Application Note: 52106

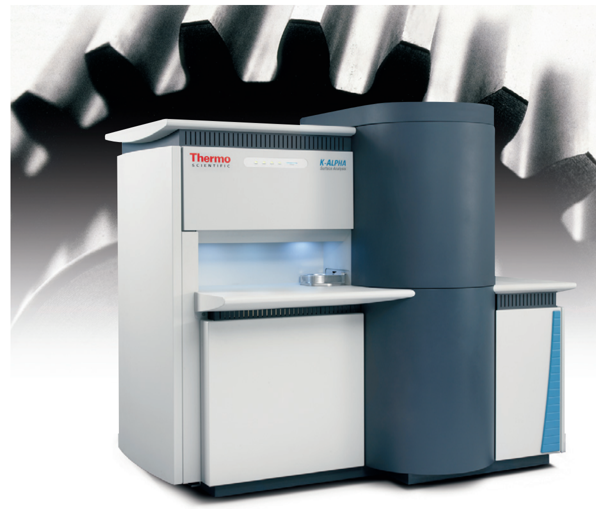
XPS Evaluation of Wear Resistant Coatings

Paul Mack, Thermo Fisher Scientific, East Grinstead, West Sussex, UK

Key Words

- K-Alpha
- Metal
- Steel
- Surface Analysis
- Tribology
- XPS

Thermo Scientific K-Alpha, an integrated XPS tool was used to correlate the behavior of wear resistant coatings with their elemental and chemical composition.



Introduction

Additives in lubricating oils play an important role in forming friction modifying layers on metal surfaces. Overbased calcium sulfonate additives are used to deposit wear resistant layers on steel surfaces, for example, and zinc dialkyldiphosphonate (ZDDP) has been observed to form a protective, glassy phosphonate coating on surfaces under tribological load.[1] Layers formed on surfaces under load are unlikely to have a uniform distribution across the sample. Optical images of worn surfaces (Figure 1) show darker and brighter tracks (50–100 µm wide) caused by non-uniform processes during tribological testing.

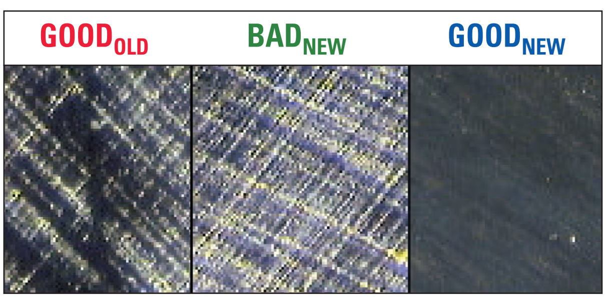


Figure 1: Optical images taken by the instrument of the analyzed surfaces

The samples used in tribological testing may have a large surface area (several cm²) compared to the size of a typical high quality X-ray spot (30–400 µm). An experimental protocol which includes both micro and macro analyses is therefore required to characterize the wear tracks. Small spot X-ray analysis can be used to detect and distinguish different chemical bonding states within narrow interesting features and large area mapping can be used to investigate the distribution of these states across the surface.

Thermo Scientific K-Alpha is the ideal analytical tool for investigating the elemental and chemical composition of these surfaces, combining imaging capability with surface sensitivity and chemical selectivity. The design philosophy of K-Alpha means that even when the anti-wear coatings are electrically insulating or have magnetizable substrates, such as steel, straightforward analysis with high sensitivity is still possible even for small spot analysis.

Experimental and Results

Three steel samples were tested for friction stability. One of the samples, labelled as $GOOD_{OLD}$, had already been under consistent tribological load throughout its lifetime, whereas the other two samples ($GOOD_{NEW}$ and BAD_{NEW}) had not been worn prior to the test. The $GOOD_{OLD}$ sample was tested to see whether aging under load had detrimentally affected its friction stability behavior. It was found that the $GOOD_{NEW}$ sample behaved very well under tribological test. One of the samples (BAD_{NEW}), however, was found to have abnormal friction properties. K-Alpha XPS was used to correlate surface composition and chemistry to these different tribological characteristics.

Survey spectra (Figure 2) were acquired over wide areas on each sample to identify and quantify the elements present on the surfaces. Although the oil contained a high

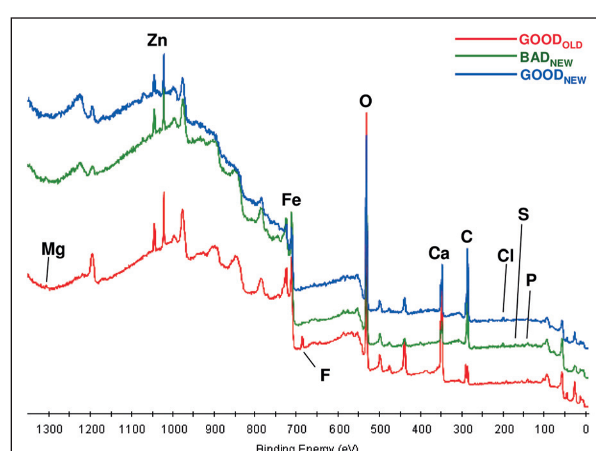
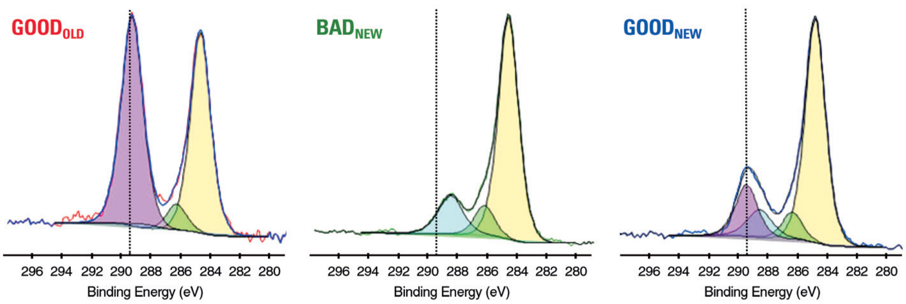


Figure 2: Elemental identification of the elements on the steel surfaces



Carbon Bonding States Quantification

Chemical State	Relative Amounts of Carbon Bonding States		
	GOOD$_{OLD}$	BAD$_{NEW}$	GOOD$_{NEW}$
C-C	44.03	74.07	65.97
C-O	5.52	9.81	7.68
C=O	1.13	15.61	10.04
CO_3^{2-}	49.32	0.51	16.31

Figure 3: Chemometric analysis of carbon

level of ZDDP additive, the actual amount of zinc on the samples after tribological testing is quite small. (See quantification in Table 1.) In contrast, the GOOD$_{OLD}$ and GOOD$_{NEW}$ samples have a significant quantity of calcium. The source of calcium was the overbased detergents that had been mixed, in differing ratios, with the ZDDP into the oil. The GOOD$_{OLD}$ sample was found to have significantly more calcium on the surface than the BAD$_{NEW}$ and GOOD$_{NEW}$ samples, but significantly less total carbon. The carbon chemistry on each sample was therefore investigated more thoroughly.

Atomic Concentration

Element	GOOD$_{OLD}$	BAD$_{NEW}$	GOOD$_{NEW}$
P	0.29	0.28	0.21
S	0.29	0.59	–
Cl	0.22	0.80	0.83
C	15.96	39.86	40.10
Ca	14.12	3.79	8.31
O	57.73	45.12	44.71
F	1.50	–	0.28
Fe	6.74	7.67	4.28
Zn	3.03	1.63	1.28
Na	–	0.26	–
Mg	0.12	(tr)	–

Table 1: Elemental surface quantification of samples

The chemical bonding states of carbon on each surface were analyzed by acquiring high energy resolution carbon spectra (Figure 3). Four chemical states were observed: organically derived C-C, C-O and C=O, and inorganic carbonate. A detailed analysis of the carbon chemistry is possible by fitting the data with a series of synthetic Lorentzian-Gaussian peakshapes. This allows a full quantification of the chemical states on the sample surfaces. The GOOD$_{OLD}$ sample has significant amounts of both carbonate and organic carbon. Peak fitting confirms that the GOOD$_{NEW}$ sample has a mixture of carbonate and C=O but that the BAD$_{NEW}$ sample has virtually no carbonate.

XPS imaging of the GOOD$_{OLD}$ sample revealed well defined wear tracks, with alternating regions of high and low carbonate (Figure 4). These regions correlate with high and low calcium concentrations, indicating that the calcium carbonate is formed in the tracks. The thickness of the carbonate film at each point in the map was measured simultaneously with the composition. In the carbonate tracks, the film can be as thick as 87 Å. XPS imaging of the GOOD$_{NEW}$ sample also revealed thick calcium carbonate tracks. These tracks were slightly thicker than for the GOOD$_{OLD}$ sample.

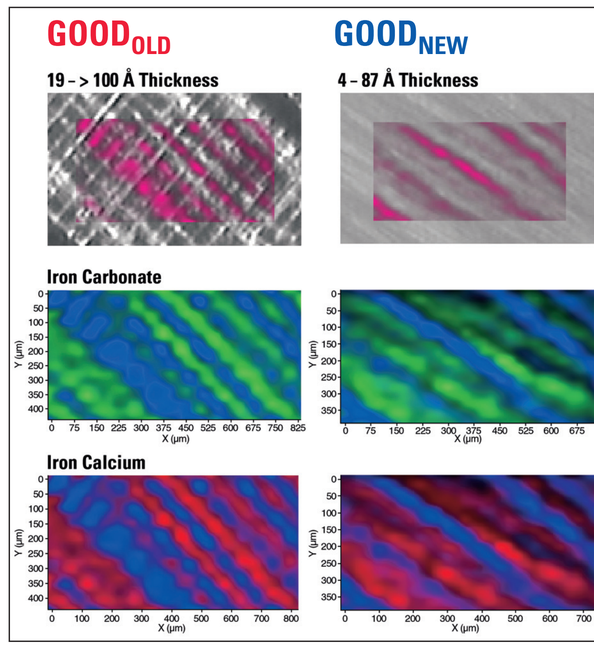


Figure 4: XPS imaging measurements of carbonate film thickness and surface composition

Summary

Thermo Scientific K-Alpha was used to comprehensively characterize the surfaces of three coated steel samples. Two of the samples, labelled $GOOD_{OLD}$ and $GOOD_{NEW}$, were known to have good friction stability properties and XPS showed the presence of calcium carbonate tracks on these samples. A third sample, which was known to have poorer friction stability properties, labelled BAD_{NEW}, had virtually no calcium carbonate on its surface.

K-Alpha XPS analysis showed that the correct ratio of ZDDP to calcium detergent will result in the formation of calcium carbonate during tribological load, and it is this carbonate that confers good friction stability properties. Calcium carbonate, however, did not form on the BAD_{NEW} sample, indicating an inappropriate ratio of ZDDP to detergent in the oil formulation.

Acknowledgements

Thermo Fisher Scientific wishes to thank the Austrian Center of Competence for Tribology (*www.ac2t.at*) for the sample.

Reference

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

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa-Other
+27 11 570 1840
Australia
+61 3 9757 4300
Austria
+43 1 333 50 34 0
Belgium
+32 53 73 42 41
Canada
+1 800 530 8447
China
+86 10 8419 3588
Denmark
+45 70 23 62 60
Europe-Other
+43 1 333 50 34 0
Finland/Norway/Sweden
+46 8 556 468 00
France
+33 1 60 92 48 00
Germany
+49 6103 408 1014
India
+91 22 6742 9434
Italy
+39 02 950 591
Japan
+81 45 453 9100
Latin America
+1 561 688 8700
Middle East
+43 1 333 50 34 0
Netherlands
+31 76 579 55 55
New Zealand
+64 9 980 6700
Russia/CIS
+43 1 333 50 34 0
South Africa
+27 11 570 1840
Spain
+34 914 845 965
Switzerland
+41 61 716 77 00
UK
+44 1442 233555
USA
+1 800 532 4752

VG Systems Ltd. Trading as Thermo Fisher Scientific, East Grinstead, UK is ISO Certified.

AN52106_E 04/11M

www.thermoscientific.com

©2011 Thermo Fisher Scientific Inc. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.

Part of Thermo Fisher Scientific

Thermo SCIENTIFIC