APPLICATION NOTE

Analysis of chemical bonding states in an ionic liquid

The Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) System was used to analyze the elemental and chemical composition of a worn steel surface coated with an ionic liquid.

Introduction

Ionic liquids have recently been identified as potential lubricants for metal/metal contacts. Tribological experiments are used to study the wear and friction behavior of the liquids, but interpreting the data from such experiments requires a detailed understanding of the surface chemistry. X-ray photoelectron spectroscopy (XPS) is the ideal analytical technique for this purpose, combining surface sensitivity with chemical selectivity.

To fully characterize the surfaces formed during tribological experiments, it is necessary to detect and distinguish different chemical bonding states within small, localized areas of the sample. Additionally, the ionic liquid may be deposited on a magnetic substrate, such as steel, which further increases the demands of the analysis. This requires an XPS tool that combines small spot capability with high sensitivity and excellent energy resolution, but which can achieve this on magnetic samples.

The K-Alpha XPS System was used to investigate the wear surface formed by the tribological action of a brass rod on a steel disc. The ionic liquid 1-hexyl-3-methyl-imidazolium tris (pentafluoroethyl) trifluorophosphate was used as the lubricant. The chemical structure of the ionic liquid is shown in **Figure** 1.
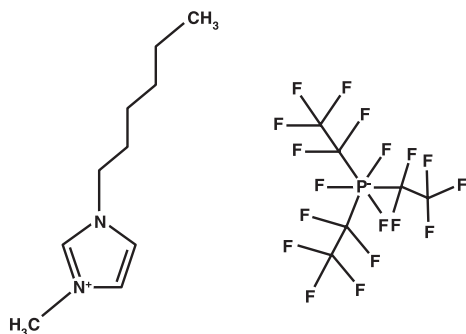
Experiment

An optical image of the worn steel surface is shown in **Figure** 2. The image was acquired using the live Reflex optics system, unique to the Thermo Scientific™ K-Alpha™ X-ray Photoelectron Spectrometer (XPS) System. With Reflex, the user can confidently select the analysis points for large- or small-area XPS analysis. The XPS probe is accurately replicated on the live optical view by a graphical marker, allowing you to easily select the most appropriate probe size for the feature of interest.

The wear track on the steel surface has dark and light stripes of differing widths, which are easily observed in the optical image. Using the graphical probe marker, it was straightforward to select 30 µm and 80 µm spots, respectively, for analyzing the differently sized dark and light stripes.
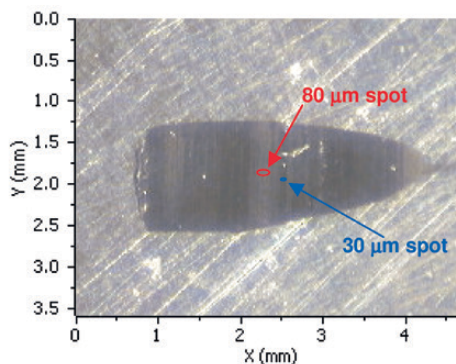

Figure 2: K-Alpha XPS System live optical image of tribologically induced wear track. The ellipses indicate the positions and sizes of the analyzed areas.

Figure 1: Chemical structure of 1-hexyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate.

Results

Elemental composition of worn surface lubricated with ionic liquid

XPS survey spectra (**Figure 3**) were acquired from the areas marked in the optical image. Survey spectra allow the elemental composition of the worn surface to be quantified at the two different analysis points (see **Table 1**).

Element	Atomic Concentration	
	Light Stripe	Dark Stripe
P	3.20	3.05
C	46.05	45.05
N	4.47	4.48
O	—	3.13
F	49.27	44.29

Table 1: Elemental quantification of worn steel surface at two analysis points.

No spectral features associated with the steel substrate were observed, indicating that the ionic liquid layer at each point was sufficiently thick to completely attenuate photoelectrons from the substrate. It can be concluded, therefore, that the ionic liquid layer is at least 10 nm thick.

The main elemental difference between the two points is the presence of oxygen in the light stripe. The quantities of the other elements identified are similar in each stripe. There is an observable difference in the shape of the C1s peak, suggesting the possibility of different carbon chemistry in the darker and lighter stripes.

Chemical bonding states in worn surface lubricated with ionic liquid

The carbon chemistry at the lighter and darker stripes was investigated using the high-energy resolution of the K-Alpha XPS System. Carbon spectra acquired at the two analysis points allow you to distinguish between the different bonding states on the worn surface (**Figure 4**).

The carbon chemistry at the lighter and darker stripes was investigated using the high-energy resolution of the K-Alpha XPS System. Carbon spectra acquired at the two analysis points allow you to distinguish between the different bonding states on the worn surface (see Figure 4).

The peaks labelled C-C and C-C-N or N-C-N are respectively due to the alkyl chain and imidazolium ring in the cationic component of the ionic liquid.[1] (A small amount of the C-C peak is also due to surface contamination.) The energy resolution of the K-Alpha XPS System is sufficient to distinguish between the two different chemical states of carbon in the imidazolium ring, which consists of carbon bonded to a single nitrogen atom and carbon bonded to two nitrogen atoms.

The CF_3 and CF_2 peaks are due to the two different carbon bonding states in the anionic fluorophosphate component of the ionic liquid. The main difference between the carbon chemistry of the pale and dark stripes is the increased amount of aliphatic carbon in the latter (indicated by the larger C-C component in Figure 4).
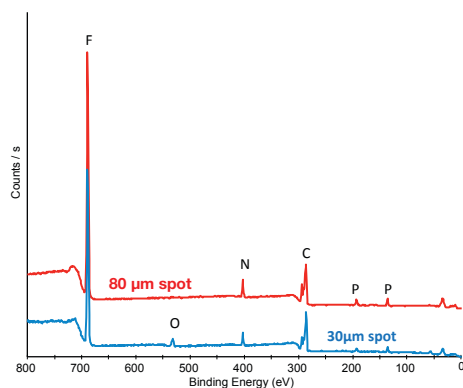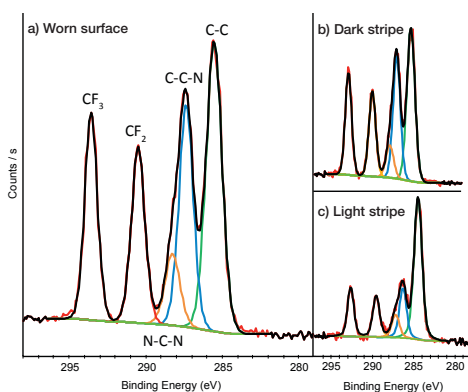

Figure 3: XPS spectra acquired from darker (blue) and lighter (red) stripes in the wear track of the steel disc. Spectra have been normalized and offset for clarity.

Figure 4: High-energy resolution C1s spectra acquired from a) worn surface using 400 µm X-ray spot b) darker stripe and c) lighter stripe on worn surface.

Summary

K-Alpha XPS System was used to analyze the elemental composition and carbon chemistry of a worn steel surface formed during a tribological experiment. The surface was coated with the ionic liquid 1-hexyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate. Different points on the worn surface were found to have different carbon chemistry, and the thickness of the ionic liquid layer was determined to be at least 10 nm.

1. S. Caporali et al., Journal of Electron Spectroscopy and Related Phenomena 151 (2006) 4-8.

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