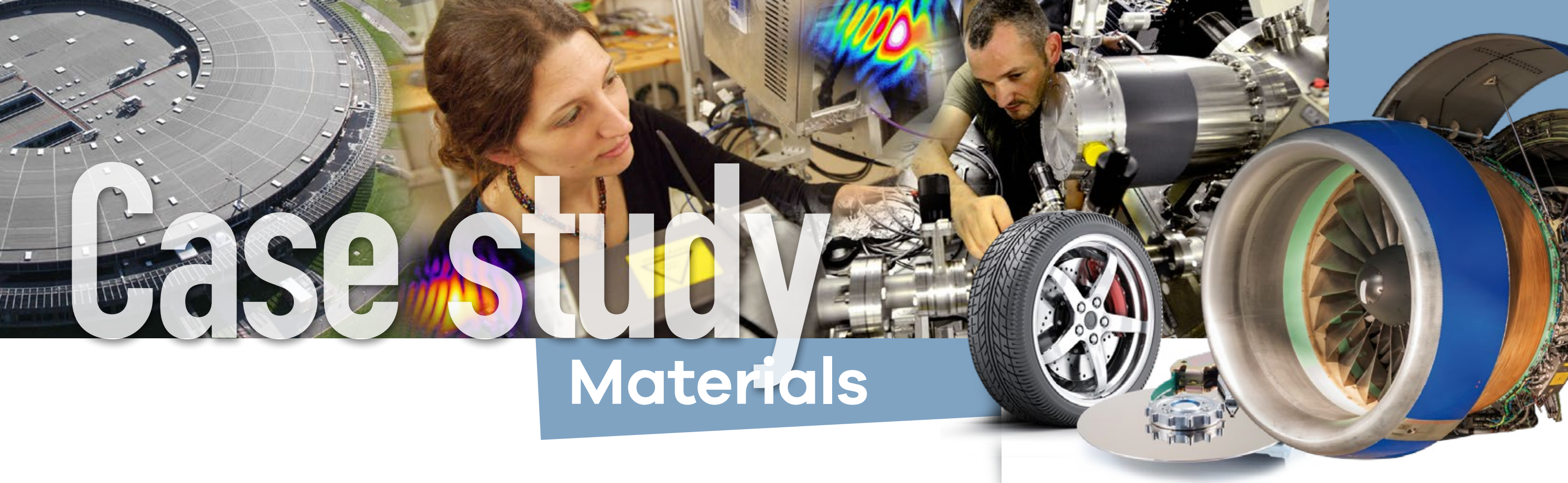
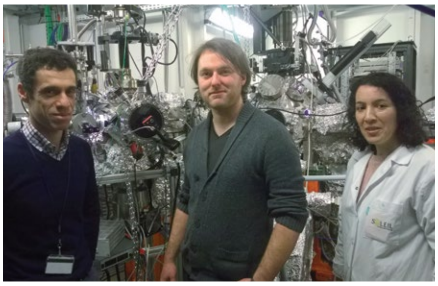


Understanding the chemical reaction mechanism in an industrial process to optimize it

Drawing on recognized expertise, Safran Electronics & Defense uses a polishing process for various hard and fragile materials with advanced manufacturing requirements (sub-nanometric roughness). Though approved and used by the company in various strategic applications (aeronautics, astronautics, defense and security), this process is not yet fully comprehended as demonstrated in this quote from Shelley R. Gilliss et al. in 2005: "Despite its widespread application, the chemical reaction mechanism (the "C" in CMP, Chemical Mechanical Polishing) is not entirely understood." [1]

Challenge:

Understanding the chemical reaction mechanism between a cerium oxide abrasive and the substrate to be polished (LAS glass-ceramic: mostly composed of lithium, silicon and aluminum oxides) would enable researchers to track back to the mechanical consequences of the process in order to try to optimize it. Experiments to identify a Ce-O-Si chemical bond, thought to form and play a key role during this process, have already been carried out on cerium oxides several nanometers in size and deposited on a silicon surface. The goal is to detect miniscule quantities of cerium from the polishing slurry present on the polished substrate (0.05 % atomic analyzed using photoemission spectroscopy (XPS) at very shallow depth) and the silicon present in the slurry residue. Detecting these trace elements and determining their oxidation state to trace back to chemical bonds is very complex using traditional surface techniques like XPS. Identifying chemical bonds present between the slurry and the substrate, before and after polishing, would strengthen current hypotheses[2].



Bastien HENAULT (center), CIFRE PhD candidate at SAFRAN in partnership with ICCF (Institut de Chimie Clermont-Ferrand), Jean-Pascal RUEFF, head of GALAXIES beamline and Karine CHAOUCHI, assistant engineer at the SOLEIL Chemistry Laboratory.

Focus

The "chemical" mechanism of Zerodur® chemical-mechanical polishing by cerium oxide

Safran is an international high technology group and a leading parts manufacturer for the aeronautic, space and defense industries.

SAFRAN

Present on all continents, the Group employs nearly 58,000 people and recorded 15.8 billion euros in revenue in 2016. Comprising many companies, Safran holds leading positions in its markets in Europe and the world, both individually and as a partner. To keep up with market changes, the Group undertakes research and development programs that represented 1.7 billion euros in spending in 2016. At the Safran Electronics & Defense site in Montluçon, optical trades witnessed the induction of 5 *Meilleurs Ouvriers de France* (MOF, Best French Craftsmen), 2 of whom are still active in optics polishing. In order to optimize production processes, it has become necessary to concentrate their skills and apply them to theoretical mechanisms.

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SOLEIL's solution:

The GALAXIES beamline (2.3 to 12 keV hard X-ray energy range) has two experimental stations, with one dedicated to hard X-ray photo-emission spectroscopy (HAXPES). With this technique, materials can be probed at a greater depth (10 nm versus the usual 1 nm for conventional low-energy photo-emission techniques) thanks to the higher kinetic energy of photo-emitted electrons. In addition, the high brilliance of synchrotron radiation enables rapid measurements with a better signal-to-noise ratio compared to laboratory sources, the objective being to obtain a viable signal from an element present in small amounts.

High resolution collection on GALAXIES

Experimental set-up: several residue samples from native and post-polishing slurries are prepared in a glovebox and transferred via a mini vacuum chamber, then attached to sample holders.

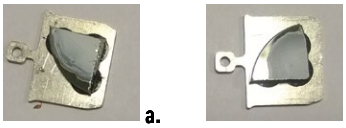
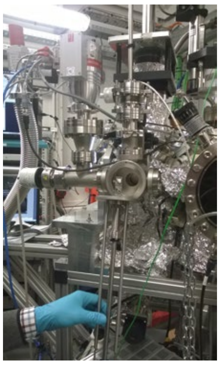


Figure 1: abrasive samples before (a) and after (b) polishing.



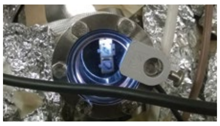


Figure 2: samples placed in a transfer chamber on the GALAXIES beamline, then transferred to the experiment chamber for analysis once vacuum conditions reached (10-9 mbars).

Results obtained:

The various elements of interest are first identified through rapid scans (Ce, Si, O), then high-resolution scans are recorded on the different samples, at element thresholds. The energy range corresponding to the Ce3d spectrum is targeted hereafter in order to highlight the oxidation state of the cerium.

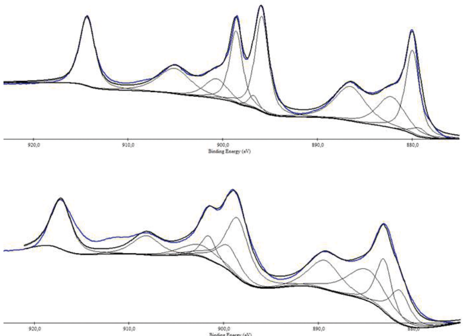


Figure 3: Ce3d spectral band of new abrasive (above) and used abrasive (below).

By carrying out a ratio of areas relative to cerium forms +III and +IV, it was possible to determine the rate of the two forms of cerium oxidation. It is 19 % in Ce^{3+} for the new abrasive and 45% for the used abrasive. The first impression suggests that the very act of polishing has a chemical influence on the abrasive (chemical-mechanical polishing hypothesis) via a reduction of cerium: Ce^{4+} to Ce^{3+}. This hypothesis is consistent with the results of a publication by Skála et al. (2013) indicating a similar result on the Ce3d band during the deposit of Si on CeO_2[3].

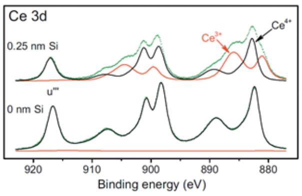


Figure 4: Ce3d of CeO_2 (below) and Si deposited on CeO_2 (above).

In connecting these publication results with measurements performed on the GALAXIES beamline, we are able to verify the hypothesis of Zerodur® chemical polishing: the production of a compound with a "Ce-O-Si"-type bond.

Sources: [1] S.R. Gilliss, J. Bentley, and C.B. Carter, "Electron energy-loss spectroscopic study of the surface of ceria abrasives," Appl. Surf. Sci., vol. 241, no. 1–2, pp. 61–67, Feb. 2005.

[2] L. M. Cook, "Chemical processes in glass polishing," J. Non-Cryst. Solids, vol. 120, no. 1–3, pp. 152–171, 1990.

[3] T. Skála and V. Matolín, "Photoemission study of cerium silicate model systems," Appl. Surf. Sci., vol. 265, pp. 817–822, Jan. 2013.

Focus follow up

For polishing, this means obtaining perfect surfaces, free of cosmetic flaws, combined with geometric planarity at the nanometer scale. For this reason, a CIFRE dissertation was initiated on "the study of polishing and superpolishing mechanisms." In more general terms, the goal of the Production Support unit in Montluçon is to support production teams in the field in order to master skills to sustain industrial activity.

New research prospects

Zerodur® polishing with cerium oxide leads to the appearance of a modified layer on the extreme surface characterized by an increase in cerium in a form as yet to be determined. Drawing on expertise with the GALAXIES beamline, we are able to demonstrate the "chemical" mechanism in Zerodur® chemical-mechanical polishing by cerium oxide. The usefulness of the method lies in the possibility to obtain a spectrum that is rich in information in a short period. The objective is to eventually obtain sufficient deconvolution of the cerium 3d peaks. These results will be followed by new studies on the impact of chemical modification on the mechanical properties of Zerodur©. Eventually, an increased understanding of extreme surface chemical-mechanical behavior will enable a deeper theoretical understanding of the polishing process.

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