

## **Oxidation and Auto-Reduction of Plutonium**

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Using X-ray photoelectron spectroscopy (XPS), the reaction kinetics which occur during the early stages of the oxidation of polycrystalline plutonium can be following in oxygen containing atmospheres. Furthermore, when subjecting these thin dioxide layers to ultra high vacuum (UHV) conditions a spontaneous, thermodynamically driven, reduction to the trivalent sesqui-oxide,  $\alpha$ -Pu<sub>2</sub>O<sub>3</sub> occurs. Kinetic information about this surface transformation, from PuO<sub>2</sub> to Pu<sub>2</sub>O<sub>3</sub>, is gained by following the changing depths of these two oxide layers, again using XPS as a probe.

A mathematical model is proposed to follow this auto-reduction reaction, based on a simple 2D layered structure. The rate of this plutonium oxide auto-reduction reaction is controlled by diffusion of oxygen across the steadily expanding Pu<sub>2</sub>O<sub>3</sub> layer. Through investigating the kinetics of this auto-reduction reaction, a value of  $1.4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$  is obtained for the diffusion coefficient of oxygen through  $\alpha$ - Pu<sub>2</sub>O<sub>3</sub> at room temperature.

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# Evidence for Differential Rates of Oxide Growth on Depleted Uranium: Implications for Uranium Corrosion

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A focused gallium ion beam was used at a grazing angle to clean surface areas of depleted uranium and remove surface oxide. Subsequent exposure of the material to air under ambient conditions for a 5 minute period allowed limited re-growth of the surface oxide.

Secondary ion mass spectrometry (SIMS) was then used to obtain depth profiles from individual metal grains at the uranium surface using signal gating to profile grains simultaneously. The recorded  $\text{UO}_2^+$  and  $\text{UO}^+$  ion cluster profiles provided strong evidence that the surface oxide film had different thicknesses over different metal grains and indicates that the initial growth of uranium oxide must occur at differential rates related to differences in the lattice orientation of the exposed metal grains on which it formed. Electron backscatter diffraction (EBSD) was then used to identify the lattice orientations of the metal grains which had been profiled to try to identify a relationship between grain orientation in the metal and the rate of oxide growth.

The observation of differential rates of oxide growth on uranium is significant because the thickness of the oxide layer on uranium is an important control on further corrosion of the metal under a wide range of conditions.

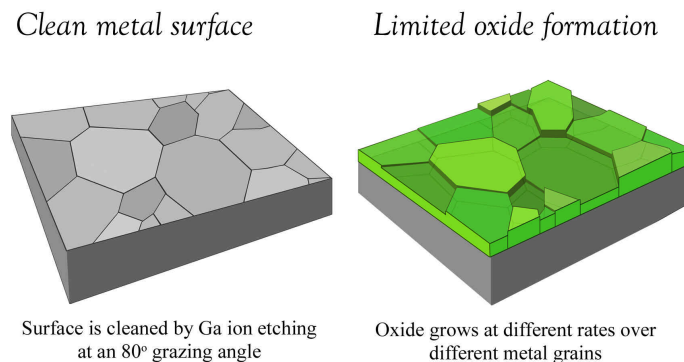


Fig. 1. Differential growth of thin film oxide ( $\text{UO}_2$ ) on depleted uranium

# **Application of Surface Analyses for Understanding Tribochemistry in Engines**

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One of the challenges that engine oil manufacturers are now facing is the reduction of engine friction losses while at the same time increasing the durability of engine components. New materials are now being used for engine components, beside the conventional ferrous materials. This makes the job of effective lubrication even more challenging knowing that existing engine oils are designed to work for ferrous materials. Engine oils are required to lubricate these materials as effective as the conventional materials, and with no environmental impact. Therefore, it is of paramount importance to understand the mechanisms by which engine oils provide low friction and high durability of boundary lubricated tribology systems build using conventional or novel materials. Surface analytical techniques are the essential tools that help in understanding these mechanisms.

In this paper, use of surface analyses in understanding the mechanisms by which engine oils additives containing Zinc Dialkyldithiophosphate (ZDDP) and Molybdenum Dialkyldithiocarbamate (MoDTC) additives form tribofilms on Steel, Chromium Nitride and Diamond like Carbon coatings is discussed. The surface films formed by testing the components in boundary lubrication regime are chemically characterised using the Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy and X-ray Photoelectron Spectroscopy while the physical properties are characterised using the Atomic Force Microscopy. It is shown that nature of the surface films depends greatly from the material lubricated.

## **Nanocomposite Coatings for Wear Resistant Applications**

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Sputter deposited nanocomposite coatings are multiphase systems which are becoming increasingly important as they offer the possibility of tailoring the coating architecture and achieving exciting new properties. These new generation coatings can extend the working conditions for tools and machine components.

Coating design is based upon thermodynamic phase diagrams. However, such coatings are deposited under non-equilibrium conditions and it is important to determine the nanostructure of the actual coating deposited. XRD, TEM and XPS have been employed to identify the phases and determine the relative phase fraction, grain size and structural defects present in nc-(Ti,Al)N/a-BN coatings.

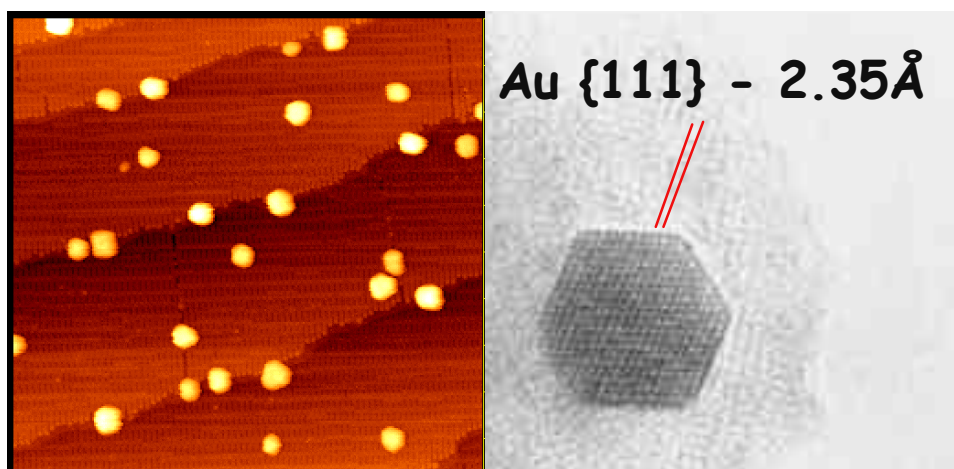
The accordance (or not) of the phase composition and relative phase fraction with the equilibrium phase diagram for this system is examined and correlations are made between the nanostructure and mechanical properties.

## The Surface of Heterogeneous Catalysts

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Heterogeneous catalysts are nanomaterials for which the nature of the very topmost surface layer is of crucial importance for economic and environmental efficiency. Hence, it is also crucial to be able to use surface-specific analysis and nanotools which are capable of resolving very small nanoparticles, and, if possible, the active site at atomic resolution. To be provocative, I will claim that many techniques are almost useless for catalysis studies (e.g. SEM) since they do not properly assess the surface layer. XPS is useful but is also very problematic, partly because it is generally only a semi-quantitative technique and partly because it is not top-layer specific. I will highlight some useful methods, including nanoprobe such as TEM, STEM and SPM.



*STM image of Pd nanoparticles on TiO<sub>2</sub>, (left, particles ~ 4nm diameter) and TEM of a Au nanoparticle in a high activity Au/TiO<sub>2</sub> catalyst for ambient temperature CO oxidation (right).*

## **The Capture and Analysis of Micrometeorites in Space using Aerogel**

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Aerogel is a silica foam with the lowest density known for a man-made material of between 5 and 150kg/m<sup>3</sup>. Aerogel has been exposed in Earth orbit for the capture of dust particles from space on a number of experiments and most recently on the NASA 'Stardust' spacecraft flyby of the Comet Wild 2 in January 2004. Analysis of collected particles returned to earth is expected to shed light on the problems posed by space debris in Low Earth Orbit as well as the origins of the universe.

Dust particles in space collide with the aerogel material at hypervelocity speeds in the range of 5 to 70km/sec and as a consequence may be buried far below the surface of the aerogel, fragment or break up causing a void within the aerogel that is thinly coated with traces of residue from the impactor. In this talk we discuss the results of ToF-SIMS analyses aerogel of returned from space and analogue sample prepared in terrestrial laboratories in conditions that match space collection.

# **Surface Science Studies of Metalliferous Minerals in the Extreme Environments Associated with Acid Mine Drainage.**

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Metalliferous and coal mining has left a global legacy of sites contaminated by acid waters and toxic metals generated by the breakdown of sulphide minerals. The environment in such areas can show pH values from as low as -3.6 to typically 1-3. Particular problems are seen in parts of North and South America and in the UK. The release, transport and re-precipitation of contaminants are ultimately controlled by processes involving interactions between mineral surfaces and fluids and can be rapidly accelerated by the presence of microbial communities (called extremophiles) but are poorly understood in many cases.

This report focuses on minerals involved in mine waste systems involving arsenic and sulphur, with experimental studies of the oxidative breakdown reactions, in the presence or absence of bacteria, of arsenopyrite (FeAsS) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>) to form iron and copper (oxy)hydroxides. The fate of arsenic in these minerals is investigated.

This study makes use of experimental and computational resources and we focus here on surface investigations using XPS of the breakdown and precipitation reactions, contrasting bio and inorganically mediated systems.