EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report")*,
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Published papers

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** The Effects of Temperature, Pressure and Shear on the Oxidation States and Local Structure of Oil Lubricant Additives: A VK-edge Operando XAS Tribology Study	**Experiment number**: MA-5042
Beamline: BM23	**Date of experiment**: from: 01-12-21 to: 05-12-21	**Date of report**: 19-08-22
Shifts: 9	**Local contact(s)**: Olivier Mathon	*Received at ESRF:*

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Report:

Summary. V K-edge XAS experiments were performed to chemically characterise the interfacial phases formed on steel by novel vanadium (IV) lubricant additives, under friction conditions in a tribological contact. The chemical composition of the V phases, which are likely formed by complex mechanochemistry in the tribological contact, were followed as a function of high temperature, pressure, and shear. The *in situ* XANES results, complemented by previous *ex* and *in situ* XPS and NEXAFS studies, indicate the tribochemical formation of a composite mixed valence tribofilm, comprising of V(III), V(IV) and V(V), with notable variations between the bulk and surface of the tribofilm.

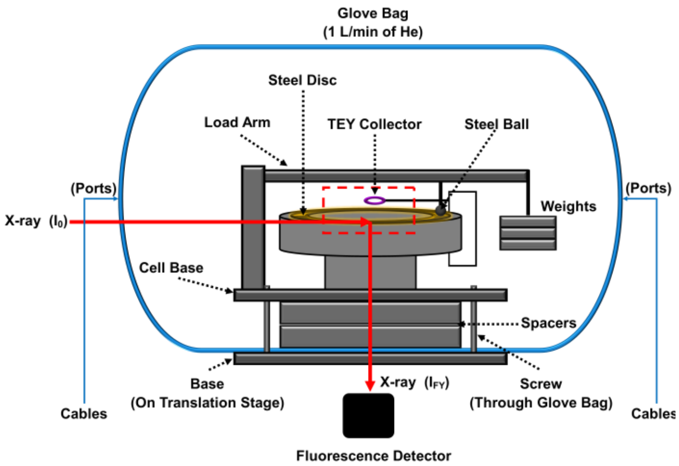

Fig 1. Sketch of the Tribometer set-up used for the *in situ* V K-edge XAS experiments at beamline BM23.

Experiment Details. We used a custom-built tribometer (Fig. 1) to analyse time-resolved structural variations as a function of process conditions by micro-focused fluorescence yield XAS inside and outside the wear scars.[1,2] Scanning XRF mapping was used to identify the wear scar location where the V-containing oil is present.

Results. We analysed various vanadium containing compounds with varying oxidation states including $VO(acac)_2$, VButylate and VOTris lubricant additives. Discernible differences were observed in the *ex situ* XANES spectra for the materials studied, most especially the features due to the 1s → 3d and 1s → 4p electronic transitions.[3] These variations were used to elucidate the changes in the tribofilms formed from the three different additives dispersed in three different oils. The *in situ* XAS data (Fig. 2) complements previous *ex situ* XPS and NEXAFS studies, which indicate the presence of V(III), V(IV) and V(V) following tribotesting. In all three cases, triboreduction from a V(IV) to V(III) species is clearly evidenced by a decrease in intensity of the 1s → 3d peak and red shifts in both pre- and post-edge features. Notably, the three additives behave differently under the same temperature, pressure and shear conditions. V reduction is evident in the $VO(acac)_2$ system at an earlier stage of the tribotesting (Fig. 2a – 5 mins) compared to the VButylate (Fig. 2b – 15 mins) and VOTris (Fig. 2c – 60 mins) systems. This correlates with their varying anti-wear properties.

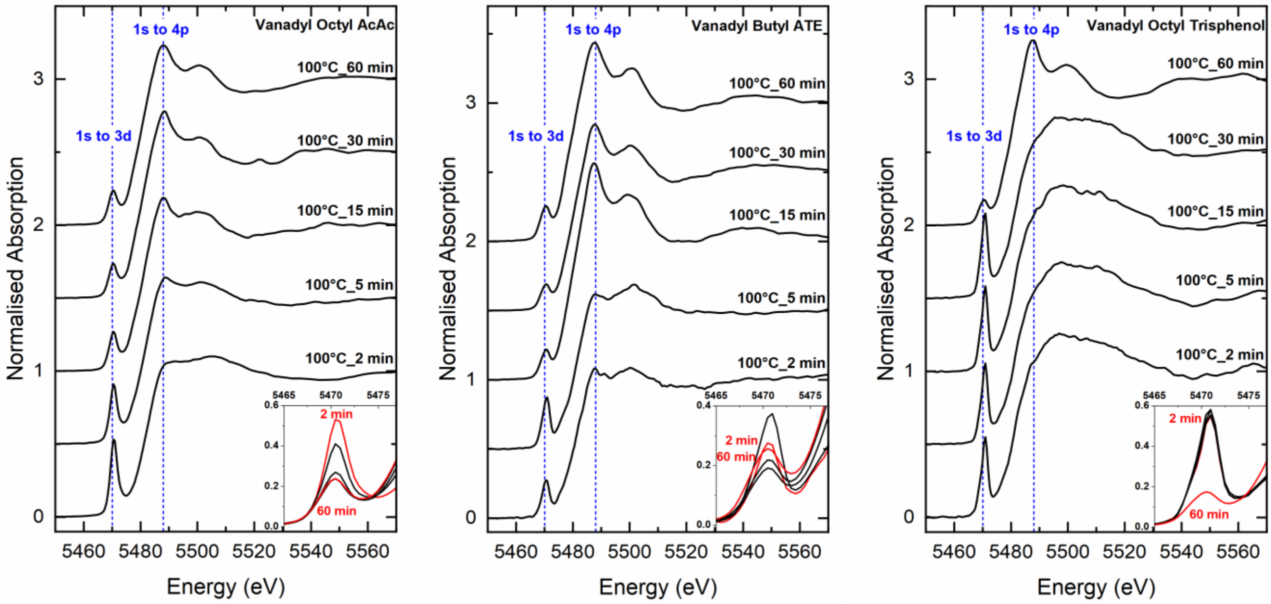

Fig 2. V K edge *in situ* XANES spectra obtained inside the wear scar during tribological testing of the (a) $VO(acac)_2$ (b) VButylate and (c) VOTris additives in base oil.

Conclusions and Future Work. Ultimately, the molecular-level mechanistic information obtained will enable the development of more effective and sustainable anti-wear additives. The results obtained from this experiment will inform future *in situ/operando* XAS studies on the tribological properties of other vanadium and/or molybdenum containing additives.

References

1. A. Dorgham, A. Neville, K. Ignatyev, F. Mosselmans and A. Morina, *Rev. Sci. Instrum.*, 2017, **88**, 015101.

2. A. Dorgham, P. Parsaeian, A. Neville, K. Ignatyev, F. Mosselmans, M. Masuko and A. Morina, *RSC Adv.*, 2018, **8**, 34168–34181.

3. J. Wong, F. W. Lytle, R. P. Messmer and D. H. Maylotte, K-edge absorption spectra of selected vanadium compounds, *Phys. Rev. B*, 1984, **30**, 5596–5610.