of the cross section of the oxide layers after oxidation in the microscope. The grains identified with colours are also identified in Fig. 5 (ESEM images).

The segmentation process allows the calculation of the average grain size in the observed area as a function of time (Fig.4). A clear increase can be observed during the first hours and then the grain size is more stable even if dynamic behaviour is observed continuously until 48 hours, as can be seen from the video.

A lamella has been extracted from the area observed in-situ. The observed area and the position of the lamella are shown in Fig.5. At this particular location, two grains appear at 35 hours in the middle of a large cubic grain. The original grains and the new grains are identified with different colours: orange and yellow for the original grains and blue and green for the newly nucleated grains.

The same colour code is used in the TEM observation, Fig.6 and the EDX analyses, Fig. 7. The TEM observation shows the microstructures of the oxide layers close to the surface. The EDX reveals that the old grains contain only cobalt oxide while the new grains also contain manganese, iron and chromium. However, it seems that the chromium diffusion into the coating only occurs in a few new grains. Indeed, looking at the grains on the external side of the original grains on the TEM lamella (identified in red in Fig. 7), they contain cobalt, manganese and Iron but no chromium.

Diffusion of manganese and iron from the bulk to the coating were observed before. This study confirms the link between new grains and the diffusion of those elements.

The techniques combination allows concluding that:

- New grains appear with a different composition compared to the original cobalt oxide grains.
- The new grains contain manganese, iron and may contain some chromium.

The technique may still be improved in several ways. The temperature measurement accuracy will be improved. A 3D detector is being implemented on the microscope and should facilitate the observation of such surfaces.

The method has also some limitations, like the operation at low pressure. In-situ observation at higher pressure (5h at 800Pa pressure with around 500Pa of O_2) present some challenges regarding the in-situ observation. Higher pressure means a smaller mean free path for electrons and a worse signal/noise ratio on the detector. A difference with samples aged in real (atmospheric) conditions is still observed. However, the chemical and microstructure analyses show that in-situ results tend to converge toward ex-situ results.

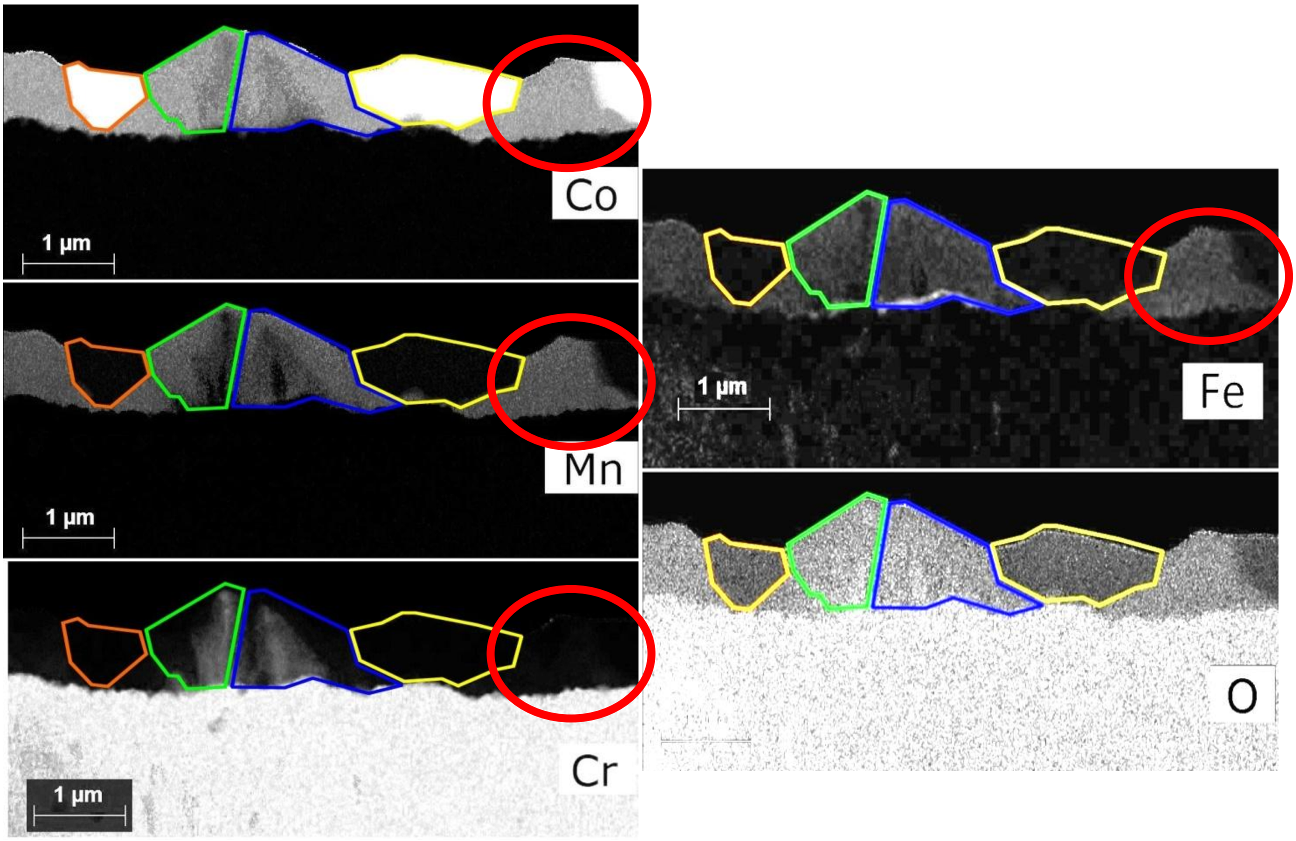

Figure 7: EDX images of the cross section of the cobalt coating (area highlighted by a red rectangle in Fig.6). The original grain is shown in yellow and orange. The new grains are shown in blue and green. The red circle shows that some grains contain manganese and iron but no chromium.

Acknowledgements

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[6] Distance transform watershed ImageJ plug-in:
https://imagej.net/Distance_Transform_Watershed