Argonne NATIONAL LABORATORY

... for a brighter future

*Superhard Coating Systems**

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Sponsored by
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and
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DOE VEHICLE TECHNOLOGIES PROGRAM
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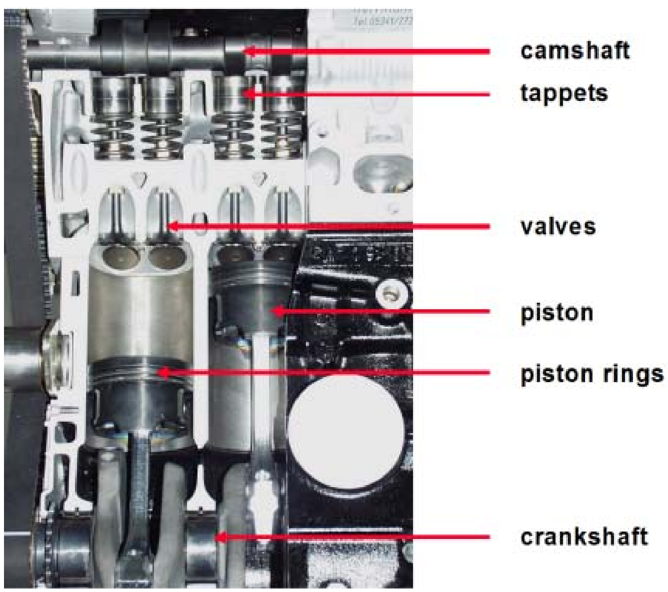
Outline

- Purpose of work
- Address Previous Review Comments (if applicable)
- Barriers
- Approach
- Performance Measures and Accomplishments
- Technology Transfer
- Publications/Patents
- Plans for Next Fiscal Year
- Summary

Purpose of Work

- Design, develop, and implement super-hard and -low-friction coatings to reduce wear and parasitic energy losses in all kinds of engine systems.
  - Demonstrate their friction and wear reducing capabilities under severe tribological conditions.
  - Demonstrate scalability and transfer technology to industry.



Piston pins

- 10-15% of fuel energy is consumed by friction in engines and ancillary components (this amounts to ~1 million barrels/ day in transportation systems alone).
- Reduction of viscosity, S- and P-bearing additives from oils is placing more demands on materials for friction and wear control.

Address Previous Review Comments (From 2006)

- **Recommendation 1:** *Fully understand mechanisms of friction reduction on sliding surfaces. Is it really related to chemical changes on surface?*
  - **We have fully characterized sliding surfaces using multiple surface-sensitive techniques and we now have a much better understanding of the lubrication mechanisms, details are provided later.**
- **Recommendation 2:** *Get a handle on running-in: it is obviously very slow and seems to involve some tribochemistry.*
  - **Running-in behavior was found to be controlled by physical (such as surface roughness) and chemical (coating composition) effects.**
    - ***To control physical effects, we refined grain size/morphology of coatings further and used smoother substrates.***
    - ***To control chemical effects, we optimized Cu content and used different metals as alloying elements.***

Barriers

- ***Predictive Models for Lubricious Coating Design:*** There exist no fundamental design or modeling tools available for the formulation of new coating systems with predictable tribological properties.
  - In this project, a crystal-chemical model has been developed to predict the kinds of coating ingredients that are needed for achieving super-low friction and wear under lubricated sliding conditions.
- ***Reproducibility/Scalability/Manufacturability:*** Large-volume productions of coatings at reasonable costs with a high degree of reproducibility in thickness, uniformity, adhesion, surface finish, chemical composition, etc. are extremely important for long-term performance and durability.
  - We are working very closely with a leading industrial coating manufacturer to address these barriers.
- ***Performance:*** Coatings represent a class of relatively new materials for engine applications and they may not meet the increasingly more stringent performance and durability requirements of future engines and ancillary components.
  - By virtue of their superhardness and very low-friction coefficients, our coatings have the capacity to meet the long-range durability and performance objectives of future engine systems. Recent field test results from fired engines seem to prove this point.

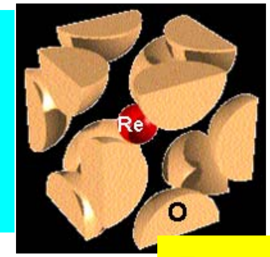
Approach (bottom-up)

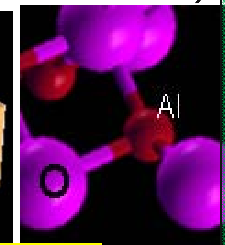
- Use a crystal-chemical model as a predictive tool for the design of next-generation coatings
  - Specifically select right ingredients for coating compositions so that they can react favorably with S, P, Cl-bearing additives in oils to form low-shear boundary films on sliding surfaces.
  - Mo was predicted as the main coating ingredient and Cu, Ag, Sb, and Sn as the secondary ingredients in a nitride-based coating system.
- Demonstrate production/deposition
- Characterize structure and properties
- Verify tribological performance
  - Lab-scale/bench top
- Identify and resolve technical barriers
  - Thickness, uniformity, adhesion, surface roughness, composition
- Perform motored/fired engine tests and demonstrate efficiency/durability
- Scale-up/Technology Transfer

Model

MeX (Me=metal; X=O, S, P, Cl, etc)

Ionic Potential:
φ = Z/r where;
Z is cationic charge and
r is the radius of the cation

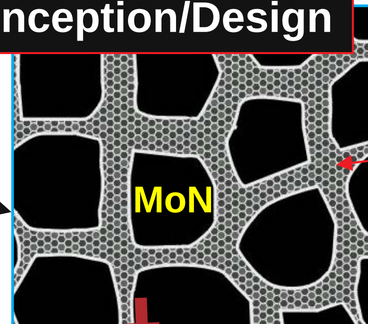




φ = 10.5 Re vs Al φ = 5.4

μ = 0.2 μ = 0.56

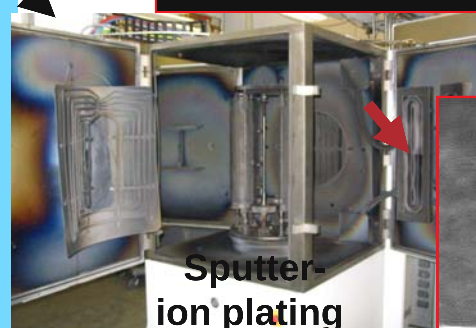
Inception/Design



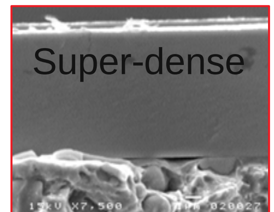
Cu and/or Ag, Sb, Sn

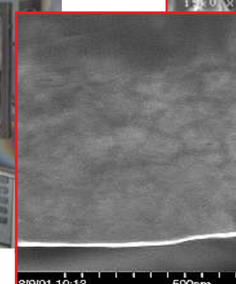
φ_{MoN-Cu} = 8.7

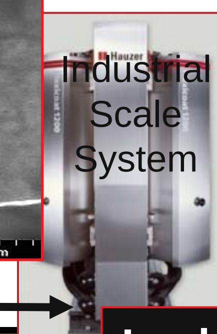
Demonstration/ Realization

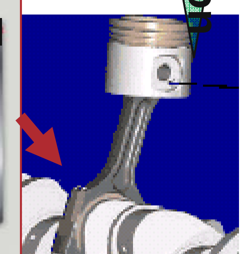


Sputter-ion plating system





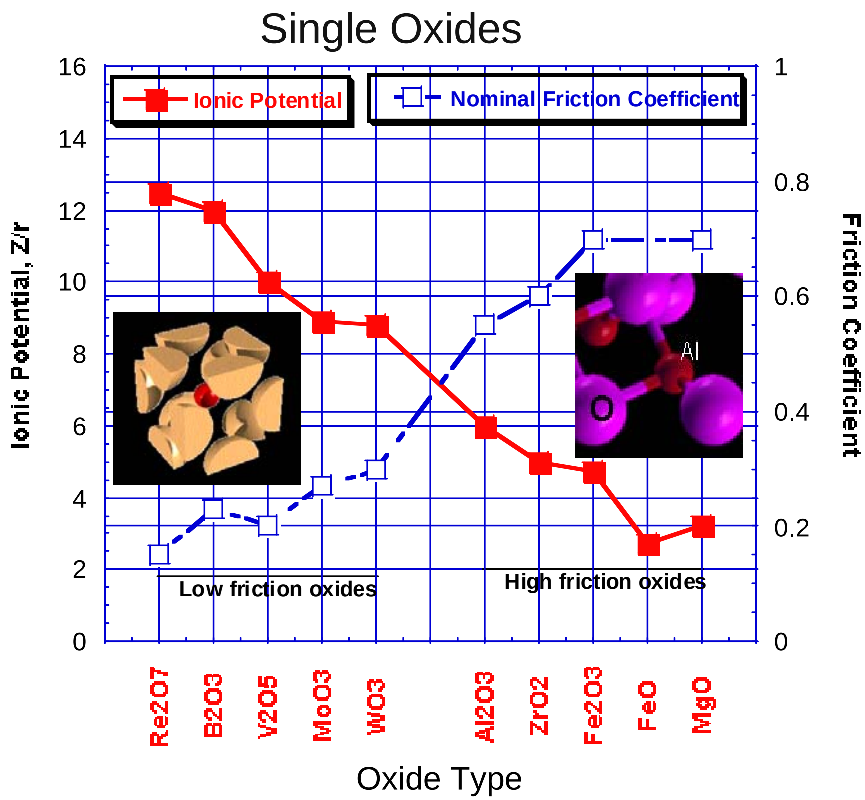




From inception to implementation

Implementation

Approach Cont'd:
Relation of Ionic Potential to Friction (The Case of Oxides)



Binary Oxides

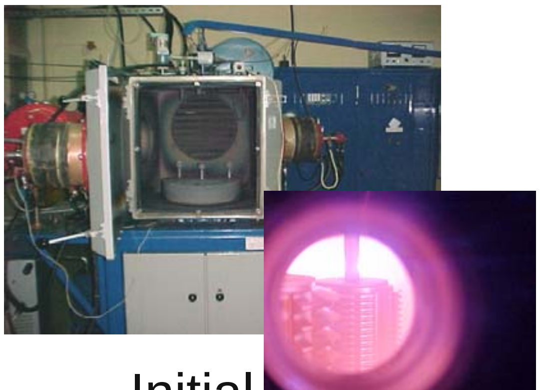
Oxide System	Difference in Ionic Potential, f	Average Friction Coefficients, μ (at elevated temperatures)	Reference
Cs_2O-SiO_2	9.45	0.1	Rosado, et al., 2000
Cs_2O-MoO_3	7.65	0.15	Strong and Zabinski, 2002
Ag_2O-MoO_3	7.43	0.25	Gulbinski, et al., 2003
CuO-MoO_3	6.5	0.3	Wahl, et al., 1997
NiO-Re_2O_7	9.8	0.2	Peterson, et.al. 1994
CuO-V_2O_5	4.75	0.35	Gulbinski, et al., 2003

Erdemir, Surf. Coat. Technol., 200(2005)1792

The higher the ionic potential (or difference in ionic potential in the case of binary oxides), the lower the friction coefficient.

In the case of lubricated systems, sulfides, phosphides, chlorides, etc. may also form.

Demonstrate Production

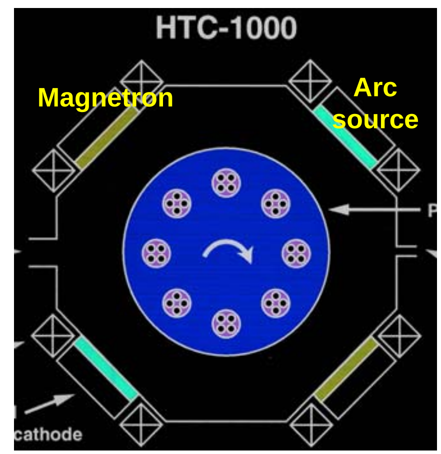


Initial
R&D Scale

Intermediate

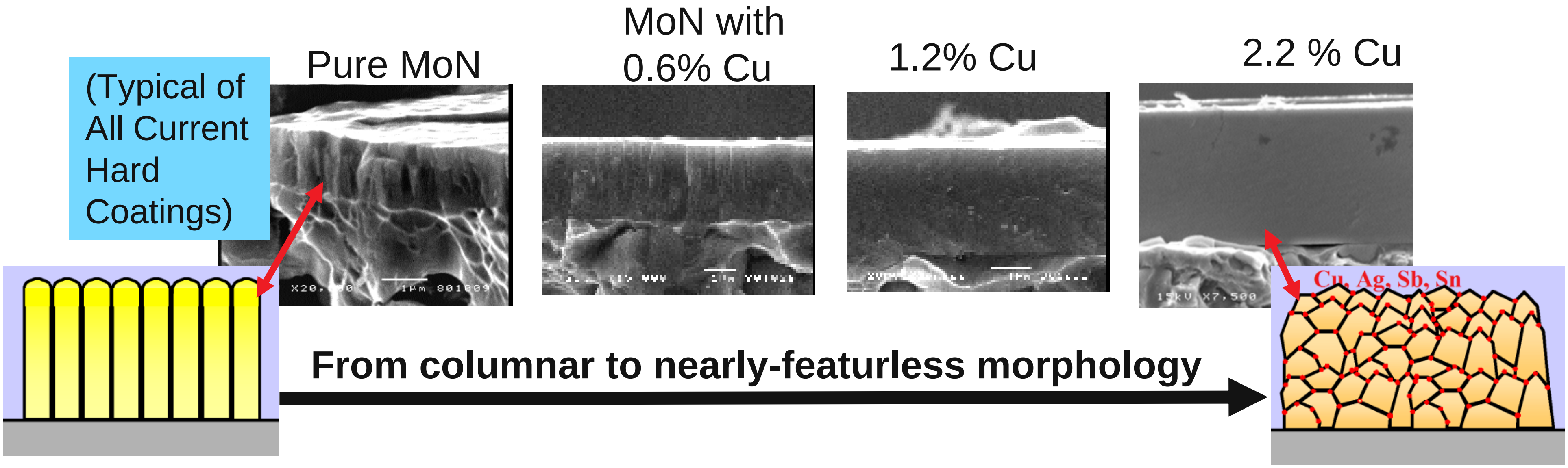
Large/Full Scale

Inside

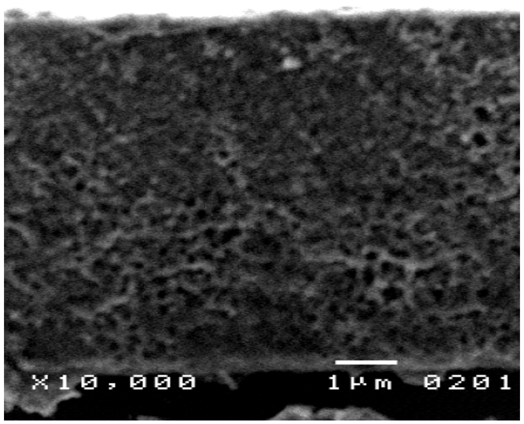


Optimization of deposition process parameters was found to be extremely important for achieving superhardness, toughness, and exceptional friction and wear properties in these designer coatings.

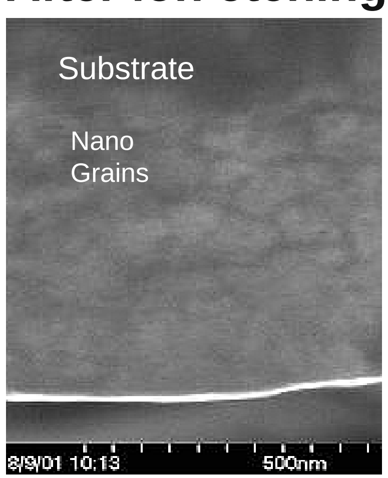
Coating Design, Development, and Characterization



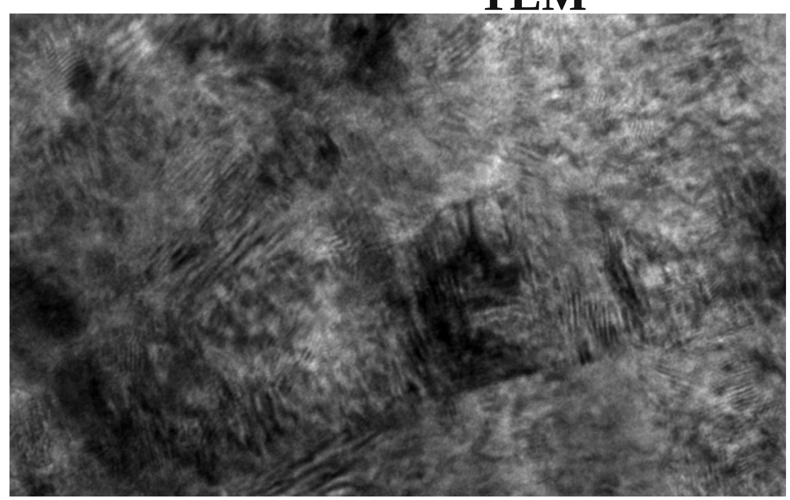
After acid etching



After ion etching

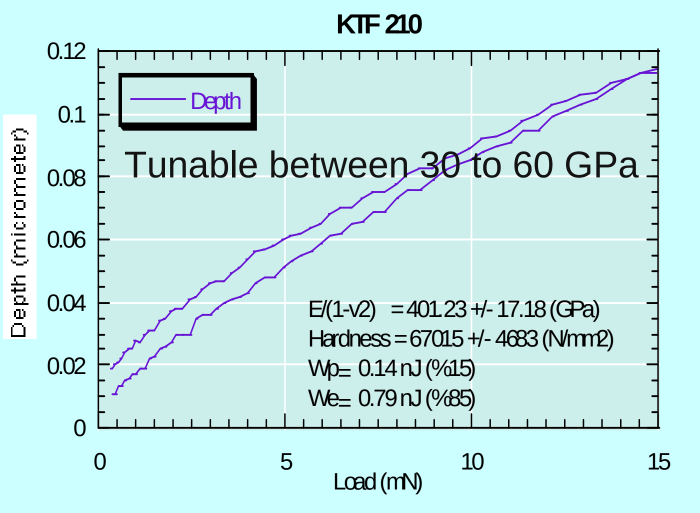


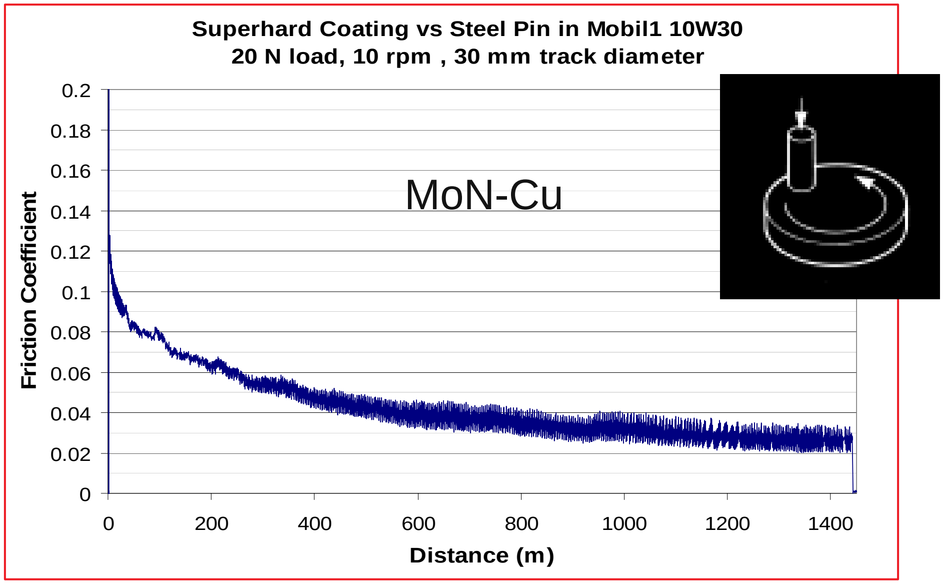
TEM

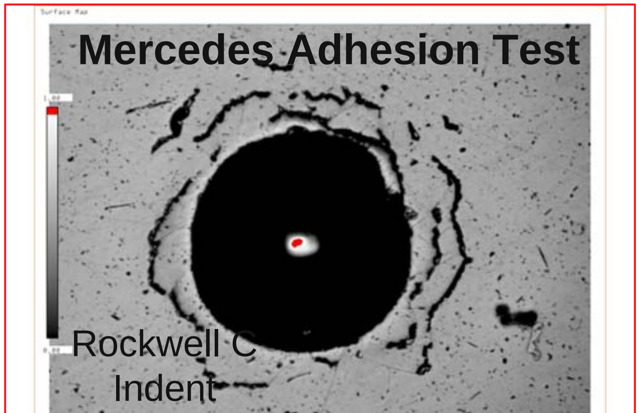


Mechanical/Tribological Characterization

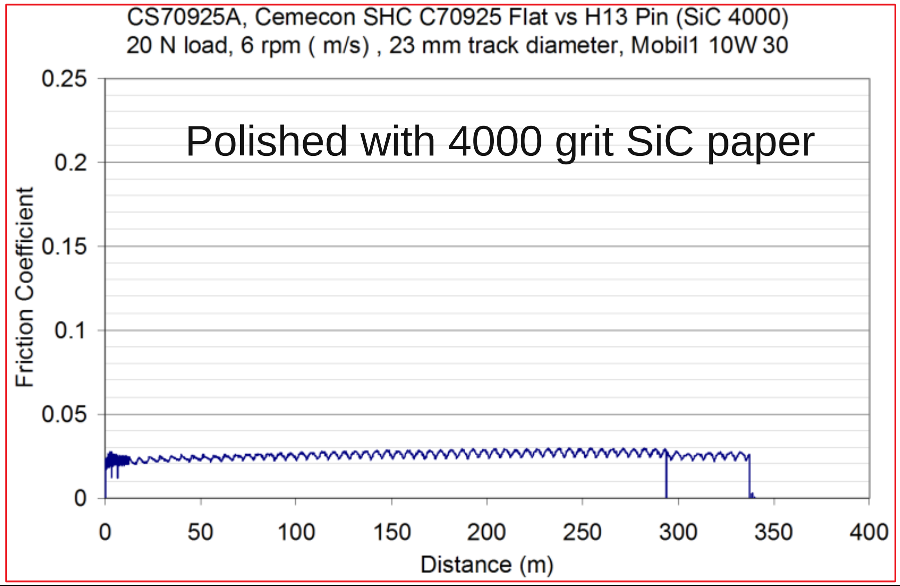
Hardness Behavior



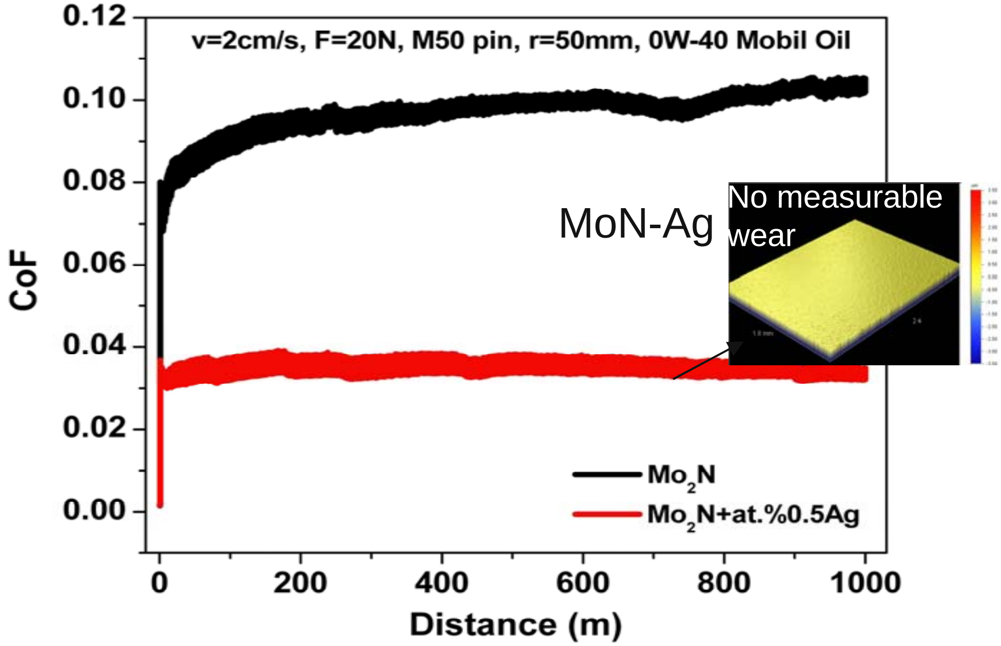


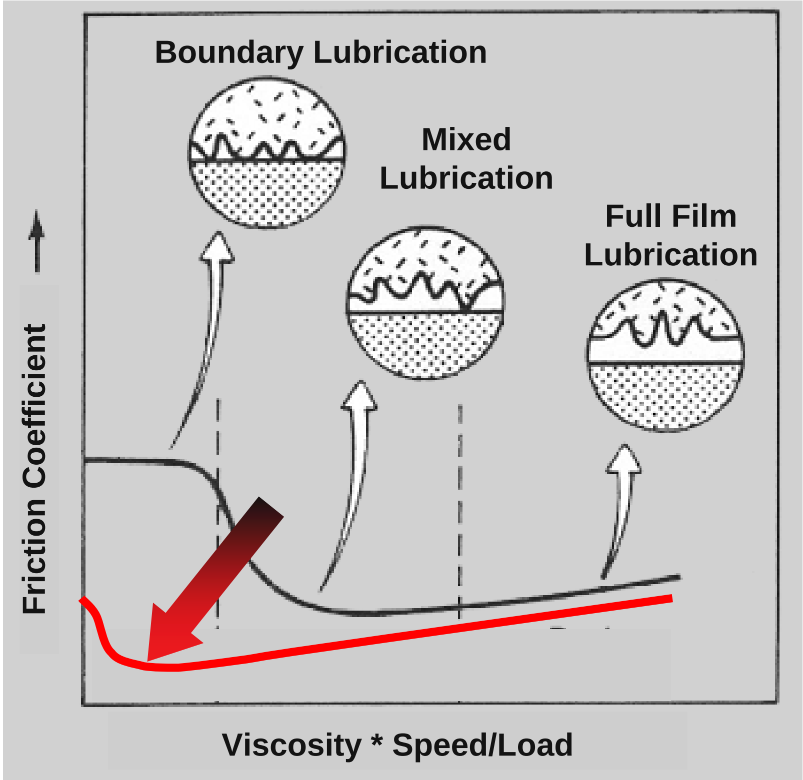


Note that coating fractures, but do not delaminate, "good sign for strong adhesion"



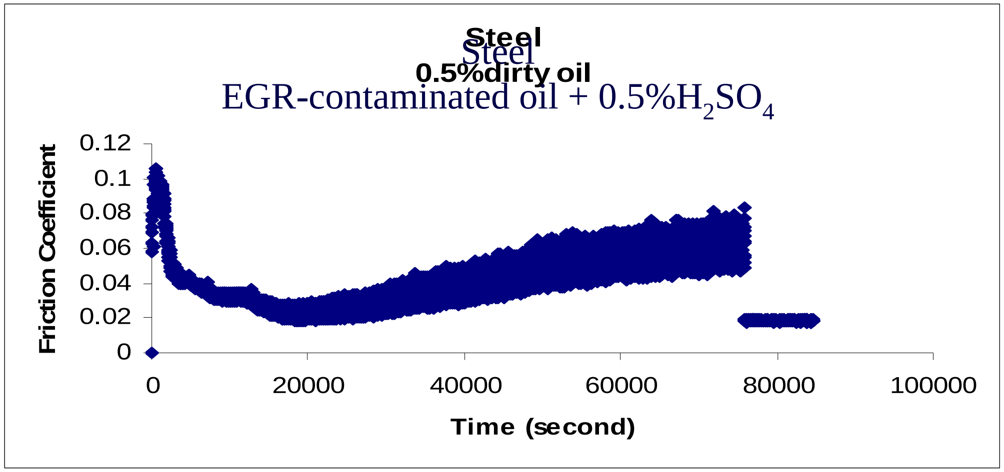
Friction and Wear: Effect of Nano-alloying with Ag, Sb, and Sn

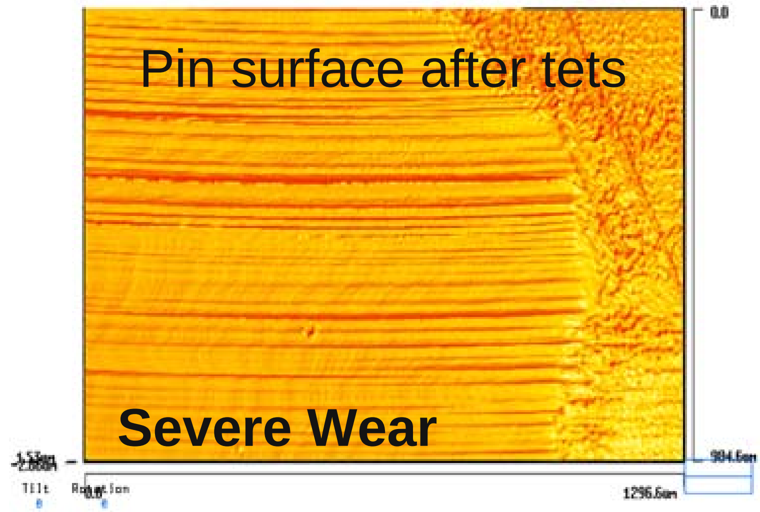


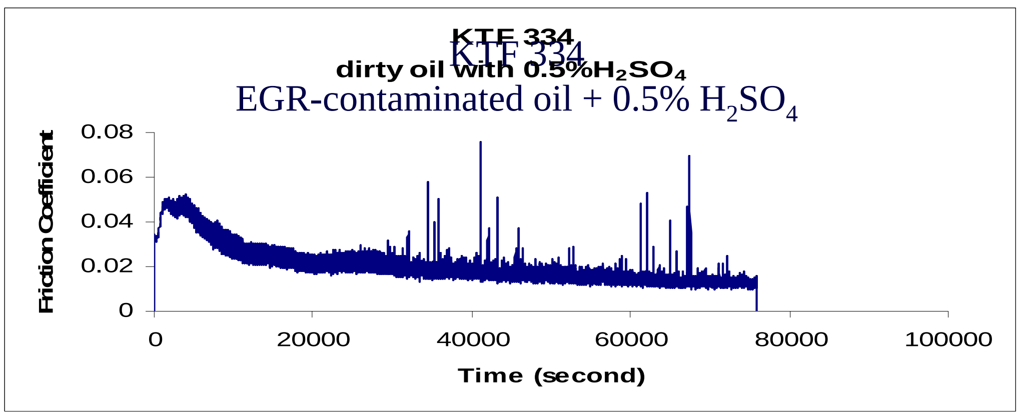


Similar levels of reductions in friction were also achieved with Sb- and Sn-alloyed MoN films under boundary lubricated sliding conditions where much of the parasitic energy losses occur in engines.

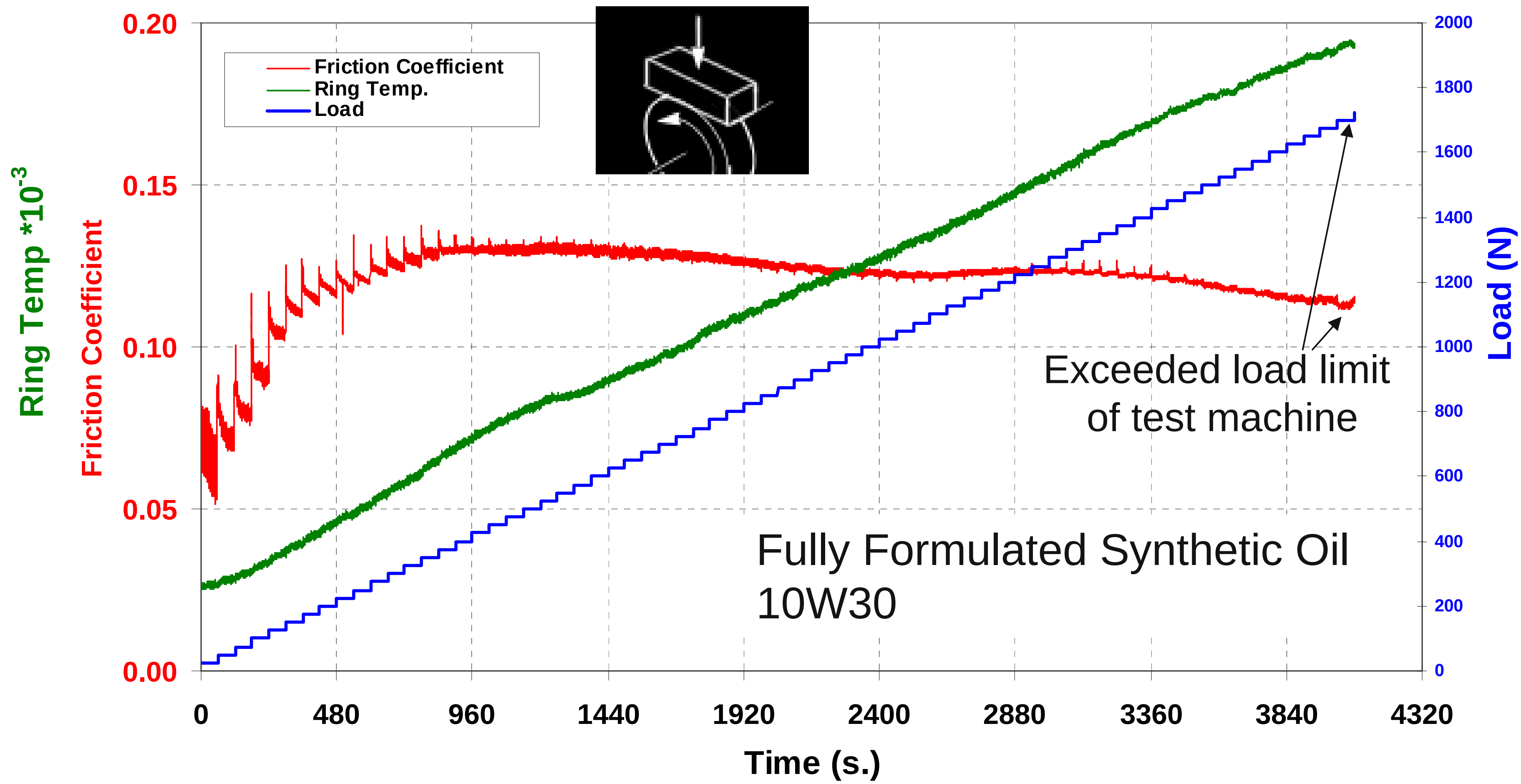
Performance in EGR-contaminated/acidified Oil



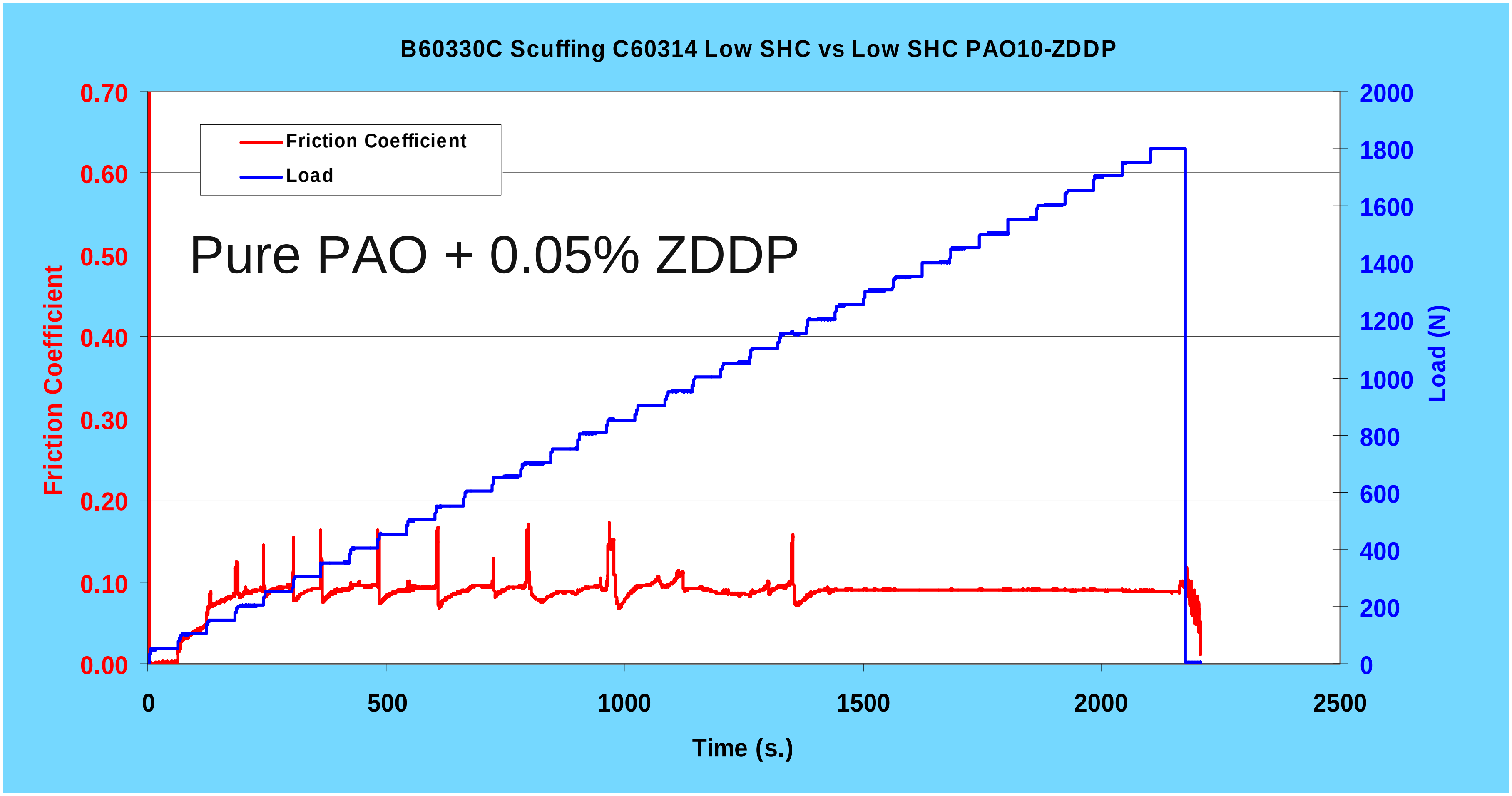




Resistance to Scuffing

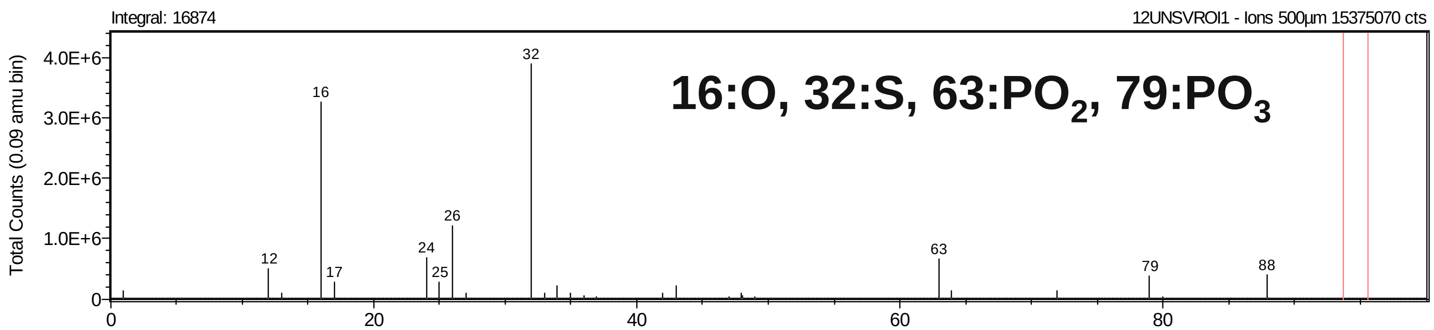


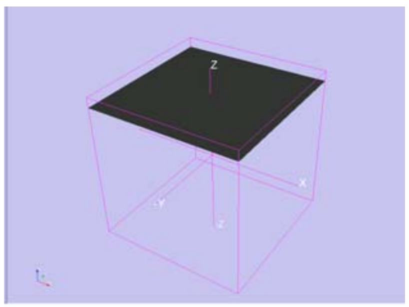
Resistance to Scuffing Cont'd

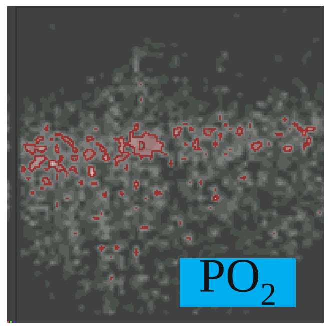


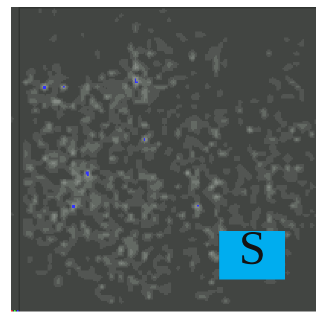
Tribochemical Studies: ToF-SIMS

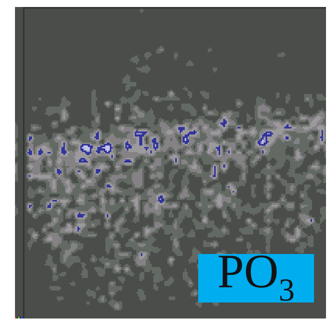
Inside Wear Track



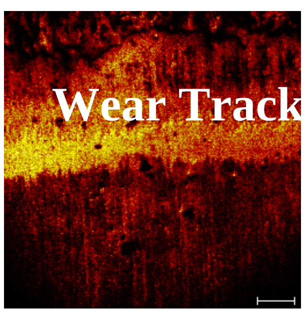




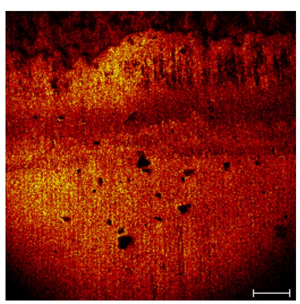




Note that tribochemical or boundary films are extremely thin (5 to 10 nm), hence hard to analyze with more conventional methods.



PO_2



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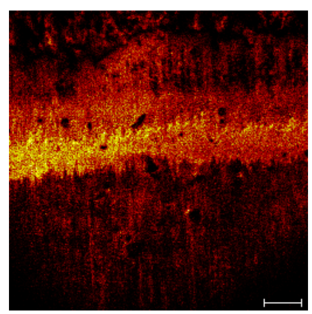
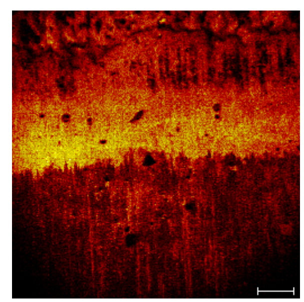


PO_3



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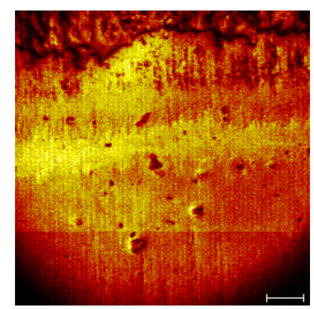
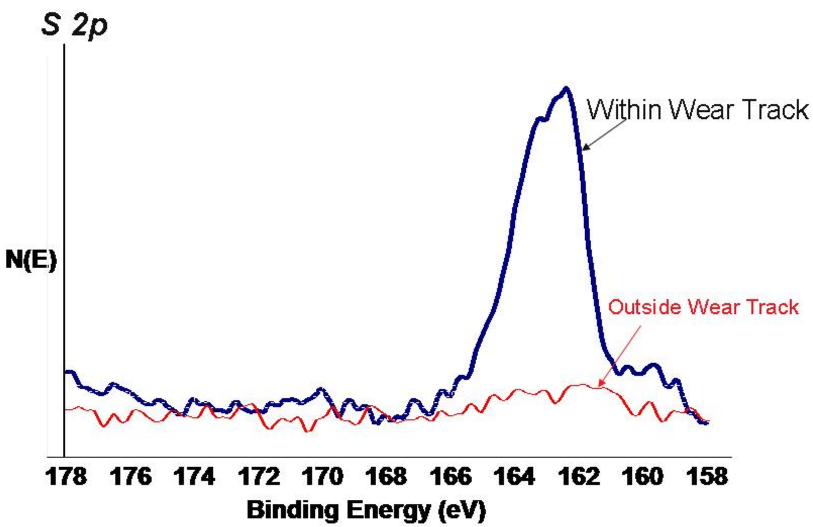
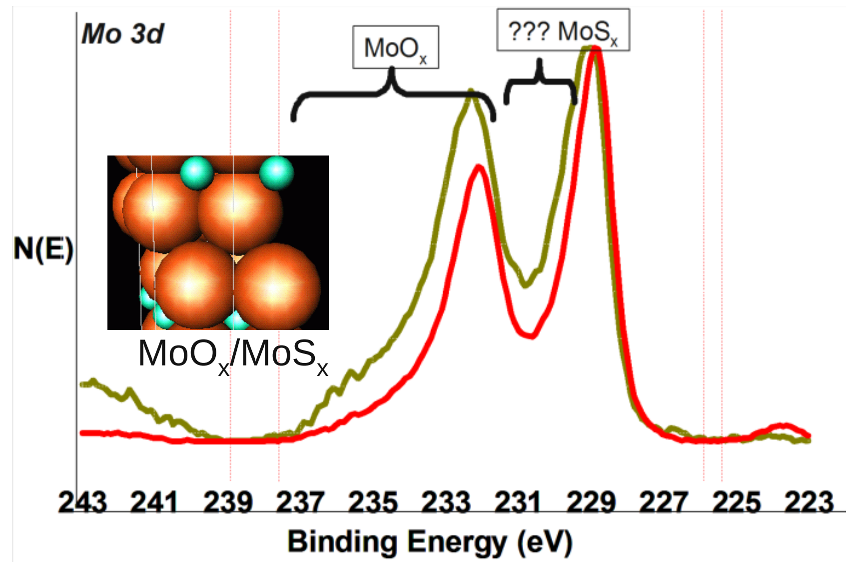
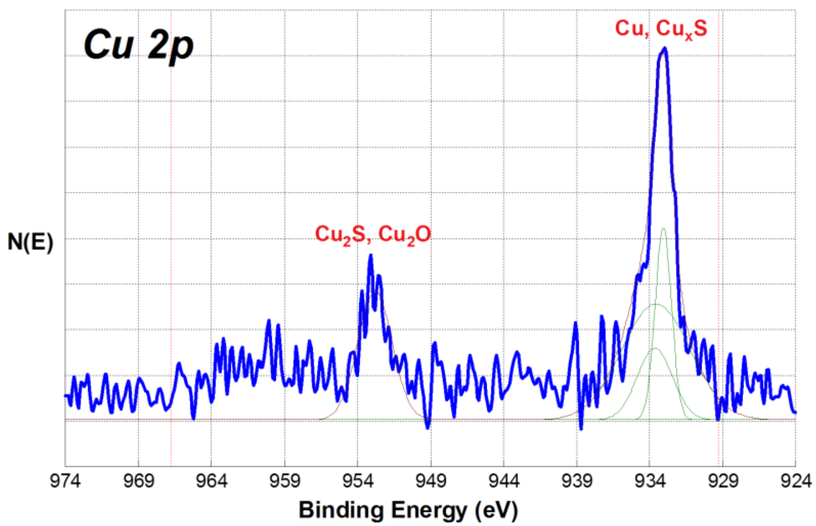


Total Ion

XPS Studies – Lubrication Mechanism



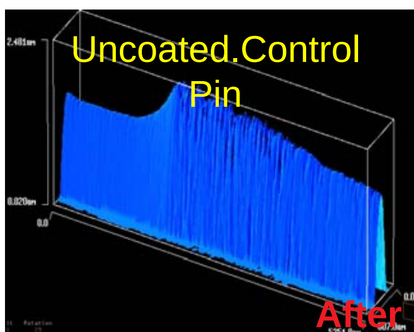


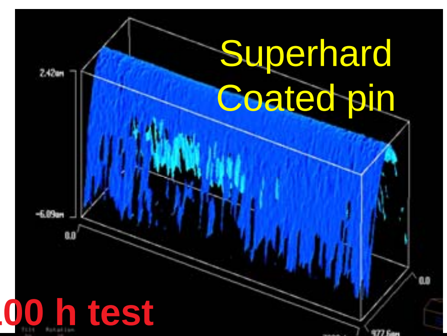


Scale-Up/Tech Transfer

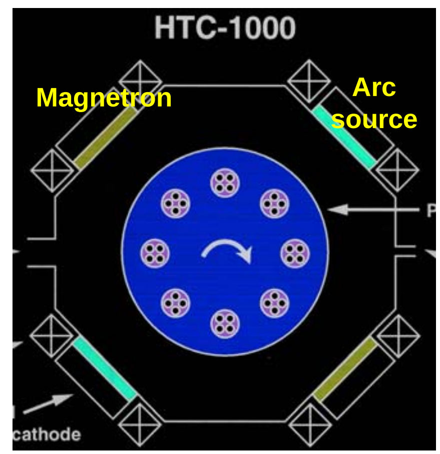
- **Working with a major industrial coating manufacturer to scale-up and offer these coatings to many engine companies including:**
  - **Burgess-Norton (world's largest wrist pin manufacturer)**
  - **Automotive OEMs (Eaton (powertrain/transaxle components), Mahle, Westport).**
  - **Caterpillar, Honda, Hyundai**
  - **Several Racing car teams**
- **Option to license agreement with a company**
  - **Provided additional funds to leverage our DOE-effort**
  - **Will donate a production-scale deposition system to Argonne**

Fired-engine tests
With piston pins



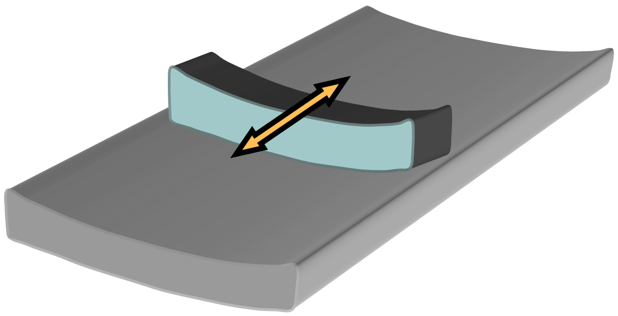


After 100 h test



Future Work:

- Determine long-term friction and wear performance as a function of temperature and in low viscosity engine oils with much-reduced phosphorous and sulfur-levels.
- Demonstrate performance under actual engine conditions (motored/fired).
- Confirm long-term durability
- Concentrate on technology transfer
  - Increase collaboration with industrial partners
  - Demonstrate cost-competitiveness
  - Demonstrate fuel-saving and emission-reducing benefits.
  - We have had several meetings with the representatives of our partner companies in recent months and they are extremely interested in this technology.







Types of engine components that we are working on at present

Publications & Patents/Inventions

- Books:
  - "Superlubricity", A. Erdemir and J. M. Martin (Editors), Elsevier, Amsterdam, 2007.
  - "Tribology of Diamondlike Carbon Films: Fundamentals and Applications," C. Donnet and A. Erdemir (Editors), Springer, 2008.
- Patents/Inventions
  - "US Patent # 7211323: Hard And Low Friction Nitride Coatings and the Methods For Forming the Same"
  - "Modulated Composite Coating Surfaces," Pending.
- Technical Papers:
  - A.Öztürk, K. V. Ezirmik, K. Kazmanlı and M. Ürgen, O. L. Eryilmaz, and A. Erdemir, Comparative Tribological Behaviors of TiN-, CrN- and MoN-Cu Nanocomposite Coatings, Tribology International, 41(2008)49-59.
  - V. Ezirmik, E. Senel, K. Kazmanli, A. Erdemir, and M. Ürgen" Effect of Copper Addition on the Temperature Dependent Reciprocating Wear Behaviour of CrN Coatings",, Surface and Coatings Technology, 202(2007)866-870.
  - P. Basnyat, B. Luster, Z. Kertzman, S. Stadler, S.M. Aouadi, J. Xu, S.R. Mishra, O. L. Eryilmaz, A. Erdemir "Mechanical and Tribological Properties of CrAlN-Ag Self-Lubricating Films," Surface and Coatings Technology, 202(2007)1011.
  - A. Erdemir, O. L. Eryilmaz, M. Urgen, and K. Kazmanli, "Development of Multi-functional Nano-composite Coatings for Advanced Automotive Applications," Plenary Paper, 16th International Colloquium on Tribology, Stuttgart, Germany, January 12-14, 2008.
  - A. Erdemir,O. L. Eryilmaz, and O. O. Ajayi, "Superhard Coatings," *2007 Annual Progress Report, Automotive Propulsion Materials,* U.S. Department of Energy, Washington, D.C., 2008.
  - A. Erdemir, "Design of Novel Nanocomposite Coatings for Extreme Tribological Applications," Keynote paper, European Conference on Tribology, Ljubljana, Slovenia, June 11-15, 2007
  - A. Erdemir, O. L. Eryilmaz., M. Urgen, K. Kazmanli, "Lubricant-Friendly MoN-Cu Coatings for Extreme Tribological Applications", AVS 54th International Symposium and Exhibition, October 14-19 2007, Seattle, WA., USA.
  - O. L. Erylimaz, A. Erdemir, O. O. Ajayi, K. Kazmanli, O.Keles, and M. Urgen,"Superhard and EGR-resistant Coatings for Advanced Diesel Engine Applications," International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 23-27, 2007.
  - A. Erdemir, O. L. Eryilmaz., M. Urgen, K. Kazmanli"A Surface Analytical Study of the Effects of Anti-Friction And Anti-Wear Additives on Oil Lubricated Tribological Behavior of MoN-Cu Nanocomposite Films", Annual Meeting of the Society of Tribologists and Lubrication Engineers, Philadelphia, PA, May 6-10, 2007.

Summary

- Superhard coating systems developed in this project have high potentials for further reducing friction and wear in engine systems and thus improving their fuel economy and durability (2 to 4% improvement in fuel economy seems feasible and will amount to 200,000 to 400,000 barrels less oil being imported per day).
- These coatings are also extremely resistant to scuffing, hence are very ideal for extreme tribological applications involving severe loading, EGR-contaminated oil environments, and starved lubrication conditions.
- Crystal chemical model eliminated guesswork and was very important for the identification of those coating ingredients which resulted in such impressive tribological properties.
- Fundamental surface analytical studies with ToF-SIMS and XPS revealed the lubrication mechanisms of superhard coatings under such extreme tribological conditions.
- FY08 effort will concentrate on:
  - Long-term durability tests
  - Engine/component tests
  - Scale-up, cost analysis, and commercialization activities