ORNL/LTR-2022/2577
NFE-19-07831
Final Report

Tribological Evaluation of Candidate Coatings

Jun Qu
Tomas Grejtak
Joel Harringa
Bruce Cook

September 2022

Approved For Public Release

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

ORNL/LTR-2022/2577
NFE-19-07831

Tribological Evaluation of Candidate Coatings

Jun Qu, Tomas Grejtak
Materials Science and Technology Division

Joel Harringa, Bruce Cook
Novus Energy Technologies, Inc

Date Published: September 2022

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

Approved for Public Release

Abstract

This SPP project with Novus was to investigate tribological properties of candidate ceramic composites. Systematic tribological bench tests and surface characterization were performed to determine composition-property relationships of several boride-based ceramic composites of different compositions. The lowest friction coefficient composition was C3 tested in hydraulic oil. Surface characterization suggests a formation of ZDDP tribofilm in the worn region when tested with a hydraulic oil. In all experiments, the ceramic composites did not have measurable wear, but caused material loss of the steel counter-surface.

Objectives

Novus Energy Technologies, Inc. (Novus) received an award in response to a U.S. Department of Energy (DOE) FY 2019 Phase I Release 2 Small Business Innovation Research (SBIR)/Small Business Technology Transfer (STTR) DOE Funding Opportunity Announcement (FOA): DE-FOA-0001941, Topic 13c, “Vehicles, Reduction of Thermal and Friction Losses in Internal Combustion Engines.” and requested Oak Ridge National Laboratory’s (ORNL) assistance to conduct tribological bench testing and analysis of candidate composite materials to gain fundamental understanding of the friction and wear properties.

In this project, materials characterizations including X-ray diffraction (XRD), hardness and roughness measurements, tribological testing, and surface characterization were performed on several boride based ceramic composites provided by Novus.

Experimental and materials

Two hot pressed compact discs were prepared by Novus and delivered to ORNL for tribological characterization. Each compact consisted of two compositions with a separation layer of grafoil in between. The four samples were ternary composites of boron with two transition metals, designated C1, C2, C3 and C4. The grafoil serves as a barrier coating and die lubricant in hot pressing. The ceramic powders at the interface are pressed into the grafoil and form a rough sample/grafoil surface that were ground off to expose the sample underneath. The compact discs were polished using a diamond wheel grinder with a 220 grit to achieve a roughness of R_a <1 µm.

Roughness was measured using a profiler (Mahr, Pocket Surf IV). Vickers hardness measurements were performed using a microindenter (Buehler, Micromet 2103). The composites are very hard and difficult to machine and polish. A diamond wheel grinder is necessary. Two of the composites appeared to be rather brittle with one sample having fractured during polishing and the edges of other samples chipped off during sample mounting for tribological testing.

X-ray diffraction (XRD, PANalytical Xpert diffractometer) was performed for chemical compound/phase identification.

Ball-on-flat reciprocating sliding boundary lubrication tests were carried out using a tribometer (Phoenix Tribology, Plint TE-77), Figure 1a. In each test, a hardened AISI 52100 bearing steel ball (10 mm diameter, HRC 60) was used to slide against the ceramic composites disc. Test was conducted at 10 Hz oscillation frequency with 10 mm stroke (average speed: 0.2 m/s), under a 100 N load and 100°C oil temperature for 1 km of reciprocating sliding. The experiments were performed using two different lubricants: PAO 4 cSt base oil and Mobil DTE™ 25 hydraulic oil (ISO VG 46). After a completion of the tribological testing, the worn surface topography of the ceramic composites and the steel ball was measured with an optical profilometer white light interferometer (Wyko NT9100) to determine the wear volume. The worn contact surfaces of the composite samples and the steel balls were also imaged with optical microscopes (Nikon Labophot-2). A scanning electron microscope (Hitachi S4800 SEM) equipped with energy-dispersive X-ray spectroscopy (EDS, AMETEK) was used to analyze the tribo-chemistry of the contact surfaces.

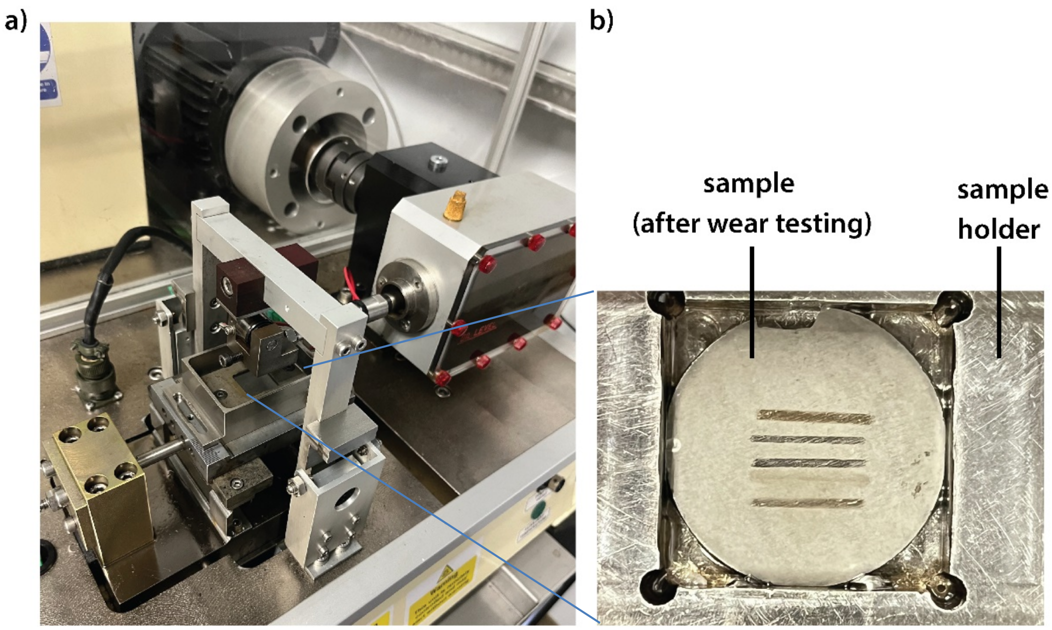

Figure 1. Left) Plint TE-77 tribometer. Right) Composite sample C4 after tribological testing placed in a sample holder.

Results and Discussion

Surface roughness & hardness

Both sides of the hot-pressed compact discs were polished with a diamond grinding wheel to achieve a desired surface roughness (Ra<1 μm) for a tribological testing. The lowest surface roughness was measured in C2 and C3 samples, R_a of ~0.25 and ~0.21 μm, respectively, Table 1. C4 had the highest surface roughness of ~ 0.61 μm. The surface roughness of the C1 sample was ~ 0.51 μm. Unfortunately, the sample broke during the grinding procedure and the geometry of the sample prevented further tribological evaluations.

The hardness of the C3, C4 and C1 composites was very similar, roughly 3000 HV. The hardness of the C2 was lower, around 2350 HV. This could be due to a presence of a low-hardness carbonaceous residue that could have been embedded in the material during hot-pressing process.

Table 1. Surface roughness and Vickers hardness of candidate composite ceramics.

Composite	*#1	#2	#3	#4
Roughness (R_a μm)	0.51 ± 0.10	0.25 ± 0.03	0.21 ± 0.04	0.61 ± 0.03
Hardness (HV 500)	2928.2 ± 224.5	2351.4 ± 353.1	3036.2 ± 260.8	2934.8 ± 212.0

**Note: C1 sample broke during polishing and was not suitable for tribological testing.*

XRD analysis

X-ray diffraction patterns revealed a presence of M1B2 phase and M1 in all four ceramic composites, Figure 2, where M1 =transition metal1. C1 composite exhibited only primitive cubic M1. M2B2 phase was present in C2and C3 composites, however, the a and c lattice parameters from the M2B2 were smaller than the reference pdf database, which could indicate some substitution of M1 for M2 and a possible intermediate composition phase. M3B2 phase was identified in C4 composite. This is somewhat unexpected because the intention was to formulate a solid solution of M1, B and M2.

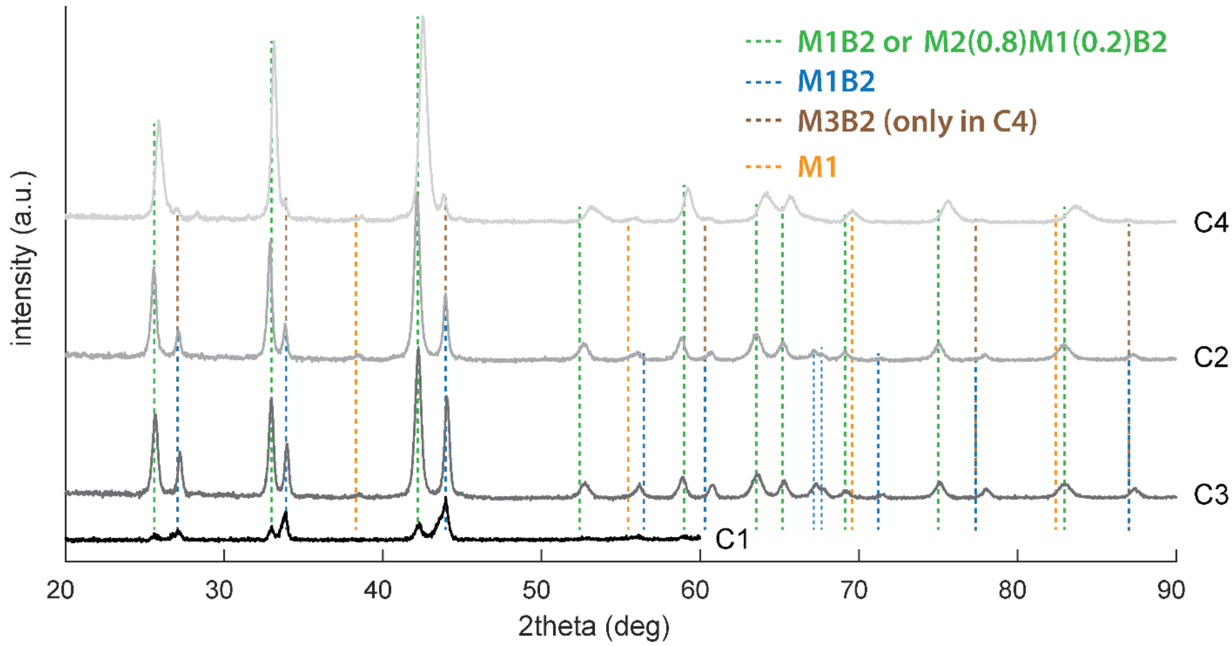

Figure 2. XRD analysis of candidate composite ceramics.

Tribological testing using a base oil

Wear and friction properties of two ceramic composites, C3 and C4, were tested with a base oil (PAO 4 cSt) using the test conditions described in the Experimental and materials section above. Two repeats were performed on each material. The testing revealed no significant difference in friction or wear performance for the two composites. The evolution in the friction coefficient with increasing sliding distance was very similar in both composites, Figure 3. The steady-state friction coefficient was maintained between 0.12 and 0.13. The C4 appeared to have a lower initial friction coefficient during the first 200 m of sliding than the C3.

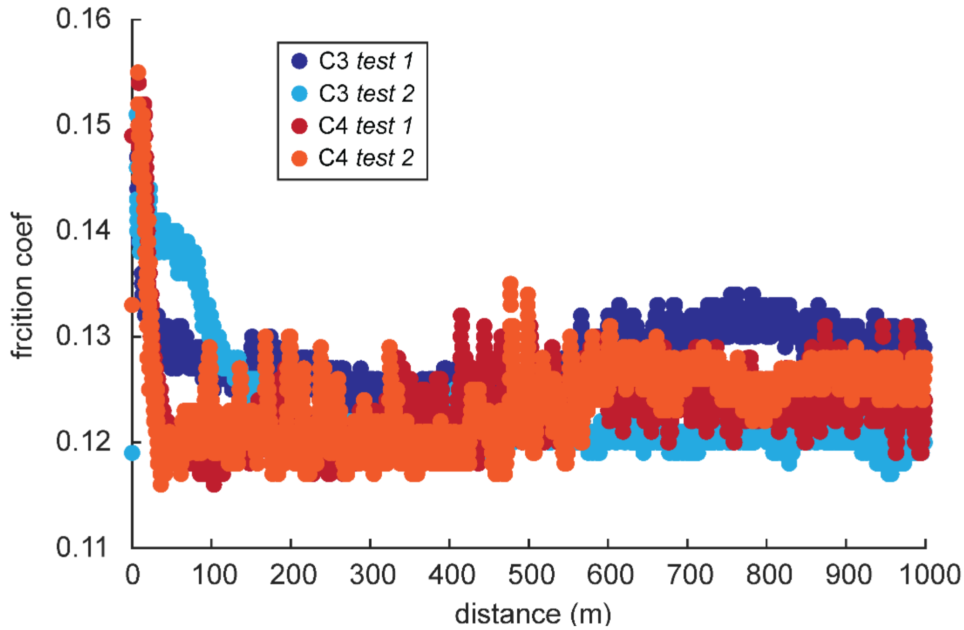

Figure 3. Evolution of friction coefficient as a function of sliding distance for C3 and C4 composites tested with a base oil.

The analysis of the contact surface region revealed that both C3 and C4 had a very similar width of the contact surface, ~900 µm, Figure 4a. Surface topography measured across the contact surface of the composites did not show any measurable wear, i.e., the height difference between the region inside and outside of the contact surface is minimal, Figure 4b. However, there was a considerable wear loss of the steel ball, Figure 4c. The ball wear rates were 1.41×10^{-7} and 1.67×10^{-7} $mm^3/(N\text{-}m)$ sliding against the C3 and C4 composites, respectively, Table 2.

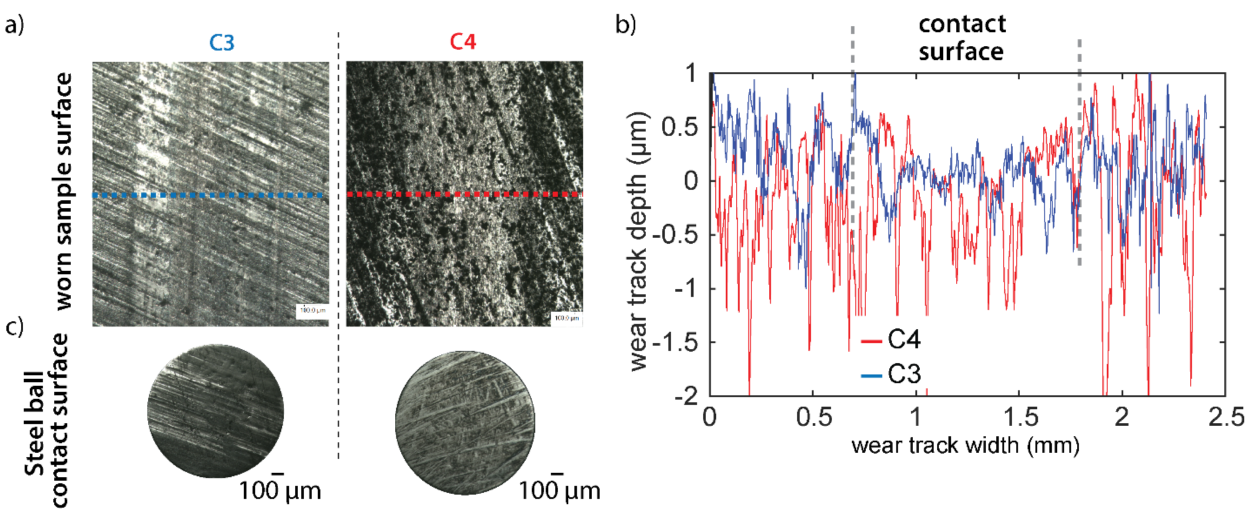

Figure 4. Wear properties of C3 and C4 composites tested with a PAO base oil. a) Worn contact area, b) Worn surface profile, and c) Wear scars of the steel balls.

Table 2. Friction and wear results in the base oil.

Sample	Steady-state friction coefficient (after 200m of sliding)	Steel ball wear rate ($mm^3/(N\text{-}m)$)
C3	0.12	1.41 E-7 ± 3.5 E-8
C4	0.12	1.67 E-7 ± 9.2 E-9

EDS elemental mapping of the C3 and C4 composites shows a higher concentration of iron and oxygen in the contact surface region, Figure 5. This suggests a formation of an iron oxide tribo-layer. The presence of iron in the contact surface is believed to be a result of material transfer and deposit of wear debris from the steel ball.

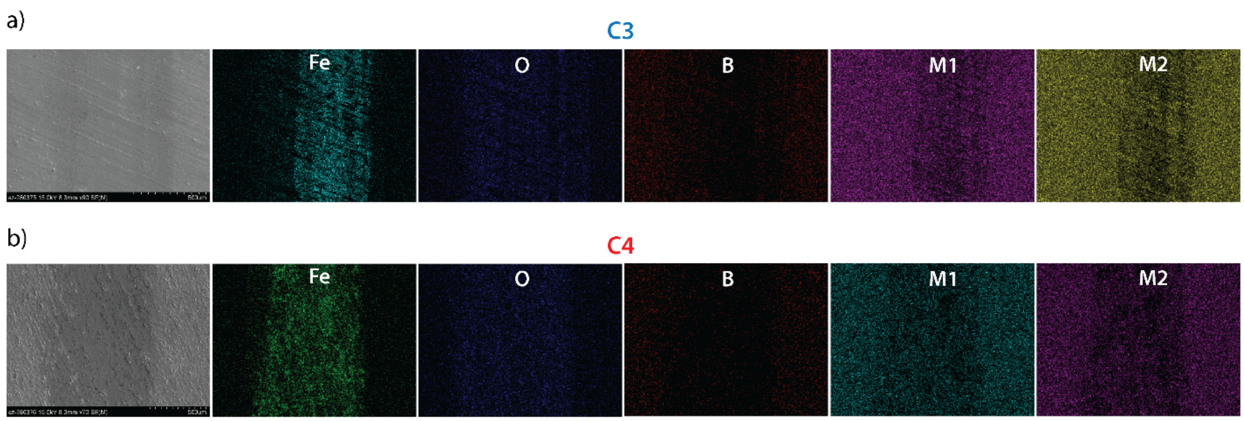

Figure 5. EDS elemental maps of a) C3 and b) C4 composites tested with a base oil.

Tribological testing using a hydraulic oil

Wear and friction properties of three ceramic composites, C2, C3 and C4 were tested with a hydraulic oil using the same test conditions as that in the base oil. While the ceramic composites showed rather similar wear and friction properties in the base oil, they exhibited more differences in the hydraulic oil (Mobil DTE 25). The C2 and C4 composites had almost identical and stable friction coefficient over the entire duration of testing, but the C3 composite had notably a lower initial friction coefficient in the first 200 m of sliding, Figure 6. The steady-state friction coefficients of the three composites eventually converged to ~0.125.

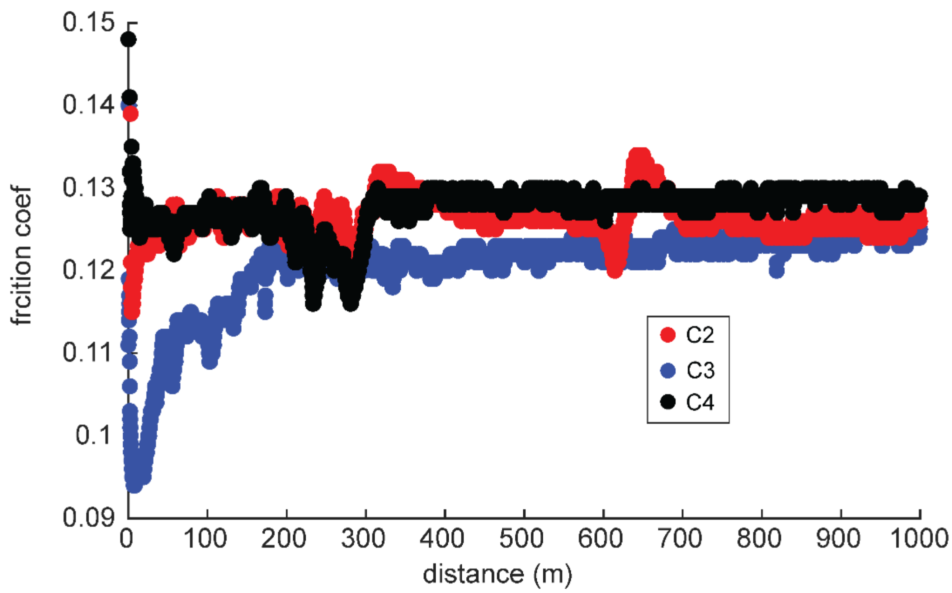

Figure 6. Evolution of friction coefficient as a function of sliding distance in a hydraulic oil.

The analysis of the worn surfaces of the ceramic composites showed that the C3 composite had the narrowest contact surface, ~470 µm, Figure 7a. The contact area widths in the C2 and C4 composites were similar, approximately 750 µm. The line profiles of the contact surface topographies in Figure 7b show that the C3 and C2 composites had no measurable wear except polishing effect. In contrast, the C4 composite has a deeper wear scar, though the wear volume was still too little to precisely quantify.

The C3 composite had not only the lowest friction coefficient and the smallest contact surface width on itself but also caused the least wear rate on the steel ball, ~9.85×10^{-9} mm^3/(N-m), which is approximately 5X lower than the ball wear rates against the C2 and C4 composites, Figure 7c and Table 3. Overall, the wear rates of the steel balls tested in the hydraulic oil were lower than those tested in the base oil, Table 2, which can be attributed to the higher oil viscosity and presence of anti-wear additives in the hydraulic oil.

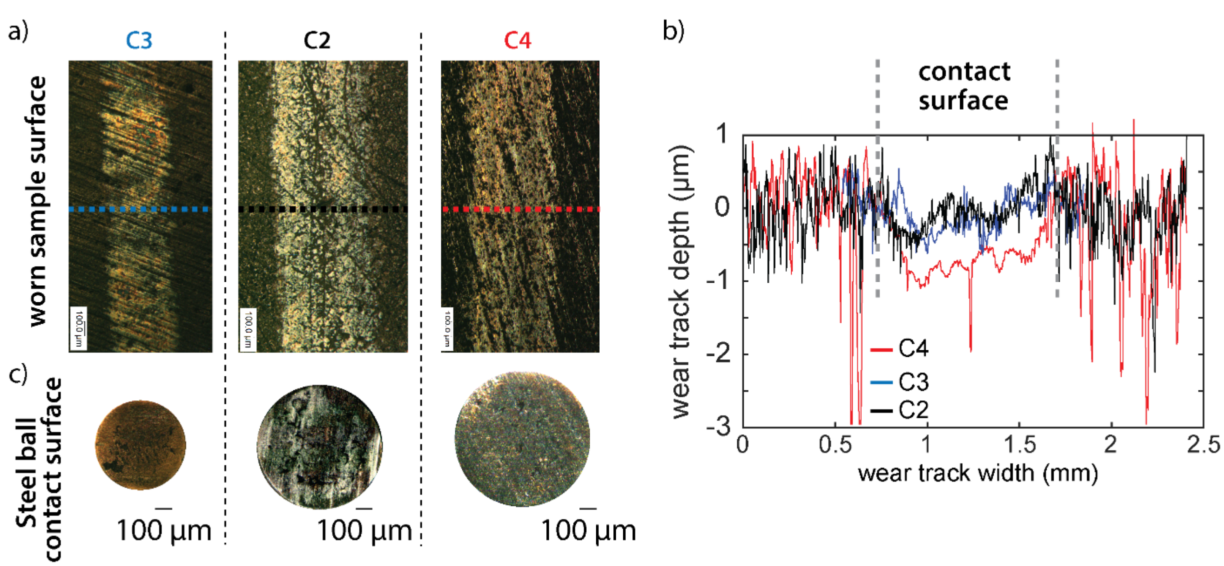

Figure 7. Wear properties of the composites tested in a hydraulic oil. a) Worn contact surface, b) Worn surface profile, and c) Wear rate of the steel ball counter-surface.

Table 3. Friction and wear results in the hydraulic oil.

Sample	Steady-state friction coefficient (after 200 m of sliding)	Steel ball counter-surface wear rate ($mm^3/(N\text{-}m)$)
C3	0.121	9.85 E-9
C4	0.126	6.25 E-8
C2	0.125	4.47 E-8

SEM imaging and EDS elemental analysis were performed on the composites tested in the hydraulic oil, Figure 8. All three composites showed a higher concentration of oxygen, zinc, and phosphorus on the worn contact surfaces, suggesting a tribofilm composed of zinc oxides and phosphates as formed by the ZDDP contained in the hydraulic oil. The concentration of M1, M2 in all three composites and M3 in the C4 was also unchanged between the worn and unworn regions. There is a lower concentration of B in the worn region in all three composites. EDS spectra confirmed a presence of all the constituent elements of the composites.

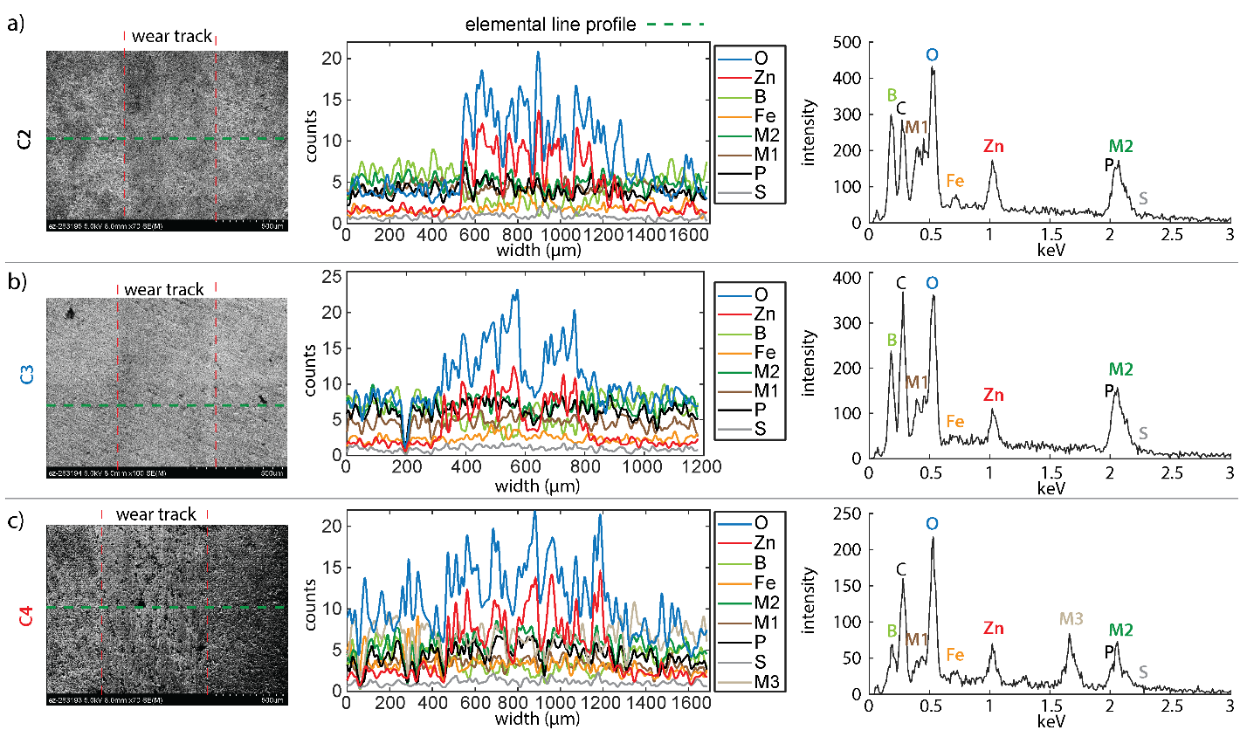

Figure 8. SEM imaging and EDS elemental analysis of the composites tested in the hydraulic oil.

Conclusions

Materials characterization and tribological bench tests were conducted at ORNL to evaluate the M1-M2-B based ceramic composites from Novus. While the intention was to formulate a solid solution of M1, B and M2, XRD suggested the composites contain significant $M1B_2$ and $M2B_2$ (or $M2_{0.8}M1_{0.2}B_2$) phases.

All composite samples maintain steady-state friction coefficient ~ 0.125 when tested with both base and hydraulic oil. The only notable difference was observed in the C3 composite tested with a hydraulic oil which had a significantly lower initial friction coefficient. No measurable wear was observed on the contact surface of the composites, though there was a considerable wear loss on the steel ball countersurfaces in all cases. Contact surface characterization of the composites revealed a formation of iron oxide tribolayer when tested with a base oil and a ZDDP tribofilm when tested with a hydraulic oil. The ceramic composites are very hard and resistant to sliding wear. On the other hand, the composites are difficult to machine and rather brittle.

Acknowledgements

The authors thank D. Heidel and D. Stringfield from ORNL for sample preparation and T. Watkins and E. Cakmak for the XRD measurements. This research was supported by U.S. Department of Energy (DOE), Small Business Innovation Research (SBIR)/Small Business Technology Transfer (STTR) via a subcontract from Novus Energy Technologies, Inc.