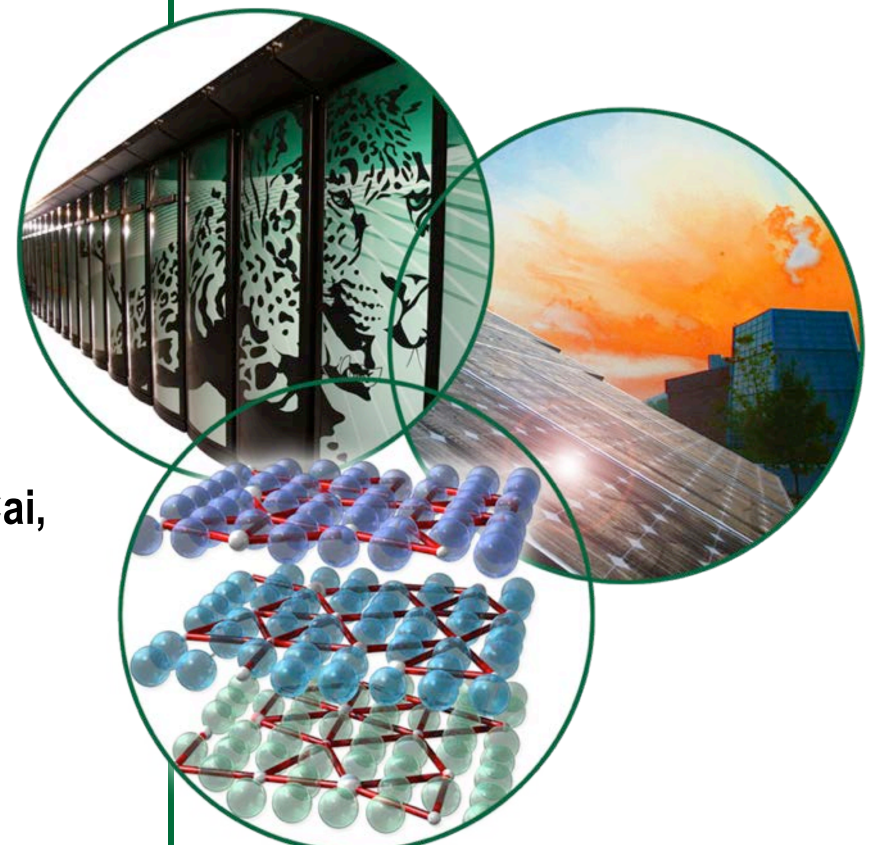
Can hard coatings and lubricant anti-wear additives work together?

Project ID: FT021



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DOE Management Team:

Steve Goguen, Kevin Stork and Steve Przesmitzki

2014 DOE Vehicle Technologies Program Annual Merit Review, June 19, 2014

Overview

Timeline

- Project start date: Oct. 1, 2012
- Project direction and continuation are evaluated annually

Budget

- FY13 DOE funding: $250K
- FY14 DOE funding: $250K

Partners

- Lubrizol
- Cytec Industries
- Northeast Coating Technologies
- Eaton
- ANL

Barriers

- 10-15% energy generated in an IC engine is lost to parasitic friction.
- Current engine lubricants and their additive packages were designed for ferrous alloy bearing surfaces.
- Compatibility between oil anti-wear additives and non-metallic hard coatings is little known.
- Fundamental understandings gained in this study will help guide future development of engine lubricants.
- A synergistic lubricant-coating combination will provide maximized benefits in fuel economy.

Relevance

- **Objective: Investigate the compatibility of engine lubricant anti-wear (AW) additives, specifically conventional ZDDP and newly developed ionic liquids, with selected hard coatings.**
- **Potential benefits:**
  - **Fundamental understandings gained in this study will help guide future development of engine lubricants**
  - **A synergistic lubricant-coating combination will provide maximized benefits in fuel economy.**

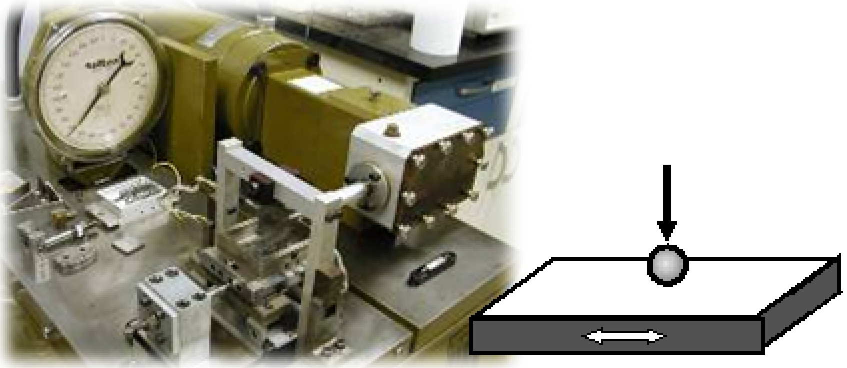
Milestones

- **Demonstrate the lubricant-coating compatibility via tribological testing and analysis at room temperature (June 30, 2013) – complete!**
- **Reveal the tribo-chemical interactions for selected lubricant-coating combinations at room temperature (September 30, 2013) – complete!**
- **Tribological testing and analysis of the AW-coating compatibility at 100 ^{o}C (June 30, 2014) – on schedule**
- **Understand the tribochemical interactions of candidate lubricant-coating combinations at 100 ^{o}C (September 30, 2014) – on schedule**

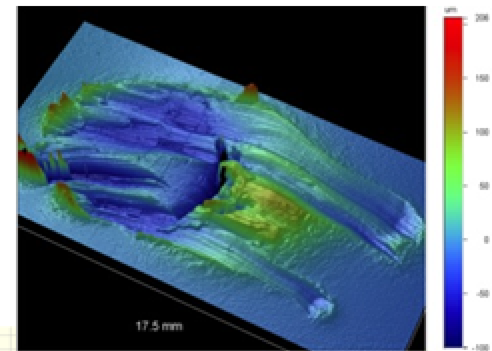
Approach

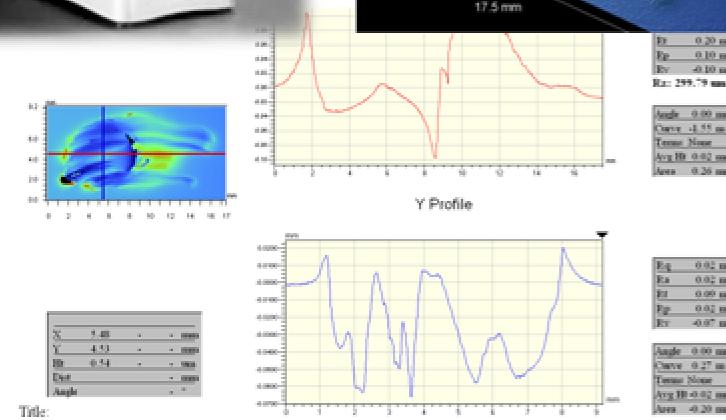
- **Experimentally study the friction and wear behavior for selected non-metallic hard coatings lubricated by selected anti-wear additives via tribological bench testing in well-defined conditions.**
  - **Anti-wear additives: ZDDP and ionic liquid**
  - **Hard coatings: Borides and DLC**
  - **Counterface material: AISI 52100 steel**
- **Mechanistically investigate the tribochemical interactions between the anti-wear additives and the coating surfaces via comprehensive tribofilm characterization.**
  - **Top surface examination:**
    - **SEM: worn surface morphology for wear mode analysis**
    - **EDS: element analysis**
  - **Tribofilm layered chemical analysis aided by ion sputtering:**
    - **XPS: composition-depth profile and binding energy spectrum**
    - **Auger: surface element mapping**
  - **Tribofilm cross-sectional examination aided by focused-ion-beam (FIB):**
    - **TEM: nanostructure and tribofilm thickness measurement**
    - **Electron diffraction: phase determination**
    - **EDS: element mapping**

Tribological testing and wear quantification



- **Boundary lubrication ball-on-flat reciprocating sliding test**
  - Plint TE-77 tribometer
  - Ball: AISI 52100 steel (10 mm dia)
  - Flat: coatings
  - Ave. sliding speed: 0.2 m/s
  - Load: 50 N
  - Sliding distance: 1000 m
  - Ambient environment



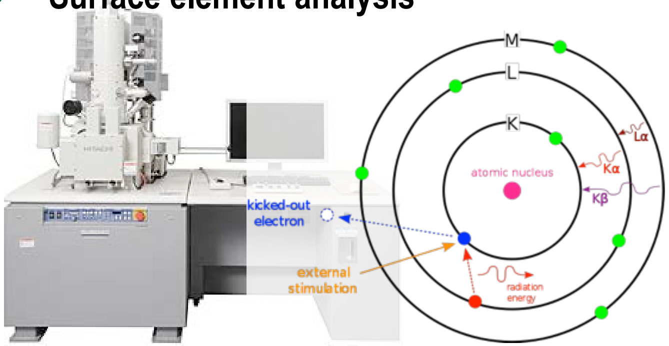


- **Wear quantification**
  - Wyko NT9100 optical profiler
  - Wear volume/depth
  - Roughness

Comprehensive tribofilm characterization

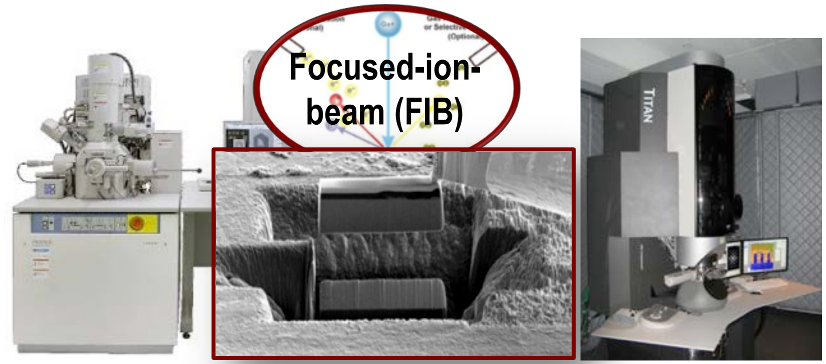
Scanning electron microscopy (SEM)/Energy-dispersive X-ray spectroscopy (EDS)

- ✓ Worn surface morphology
- ✓ Surface element analysis



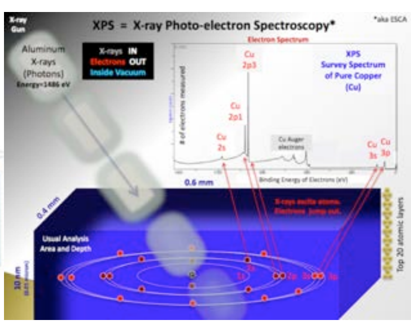
Transmission electron microscopy (TEM)/Electron Diffraction/EDS

- ✓ Tribofilm nanostructure and thickness
- ✓ Cross-sectional element mapping



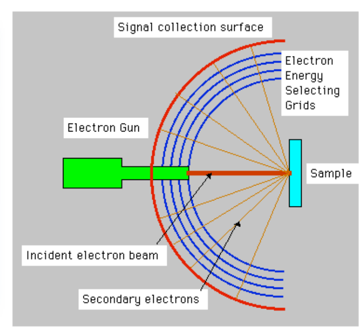
X-ray photoelectron spectroscopy (XPS):

- ✓ Composition-depth profile B
- ✓ Binding energy spectrum



Auger electron spectroscopy (AES):

- ✓ Surface element mapping (better spatial resolution than XPS)



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Technical accomplishments – summary

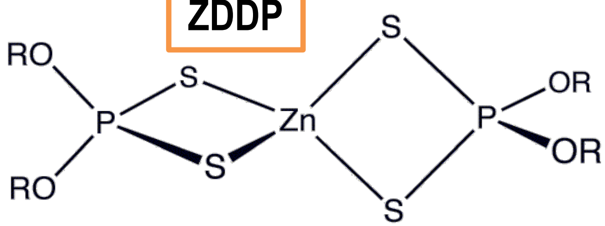
- The mechanism for the ZDDP (and ionic liquid) tribofilm formation on non-metallic coatings has been revealed: ZDDP/IL reacting with metallic wear debris and the new compounds are compressed onto the non-metallic surface.
  - This could be a significant part of the tribofilm formation on a metallic surface as well, in addition to the well-received process of ZDDP/IL directly reacting with the metallic surface.
- The ZDDP and IL formed tribofilms on both boride and DLC coatings with various surface coverage and thicknesses.
- Tribofilms on coatings are composed of reaction products of metal oxides, sulfites (ZDDP only), metal phosphates, and metallic iron (wear debris).
- Tribofilms on boride coatings cover the surface by 80-95% and are up to 60-70 nm thick.
- Tribofilms on DLC have low surface coverage (20-30%) and are <25 nm thick, probably due to poor bonding between tribochemical products and DLC.
- Surprisingly increased wear was observed on the counterface when using the ZDDP (or IL) together with the DLC coating.
  - The IL showed better protection for the steel counterface than the ZDDP though.

Selected lubricant anti-wear additives

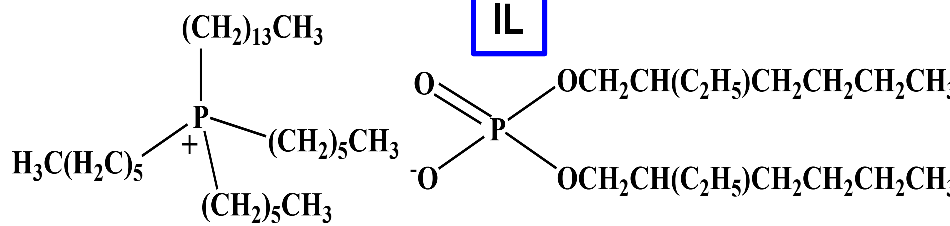
- Conventional secondary ZDDP (Lubrizol)
- New oil-miscible ionic liquid $[P_{66614}][DEHP]$ (ORNL)

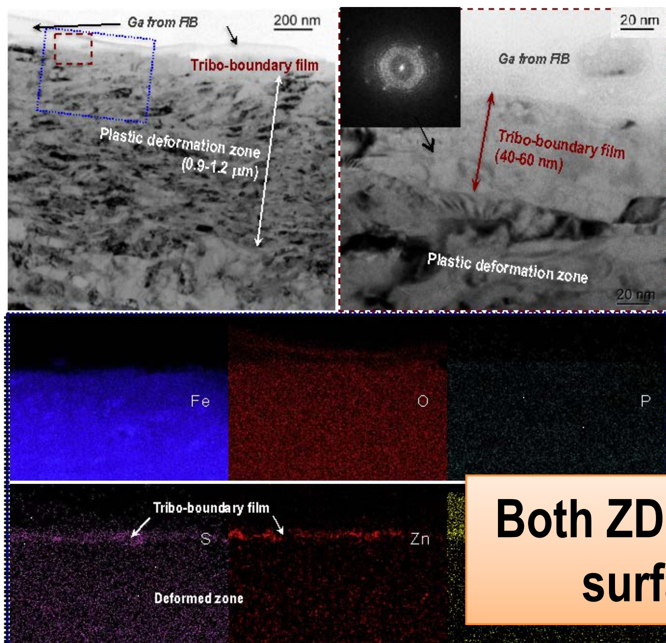
1 wt% AW treat rate in SAE 0W-30 base oil

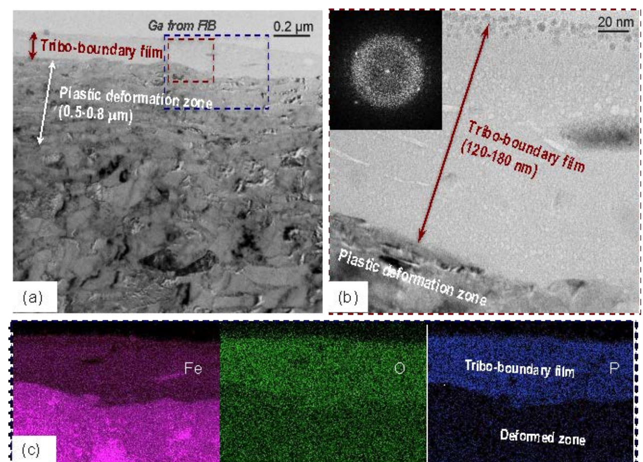
ZDDP



IL



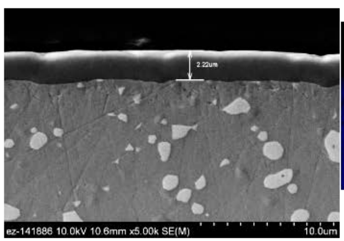




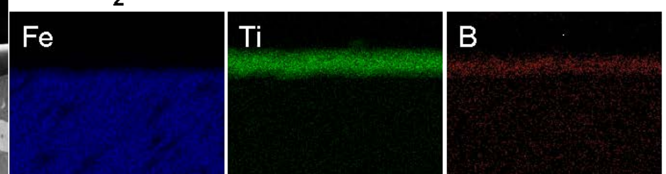
Both ZDDP and IL form anti-wear tribofilms on metallic surfaces, but will they work on hard coatings?

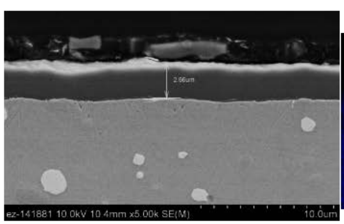
Selected hard coatings

Coating	Composition	Substrate	Process	Thick-ness (μm)	Hardness HK (GPa)	Roughness R_a (μm)	Supplier
TiB_2	TiB_2	M2 steel	PVD	2.5	21.2	0.16	Eaton
$AlMgB_{14}$-TiB_2	$AlMgB_{14}$ +50 vol% TiB_2	M2 steel	PVD	3.0	29.1	0.16	Eaton
DLC	a-C:H	M2 steel	PVD	3.5	18.7	0.16	HEF/NCT

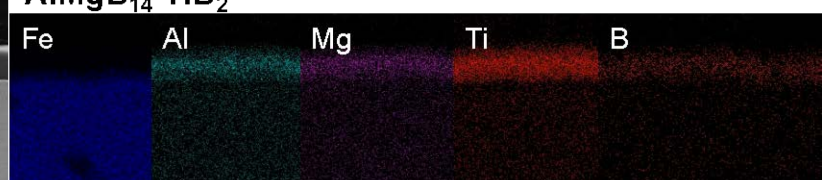


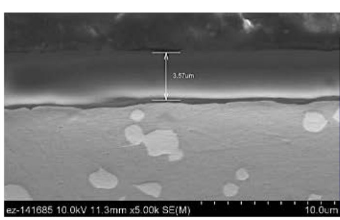
TiB_2



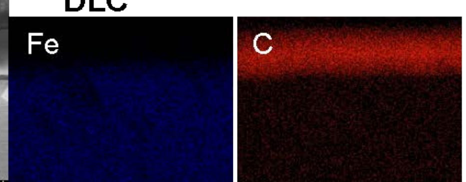


$AlMgB_{14}$-TiB_2





DLC



All three coatings possess high hardness and wear-resistance, but will they work with ZDDP or ionic liquid?

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Friction and wear results

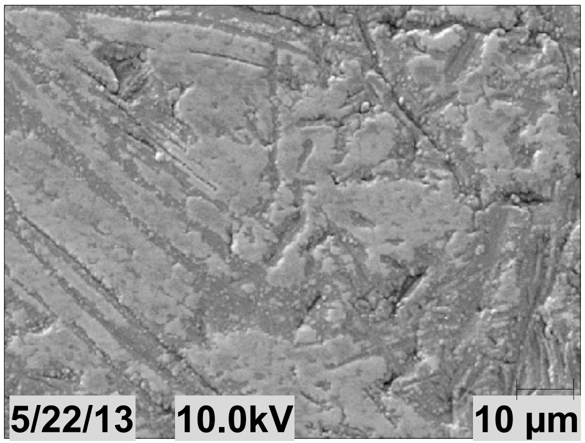
- Boride coatings generated a lightly lower friction coefficient than the DLC in both lubricants
- Similar friction coefficient between the two AW additives
- No measurable wear on coatings.
- The IL-additized oil generated lower ball (counterface) wear than the ZDDP-additized oil for all three coatings – suggesting that the IL protects the steel ball better than the ZDDP.

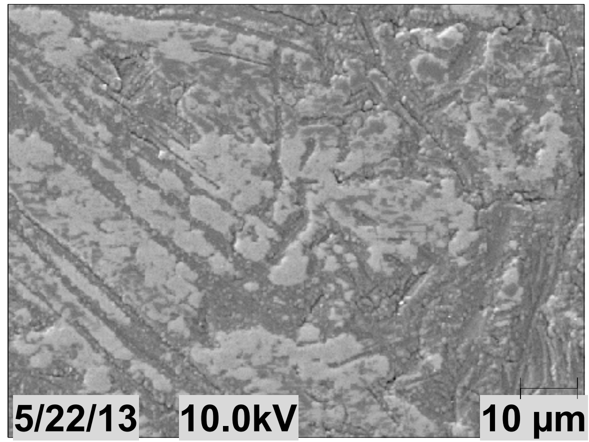
	Wear of coating		Wear rate of steel ball ($\times 10^{-8}$ mm^3/N-m)		Steady-state average friction coefficient	
	Oil+ 1%ZDDP	Oil+ 1%IL	**Oil+ 1%ZDDP**	**Oil+ 1%IL**	**Oil+ 1%ZDDP**	**Oil+ 1%IL**
TiB_2	*Not measurable*		**7.2**	**1.3**	**0.11**	**0.11**
$AlMgB_{14}$-TiB_2	*Not measurable*		**7.0**	**3.4**	**0.11**	**0.11**
DLC	*Not measurable*		**5.3**	**2.4**	**0.12**	**0.12**

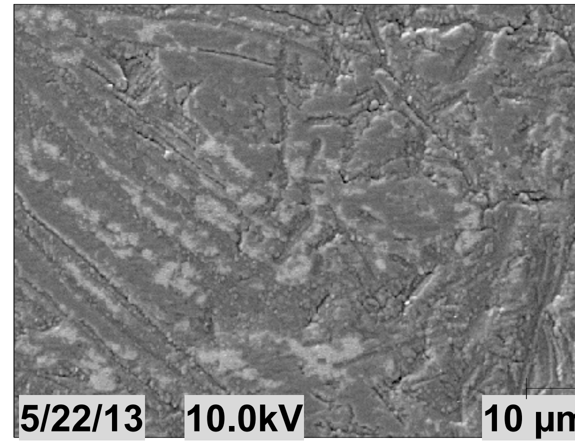
ZDDP-lubricated $AlMgB_{14}$-TiB_2 – SEM imaging and AES elemental mapping detected a tribofilm

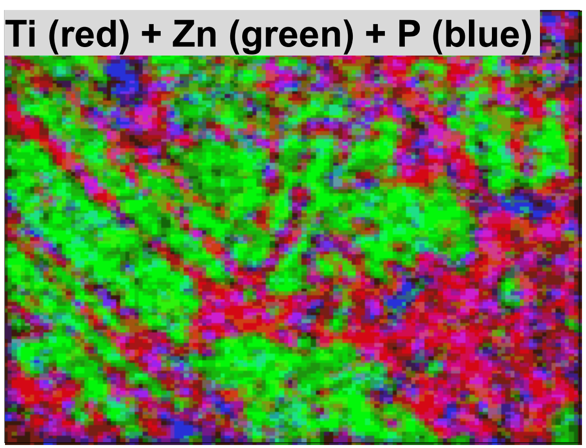
After 30 sec ion sputtering

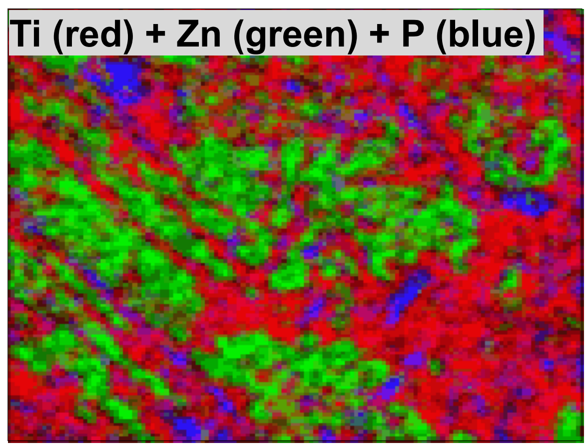
After 2 min ion sputtering

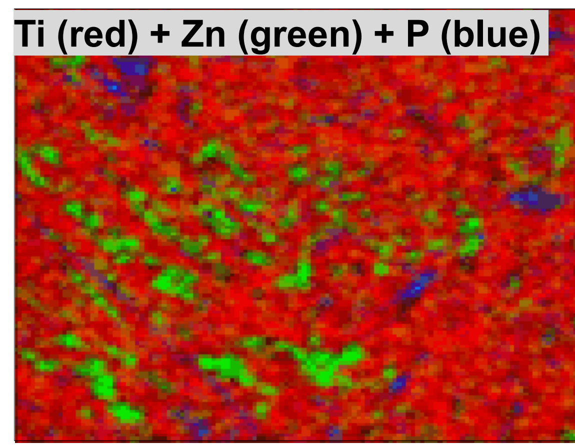






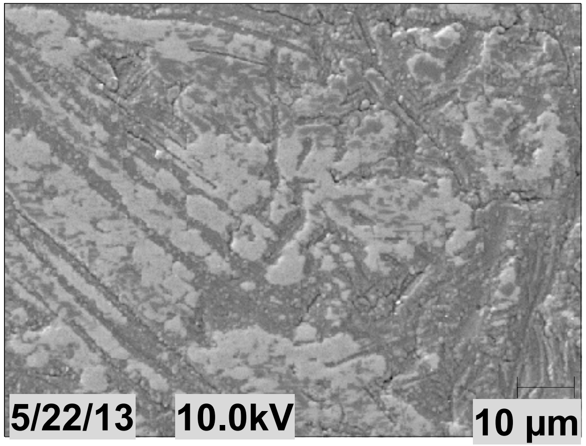




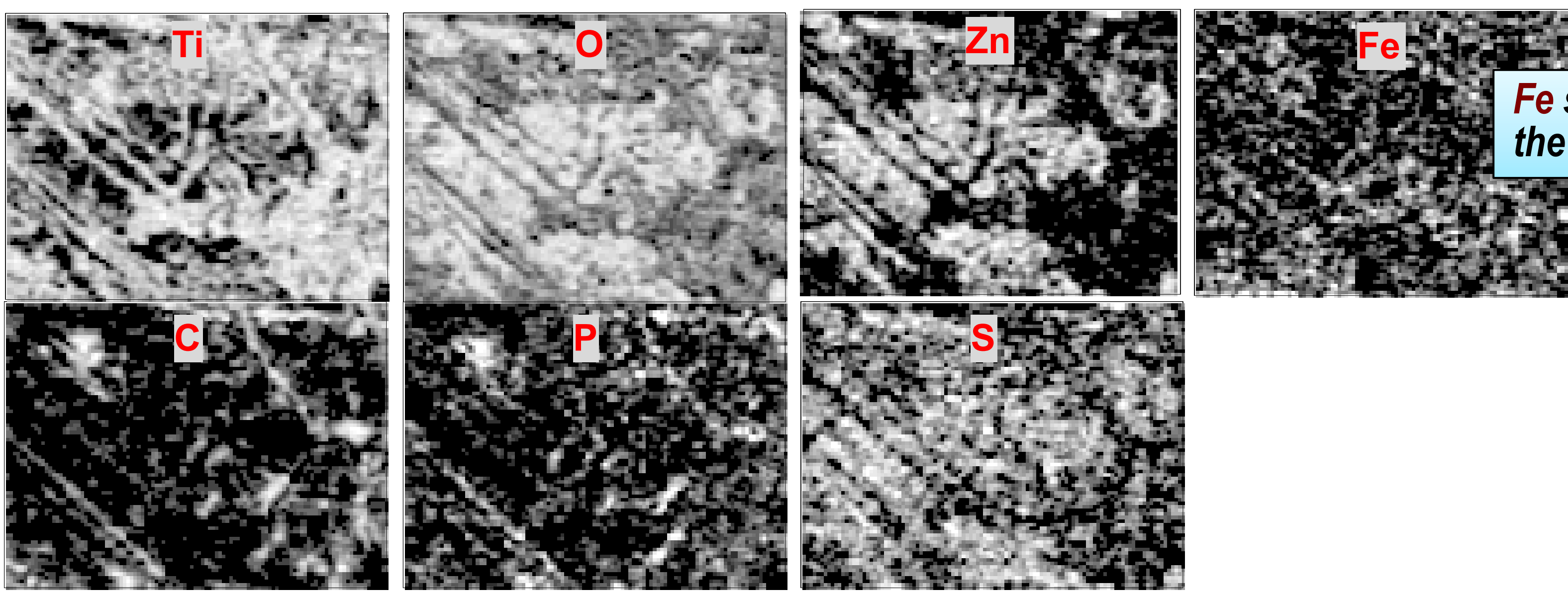


ZDDP-lubricated $AlMgB_{14}$-TiB_2 – AES elemental mapping hinted tribofilm composition

After 30 sec ion sputtering

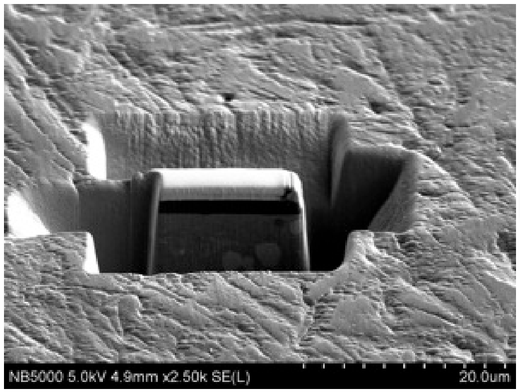


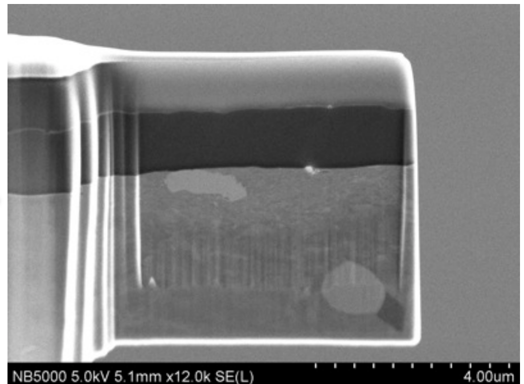
- Zn-O, Zn-S, Fe-S matching maps → zinc oxide, zinc sulfite, and iron oxide(s)
- Fe-P-C-O → maps suggest iron phosphates (inorganic and organic)



Fe supplied by the the steel ball

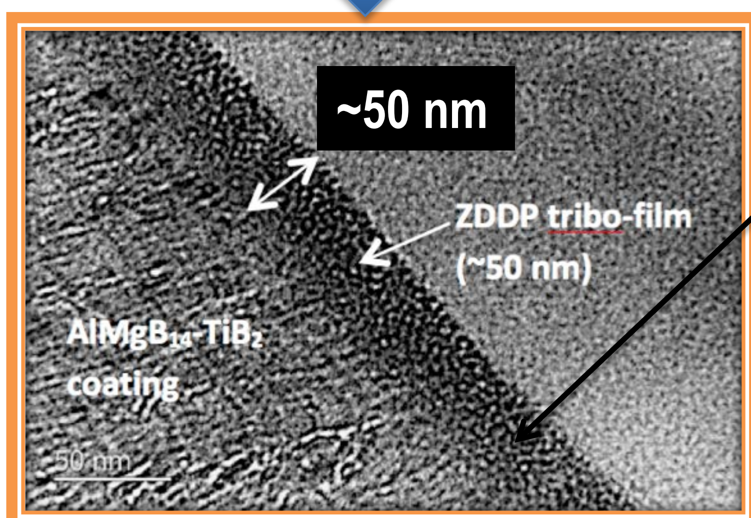
ZDDP-lubricated $AlMgB_{14}$-TiB_2 – TEM cross-sectional imaging revealed the tribofilm ~50 nm thick and dominated by amorphous phases

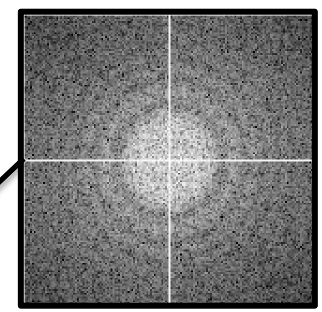




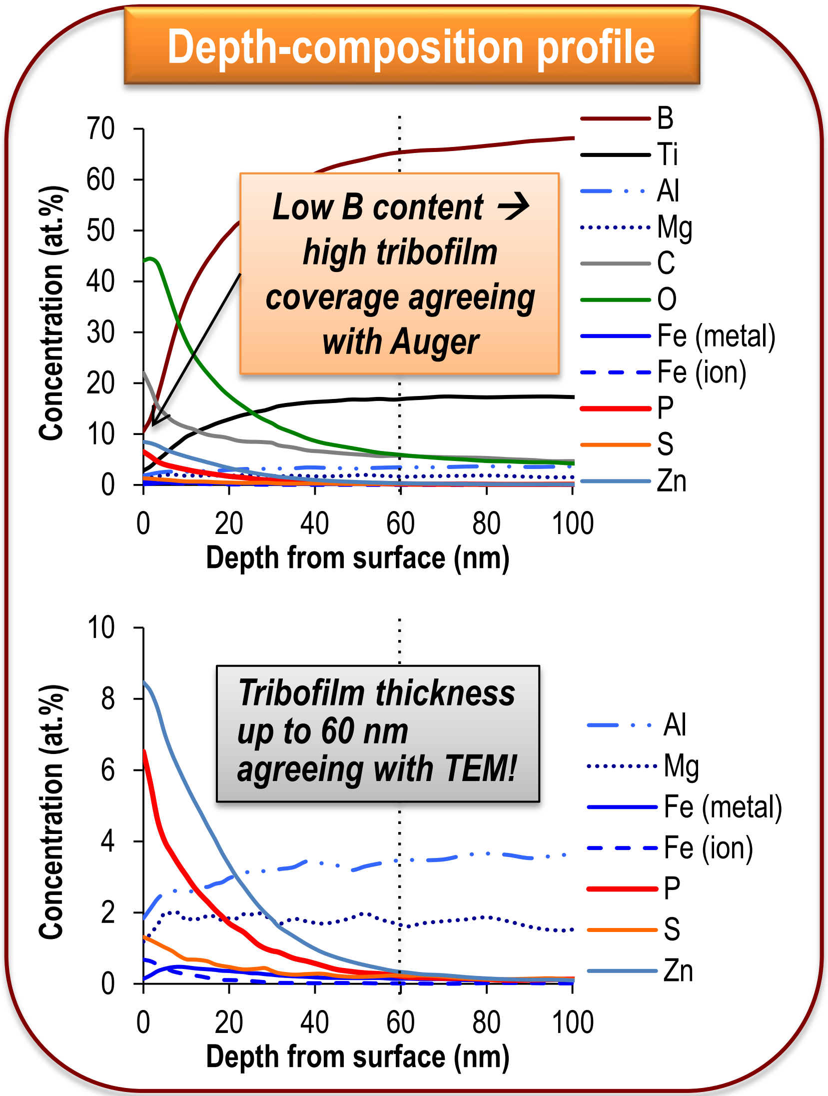
FIB sample extraction

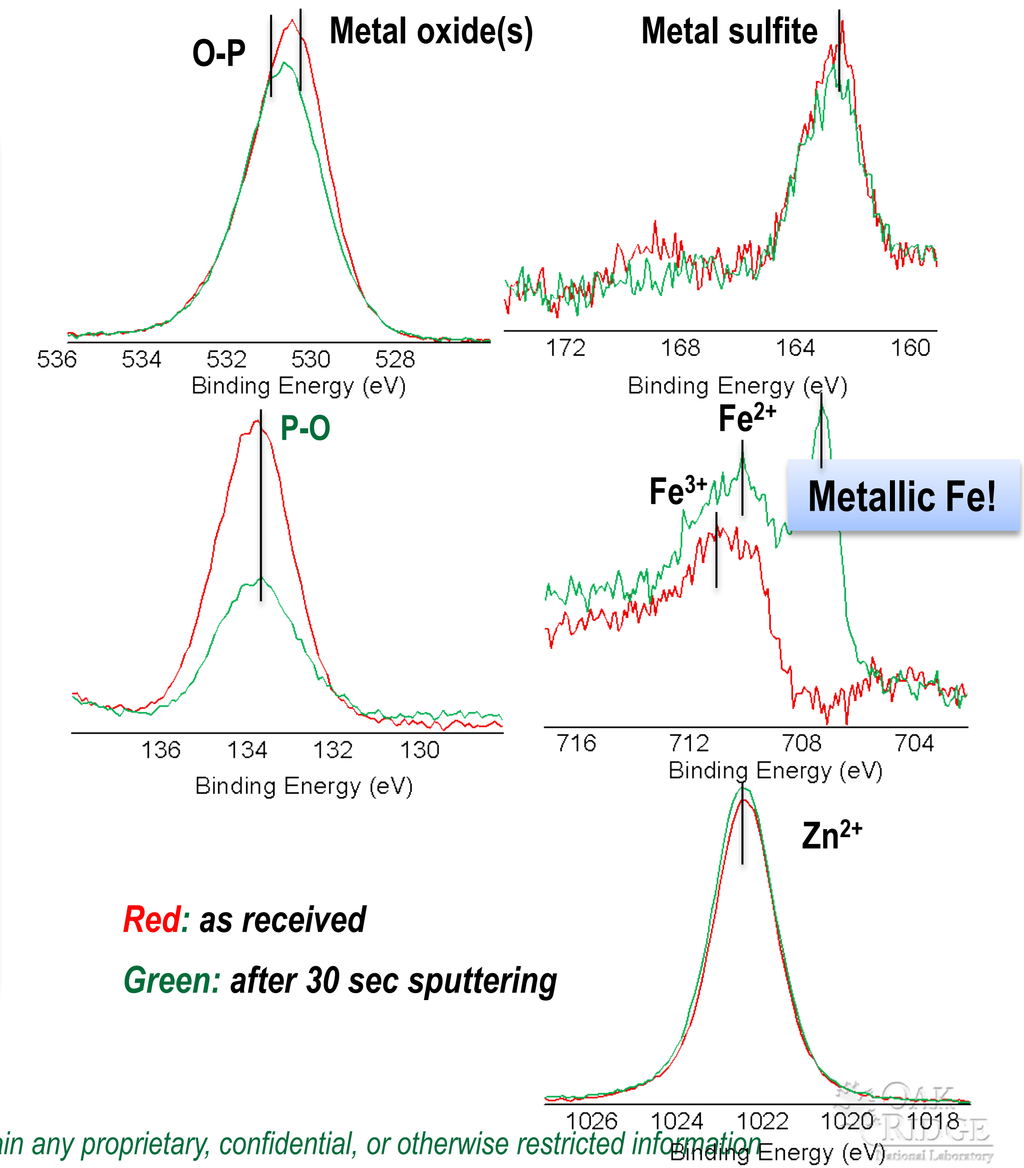
TEM image





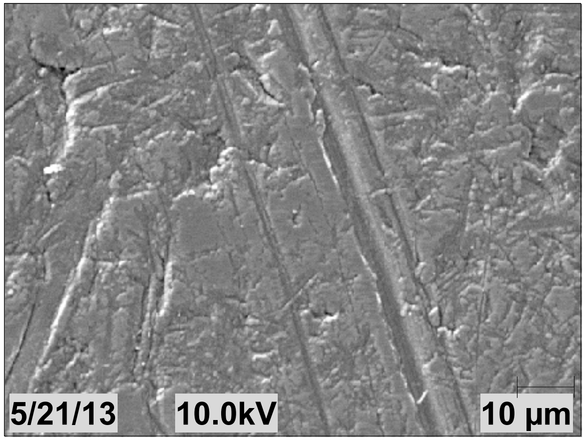
ZDDP-lubricated $AlMgB_{14}$-TiB_2 – XPS analysis provided further info of the tribofilm composition

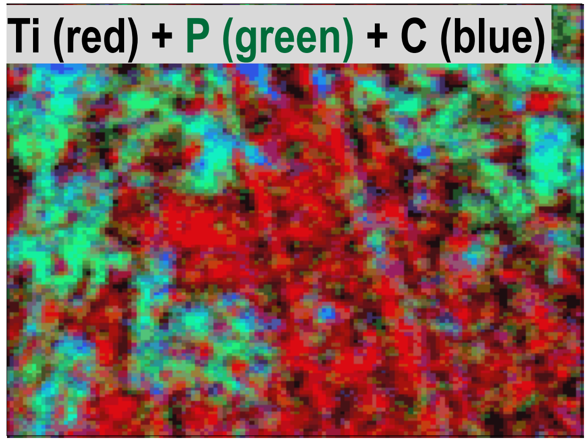


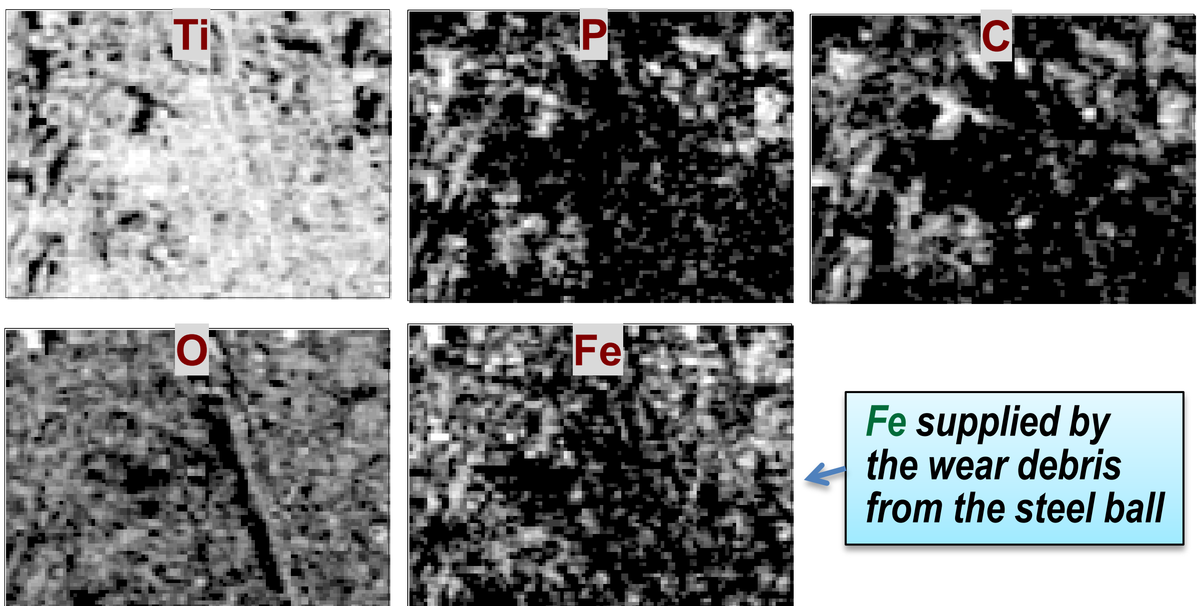


IL-lubricated AlMgB$_{14}$-TiB$_2$ – Auger elemental mapping suggested possible tribofilm composition

After 30 sec ion sputtering





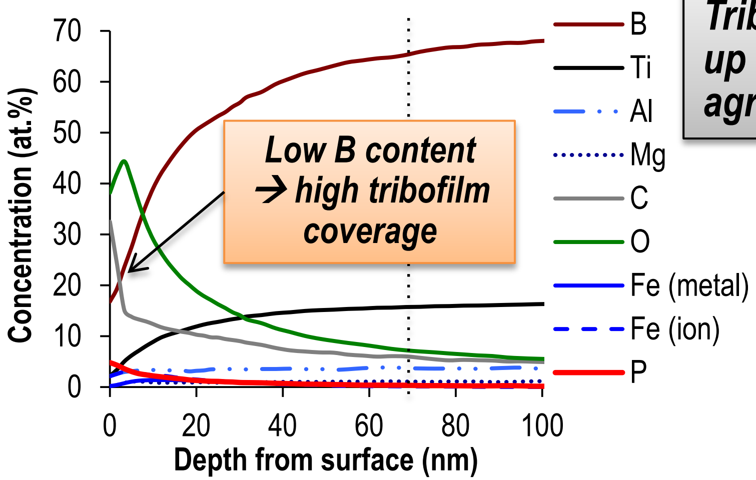


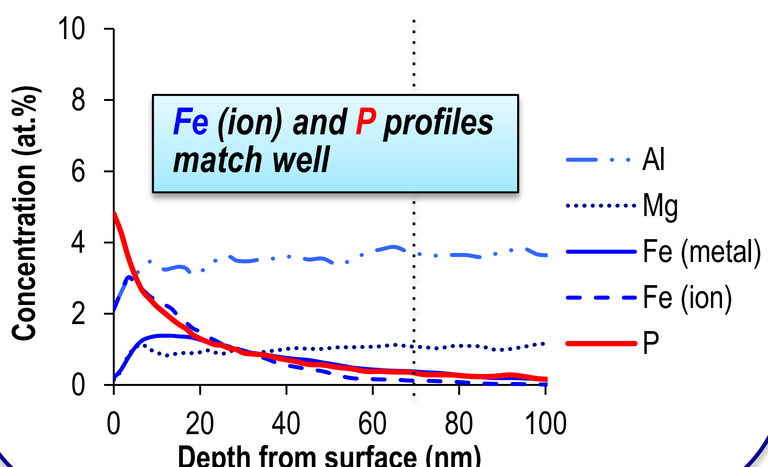
Fe supplied by the wear debris from the steel ball

- No AW self-reacted compounds like ZDDP
- All compounds are results of reactions between the IL and wear debris from the steel ball!
- Fe-P-C-O and Fe-O matching maps → iron phosphates (inorganic and organic) and iron oxides
- P-C matching maps → majority of C from non-fully decomposed organophosphate anions

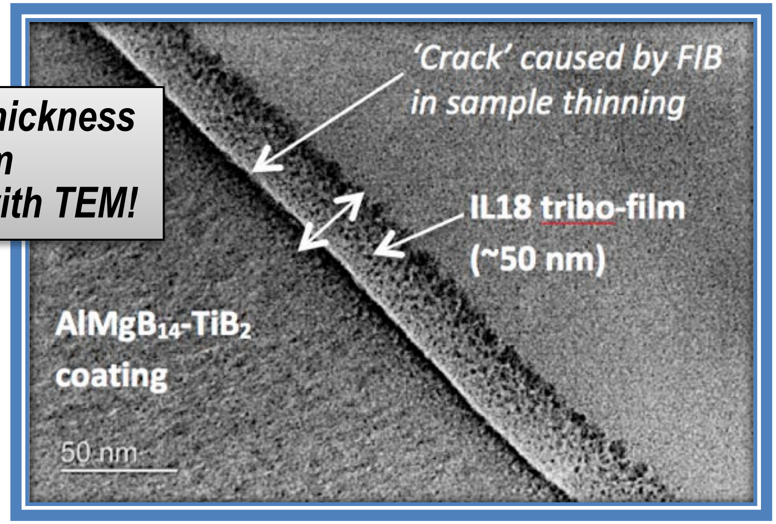
IL-lubricated $AlMgB_{14}$-TiB_2 – TEM cross-sectional imaging and XPS analysis of the tribofilm

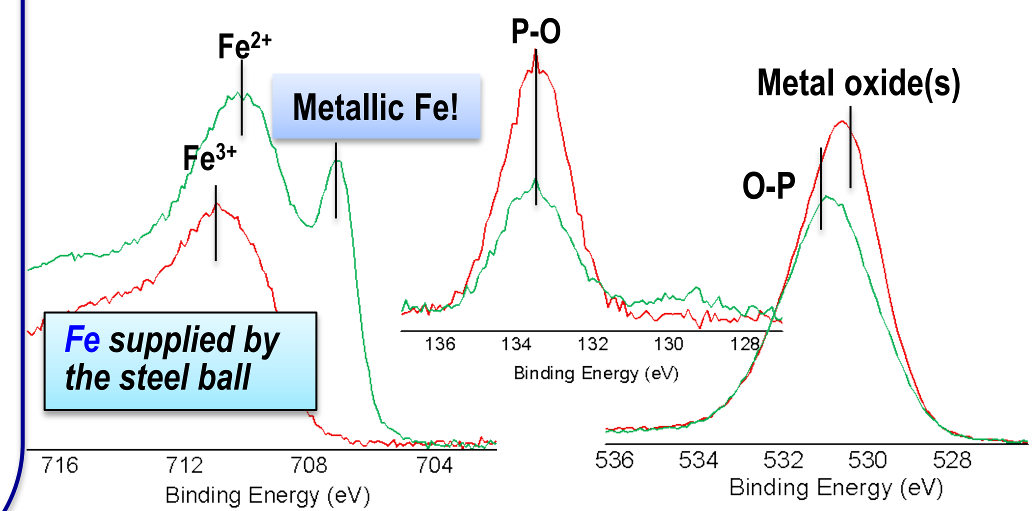
Depth-composition profile





Tribofilm thickness up to 70 nm agreeing with TEM!

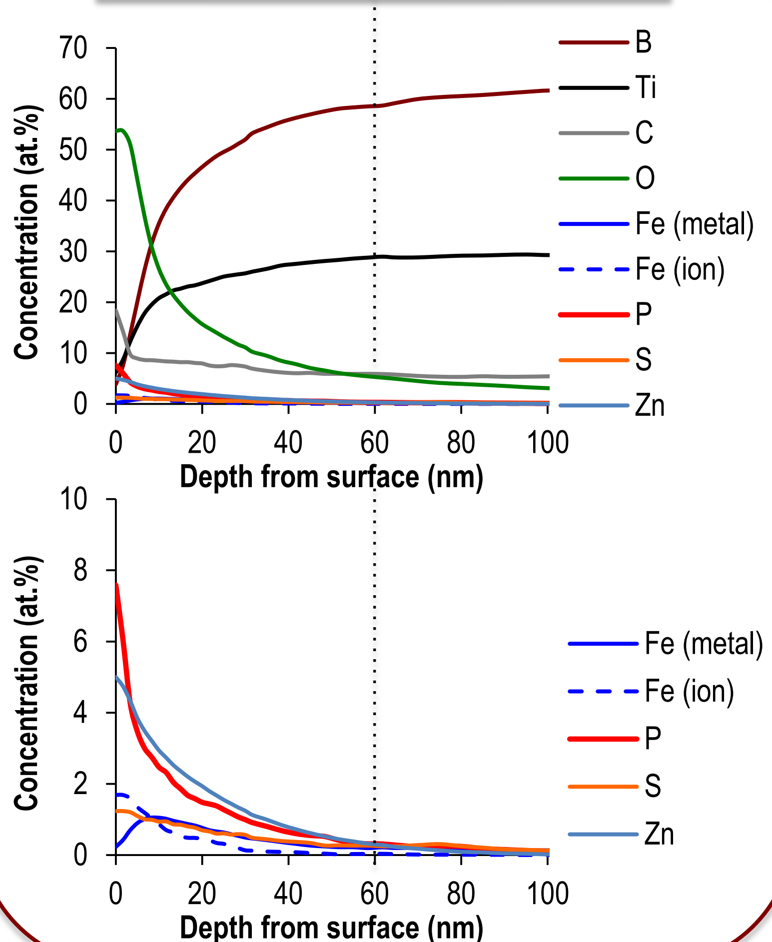




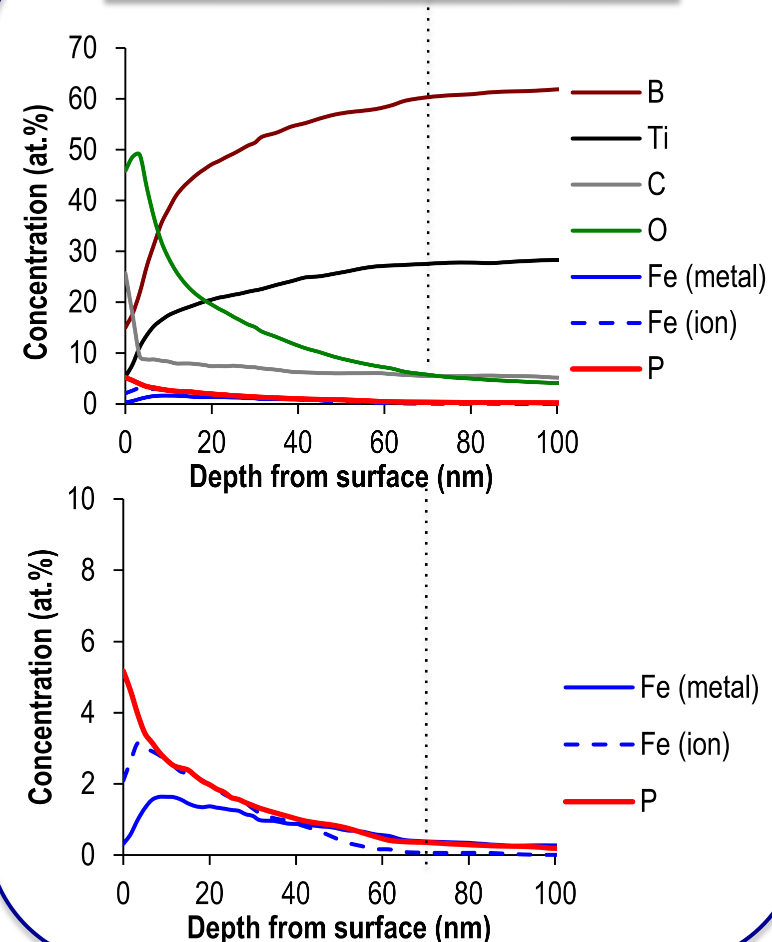
Red: as received; Green: after 30 sec sputtering

Tribofilms on TiB_2 – similar to those on $AlMgB_{14}$-TiB_2 (85-95% coverage, up to 60-70 nm thick)

ZDDP tribofilm



IL tribofilm



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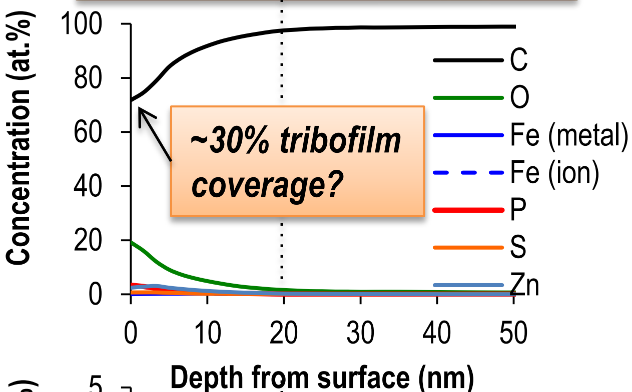
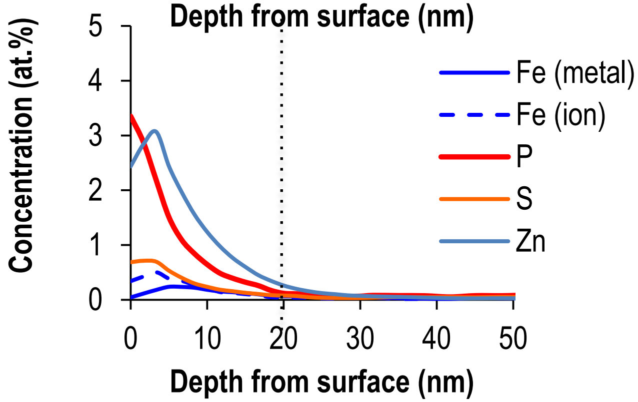
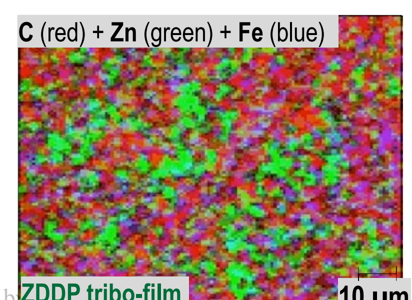
Tribofilms on DLC – lower coverage (20-30%) and thinner (<25 nm)

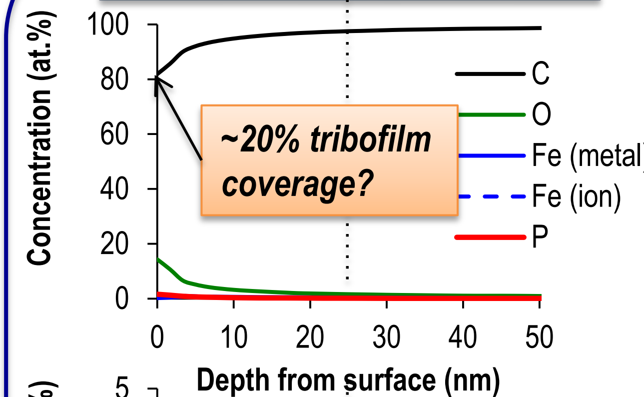
ZDDP tribofilm

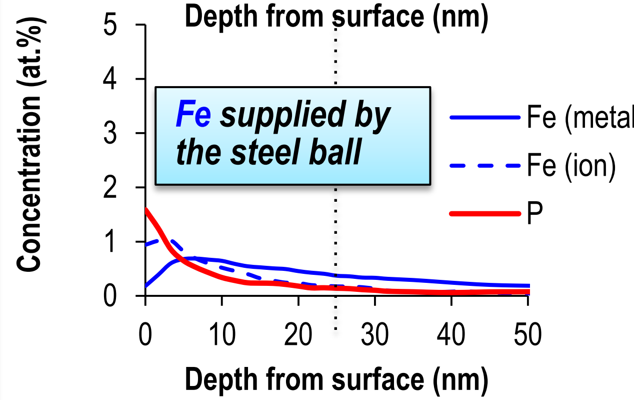


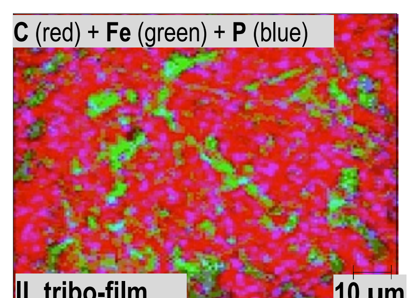




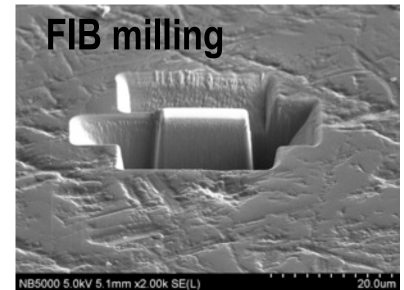
IL tribofilm

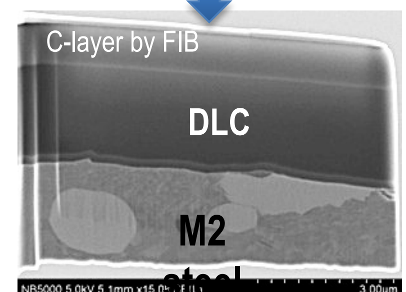


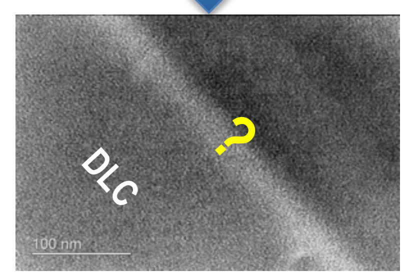




Auger elemental mapping confirmed the low tribofilm coverage!



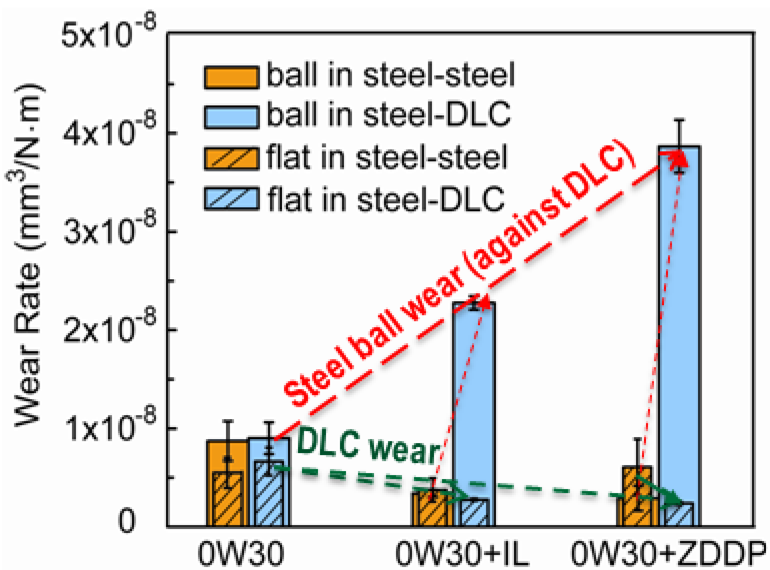


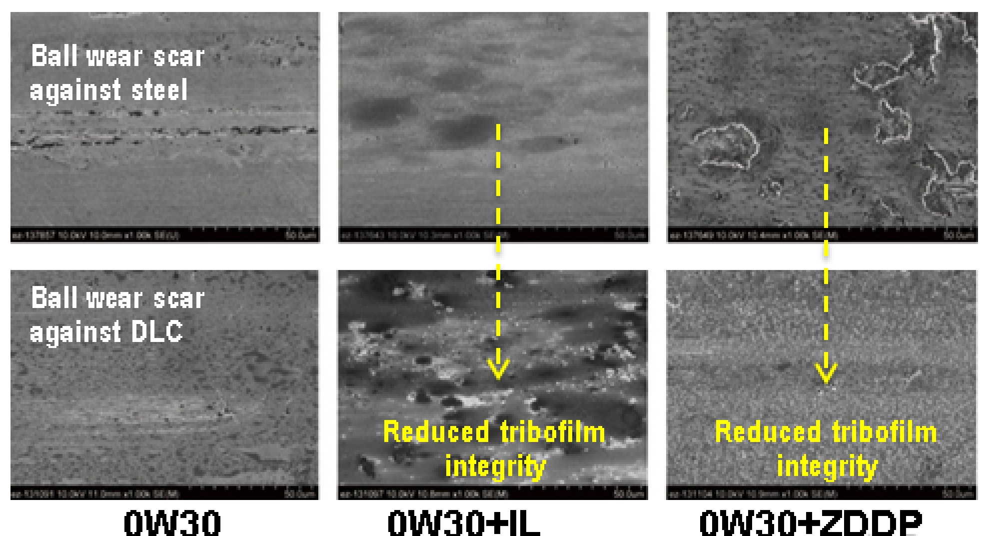


TEM cross sectional

In progress: surprisingly increased counterface wear when using ZDDP (or IL) and DLC together

- AW additive (either ZDDP or IL) alone in the steel-steel contact (w/o DLC) reduced the wear rates for <u>both the ball and flat</u>, as expected;
- DLC coating alone showed no negative impact on wear or friction;
- Combination of AW (ZDDP or IL) and DLC further reduced the <u>flat wear</u>, **however increased the steel <u>ball wear</u>!**
  - ZDDP+DLC produced 8X and 4X higher wear on the counter steel ball than using the ZDDP and DLC alone, respectively!
- ***Hypothesis***: competition between AW tribofilm formation and graphite transfer→ poor tribofilm integrity→ higher wear rate of the steel ball.





Responses to Previous Year Reviewers' Comments

- **Not applicable – this project was not reviewed last year.**

Collaboration

- Lubrizol
  - Provided a commercial secondary ZDDP
- Cytec Industries
  - Supplied feed stocks for synthesizing the ionic liquid
- Northeast Coating Technologies
  - Provided two commercial DLC coatings
- Eaton
  - Provided two commercial boride coatings
- ANL
  - Provided two research coatings

Remaining Challenges and Barriers

- Increased counterface wear when using ZDDP (or IL) and DLC together
  - Hypothesis: competition between AW tribofilm formation and graphite transfe → poor tribofilm integrity → higher wear rate of the steel ball.
  - Further characterization involving ultra-high resolution TEM to validate the hypothesis.
- Will the counterface wear increase when using ZDDP (or IL) and other hard coatings?
  - $AlMgB_{14}$-TiB_2 coating will be used to study this counterface wear issue.
- Lack of understanding of their compatibility on friction behavior in mixed lubrication.
  - Results so far have been focused on boundary lubrication.

Proposed Future Work

Rest of FY 2014

- Further investigation of the issue of increased counterface wear for both DLC and boride coatings

FY 2015

- Investigate the compatibility between ZDDP/IL and hard coatings on friction behavior in mixed lubrication.
  - The majority of literature studies were focused on boundary lubrication.
  - Literature suggests the ZDDP tribofilm commonly increases friction in mixed lubrication for a steel-steel contact. Our IL study showed much lower mixed lubrication friction than ZDDP.
  - ORNL has a newly built Variable Load/Speed Journal Bearing Tester (VLBT), suitable for this task.

Summary

- **Relevance:** Investigate the compatibility of engine lubricant anti-wear (AW) additives, specifically conventional ZDDP and newly developed ionic liquids, with selected commercial hard coatings to help guide future engine lubricants development.
- **Approach/Strategy:**
  - Experimentally study the friction and wear behavior for selected non-metallic hard coatings lubricated by selected anti-wear additives via tribological bench testing in well-defined conditions.
  - Mechanistically investigate the tribochemical interactions between the anti-wear additives and the coating surfaces via comprehensive tribofilm characterization.
- **Accomplishments:**
  - The mechanism for the ZDDP (and IL) tribofilm formation on non-metallic coatings revealed.
  - The AW tribofilms on boride and DLC coatings with various surface coverage and thicknesses.
  - Surprisingly increased wear was observed on the counterface when using the ZDDP (or IL) together with the DLC coating.
- **Collaborations:**
  - Lubrizol, Cytec Industries Coatings: NCT, Eaton, and ANL
- **Proposed Future Work:**
  - Rest of FY14: Counterface wear and roughness/temperature effects
  - FY 15: Compatibility on friction behavior in mixed lubrication

Technical Back-up Slides

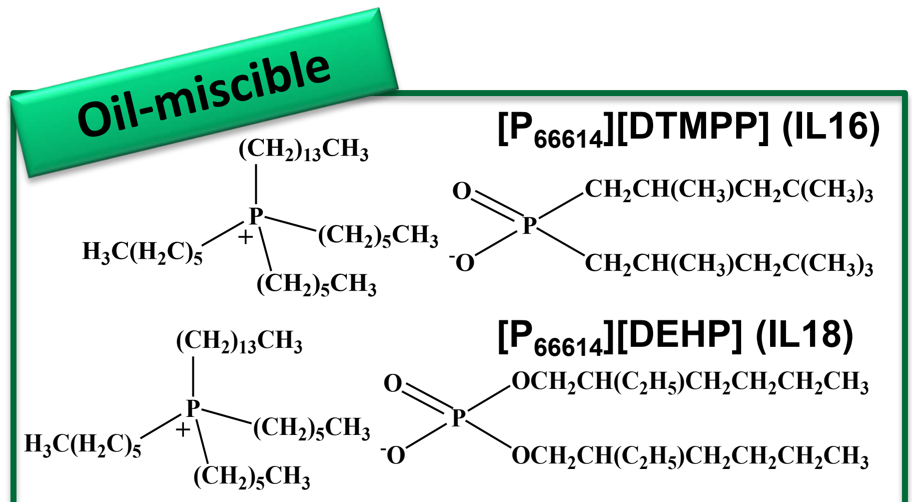
Ionic liquids (ILs) for lubrication

- **ILs as neat lubricants or base stocks**
  - **High thermal stability (up to 500 ^{o}C)**
  - **High viscosity index (120-370)**
  - **Low EHL/ML friction due to low pressure-viscosity coefficient**
  - **Wear protection by tribo-film formation**
  - **Suitable for specialty bearing components**

Ionic liquids are 'room temperature molten salts', composed of cations & anions, instead of neutral molecules.

- **ILs as oil additives**
  - **Potential multi-functions: anti-wear/EP, FM,** *corrosion inhibitor, detergent*
  - **Ashless → low sludge**
  - **Allow the use of lower viscosity oils**
  - **Advantage: cost effective and easier to penetrate into the lubricant market**
  - **Problem: most ILs insoluble in oils**

- **ORNL-developed oil-miscible ILs:**



B. Yu, and J. Qu, et al., Wear (2012) 289 (2012) 58.*
J. Qu, et al., ACS Applied Materials & Interfaces 4 (2) (2012) 997.