Final Technical Report

Boride-Carbon Hybrid Technology to Produce Ultra-Wear and Corrosion Resistant Surfaces for Applications in Harsh Conditions

DOE Award Number: DE-EE0008320

Project Period: 05/16/2018 – 11/15/2019 (extended to 11/15/2020)

Recipient Organization: Michigan State University, Department of Electrical and Computer Engineering, East Lansing, MI 48824

Partners: Fraunhofer USA, Inc., Center for Coatings and Diamond Technologies, East Lansing, MI 48824

Argonne National Laboratory, Energy Systems Division, Argonne, IL 60439

Authors: Qi Hua Fan (PI); Phone: (517) 432-4651, qfan@egr.msu.edu

Nina Baule; Phone: (517) 884-8694, nbaule@fraunhofer.org

Date of Report: December 2020

Acknowledgement: This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the the Advanced Manufacturing Office, Emerging Research Initiative award number DE-EE0008320. Many dedicated scientists, engineers, technicians, and students have contributed to the process. In particular, Thomas Schuelke, Lars Haubold, Timothy Grotjohn, Young Kim and Yun Hsiung have played significant roles in various stages of the project and contributed towards its success at MSU/Fraunhofer laboratories. Argonne National Laboratory personnel Ali Erdemir and Osman Eryilmaz played key roles in the boriding technology, coating performance and commercialization path. We also acknowledge Aaron Greco and Benjamin Gould for the micro-pitting rig tests, that are being conducted currently.

Document Availability: Reports are available free via the U.S. Department of Energy (DOE) Information Bridge Website: http://www.osti.gov/bridge.

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and Informational Nuclear Information System (INIS) representatives from the following source:

Office of Scientific and Technical Information

P.O. Box 62

Oak Ridge, TN 37831

Phone: (865) 576-8401

Fax: (865) 576-5728

E-mail: reports@osti.gov

Website: http://www.osti.gov/contract.html

Table of contents

List of Figures

List of Tables

1 Executive Summary

Engineered functional surfaces play an important role to enable new products and manufacturing processes that can endure harsh service conditions such as high impact and contact loads, highly abrasive wear, extreme temperatures, and corrosive environments. Engineered surfaces can also be instrumental to improving the efficient use of energy by reducing frictional losses and extending service life. The main objective of this project was to develop a hybrid surface engineering technology that combines the advantages of a novel ultrafast boriding process with the next generation of superhard carbon coatings. The hypothesis was that this hybrid process will offer an unprecedented combination of wear and corrosion resistance, low frictional losses and affordability for treated parts so that it can be utilized in many applications.

During this project, a duplex process was developed that combines the advantages of ultra-fast electrochemical boriding with those of hard tetrahedral amorphous carbon coatings. Both technologies can be combined to form a hybrid technology that is characterized by low friction and wear properties combined with corrosion and fatigue resistance. Good adhesion of both layers to each other was one main goal of this project, that has been achieved with HF1 adhesion through the Rockwell-C adhesion test.

In this project, the mechanical properties of the hybrid coating were modeled through a finite-element analysis approach. We can conclude that the FEA model resembles the actual samples and be utilized to predict mechanical behavior under impacts. Based on this model, application-oriented load conditions can be simulated for optimal layer design regarding thickness and mechanical properties. To exemplify, one conclusion that can be drawn from the nanoindentation model is a boride layer thickness of 50 µm is sufficient to effectively support the carbon coating on the identified AISI 1045 low carbon steel substrate material.

The duplex treatment yields wear rates as low as 6×10^{-8} mm^3 N^{-1} m^{-1} and a coefficient of friction of 0.14 when tested against a steel counter face in a ball-on-disk test setup. On the other hand, the wear rate of the only-borided AISI 1045 steel was 5×10^{-5} mm^3 N^{-1} m^{-1}, about three orders of magnitude higher than the duplex coating. At the same time, duplex treated samples experience corrosion resistance, which could not be achieved with single-layer carbon coatings. The developed surface treatment withstands a 3-hour exposure to 15% HCl, while the only carbon coated counter sample shows severe delamination of the coating due to pin hole corrosion. The boride layer is chemically stable and pin hole free because it is formed through an electrochemical process under high current densities (700 mA/cm^2) and high temperature. Additionally, the hybrid coating led to at least 3x increase in fatigue strength of the steel substrate, which exceeds the target performance of 30% improvement.

There are numerous potential applications for the duplex coatings. A representative application is bearing ball coatings for off-shore windmills. Compared to currently employed surface technologies in this field, the initial costs of applying our technology might be higher due to more process steps but the performance benefits lead to an increased life time of treated parts, which will lower the maintenance and replacement costs in the long-term. To validate the technology for this specific application, the team is currently investigating the process of white etching crack initiation of the duplex coating in collaboration with ANL.

Overall, this project successfully validated that the boride-carbon hybrid technology can withstand harsh conditions. One possible approach to commercialization under consideration is to transfer the technology to a startup or an existing coatings company.

2 Introduction

Humans are using the Earth's resources at an alarming and unsustainable rate. By mid-August of each year, we consume more water, energy and raw materials than can be replenished by natural resources [1]. Consequently, it is a matter of long-term sustainability for our society, that we must use the available resources more efficiently. To achieve this, we rely largely on technological progress. Emerging transformative technology trends (e.g. "Renewable Energy", "E-Mobility", "Industry 4.0", etc.) contribute to reducing energy consumption, to improving the utilization of raw materials, to lessening the environmental impact and to improving the quality of life in a steady and sustainable manner. But there is no "magic bullet" to solve the increasing need for energy conservation, stabilization and renewal. Our team strongly believes that these issues must necessarily be tackled in a variety of ways. One area that can clearly provide high impact is by increasing the durability and efficiency of the millions of tools and components that we use to manufacture goods, to generate and distribute energy, and to meet our transportation needs. Addressing this durability and efficiency challenge offers a clear and concrete support to achieving our society's sustainability needs.

Engineered functional surfaces in particular play an important role to enable new products and manufacturing processes that can endure harsh service conditions such as high impact and contact loads, highly abrasive wear, extreme temperatures, and corrosive environments. Engineered surfaces can also be instrumental to improving the efficient use of energy by reducing frictional losses. We propose to develop a hybrid surface engineering technology that combines the advantages of a novel ultrafast boriding process with the next generation of superhard carbon coatings. The hypothesis is that this hybrid process will offer an unprecedented combination of wear and corrosion resistance, low frictional losses and affordability for treated parts so that it can be utilized in many applications. The proposed surface treatment will enable novel mechanical systems with higher efficiency and improved durability to meet the challenges posed by increasingly harsher operating conditions across industry.

Superhard carbon coatings such as diamond and tetrahedrally bonded amorphous carbon (ta-C) already boast outstanding hardness and low friction properties, which provide such coated parts with excellent wear resistance properties. So, why would such coatings benefit from a borided support layer? One of the reasons is that these coatings are relatively thin (only a few micrometers), which causes stress fields that are imparted by high contact loads to reach deep into the substrate material (e.g. steel) and may compromise substrate integrity. Thin coatings might also contain pinholes and cracks, which expose the underlying substrate directly to corrosive attack and also compromise substrate integrity. Thus, under these extreme conditions of high contact loads and corrosive environments, the substrate material itself may become the limiting performance factor in spite of the presence of the coating. Real-world carbon coating applications, and in particular those in tough environments, have shown failure modes (individual and combined) including pinhole corrosion, substrate fatigue and delamination with potentially catastrophic consequences (e.g. gear box failures). A borided substrate supporting such carbon coatings could potentially improve the corrosion resistance and substrate fatigue strength while maintaining the advantages of the carbon coated surface. Thus, if the proposed hybrid process proves successful, the outcome will provide new levels of surface performance that should enable applications in extremely harsh service conditions. And if the application benefits outweigh the costs of producing such surfaces, the technology deployment should then be commercially feasible.

We aim at applications across industries that suffer from abrasive, adhesive, corrosive and fatigue wear, and frictional efficiency losses. The focus is on industrial manufacturing tooling (e.g. forming, drilling, excavating) and tribological (loadbearing and moving) components in mechanical assemblies (e.g. vehicle powertrain, wind turbine gear boxes).

3 Background and Project Description

Engineered surfaces play a critical role in reducing friction, wear and corrosion. The most common approaches to improve the performance of tribological systems are, in addition to design considerations, heat treatments (e.g. thermal or laser hardening), surface modifications (e.g. nitriding, carburizing, boriding) and surface coatings (e.g. chemical or physical vapor deposition, electroplating, plasma spraying). There are many processes used today, which are carefully engineered to provide durability and friction reduction advantages for specific applications. However, the environments in which tribological systems operate are also growing harsher across industries and thus pose new challenges to engineered surfaces. An important example in the field of renewable energies are wind power farms that are more frequently located offshore in a much harsher environment than inland, which reduces service life and increases maintenance costs. Gear boxes in wind turbines are designed to last for twenty years, however, frequent gearbox failures are caused by wear debris and oil-film breakdown occurring much sooner despite the use of best bearing design practices [2].

We strive to achieve an uncompromised performance by using superhard carbon coatings, which are among the hardest known surface coatings to date. Diamond and diamond-like carbon materials were first considered an emerging technology in the late 1980s [3]. Since the early 2000s the interest increased even more due to improved plasma synthesis technologies, which scaled the coating deposition process to become commercially feasible for tools and components. Due to their high hardness and low coefficient of friction superhard carbon coatings are especially interesting for tribological applications [4]. A few examples of successfully deployed applications are wear resistant diamond-like carbon coatings (ta-C:H) on large area building glazing [5], diamond tool coatings [6], diamond-like carbon coatings (a-C:H) for automotive fuel injection system components [7] and more recently tetrahedrally bonded amorphous carbon coatings (ta-C) for piston rings [8].

Boriding is a well-known and important surface technology with boron atoms diffusing into the near-surface region of workpieces made from ferrous alloys or high temperature non-ferrous alloys to form a hard layer of borides supported by a thick diffusion zone underneath. Traditional boriding processes expose the parts to high temperatures (1000°C) for very long times, typically tens of hours. In contrast, a novel process developed by Co-PI Dr. Ali Erdemir and colleagues at Argonne is fast, clean, efficient and low-cost. This ultrafast large-scale boriding process can form thick (up to 300 μm), hard (as high as 45 GPa, depending on substrate type) and uniform boride layers within less than 30 minutes of treatment time. It is based on an electrochemical cell operating at high current densities (700 mA/cm^2), works on all metallic and alloyed surfaces, provides long-lasting protection against wear, corrosion, erosion and oxidation due to the very thick, hard, and chemically stable boride layers. The Argonne group also scaled this ultrafast process from laboratory to industrially useful sizes and demonstrated its green, low cost and high-performance benefits [9,10].

The hybrid approach combines those two efficiently applicable surface treatment processes sequentially. First, a hard and corrosion resistant borided support layer is formed near the surface of the bulk material. Next, a superhard ta-C coating is deposited. **Figure 1** shows schematically hardness distributions starting at a surface depth of about 1 μm going deep into the bulk substrate at 10,000 μm. The dotted line represents a traditional “coating-only” process with a 5 μm thick and 60 GPa hard ta-C coating directly deposited on the steel (3 GPa). The dashed line shows the distribution for a part that was only treated by boriding to a surface hardness of about 20 GPa. The anticipated result of the proposed hybrid approach is presented by the thick black line, that is the hardness distribution of the duplex-treated part consisting of a boride support layer (20-300 μm thick) and a ta-C top layer (5 μm thick). The borided support layer features a very smooth and gradual transition from the hard phase near the surface toward the soft steel in the bulk substrate.

This duplex layer design is expected to contribute mechanical support to improve fatigue performance under high frequency high loading conditions. The duplex layer design is also expected to substantially increase the corrosion resistance compared to the conventional materials design.

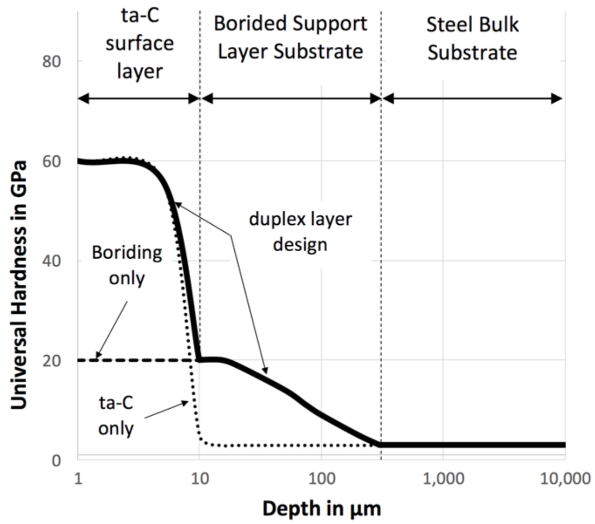

Figure 1. Schematic hardness distributions through near surface region for coated-only, borided-only and duplex treated parts.

The specific objectives of the project are to (1) create stable and adhering duplex layer boride-carbon structures on metal substrates, (2) meet specific performance targets for adhesion, wear rate, friction coefficient, corrosion resistance and fatigue strength, and (3) identify and specify the requirements for real-world applications in harsh service environments and provide a cost-benefit analysis using realistic input data. The specific project tasks and milestones (MS) are summarized in **Table 1** below.

Table 1. Project tasks and milestones.

1	**Demonstrate technical performance on laboratory scale**
1.1	Prepare laboratory test substrate samples
1.2	Process development
MS1.2	Carbon-on-boride achieved with HF1 adhesion
1.3	Iterative optimization of duplex layer design to meet target specifications
MS1.3	Targeted performance on test samples achieved
2	**Demonstrate commercialization path**
2.1	Identify and specify applications that would benefit from treatment
MS2.1	At least three relevant applications specified
2.2	Develop cost-benefit model
MS2.2	Cost-benefit models developed

4 Results and Discussion

4.1 Technical Approach

The ta-C deposition technology and electrochemical boriding technology were both studied extensively before the start of this project. These previous studies also included the characterization of tribological and corrosion properties of each individual layer. In this project, we primarily focused on the demonstration of technical performance and layer optimization on laboratory scale for a duplex technology of both layers.

The first main task focused on the process development for laboratory test substrate samples to achieve HF1 adhesion for carbon-on-boride, which also represented the Go-No-Go decision point.

Once this milestone was achieved, the next tasks concentrated on the iterative optimization of the duplex layer design to meet target specifications, which included the friction and wear properties, corrosion resistance and fatigue performance and FEA modeling.

The second main task was to demonstrate the commercialization path of the duplex technology in form of identifying and specifying applications that would benefit from the treatment and based on that show cost-benefit models for the applications.

4.2 Process Development

As mentioned in section 4.1, the processes for each individual layer were extensively tested before the start of this project. Now it was important to marry both technologies in the duplex boride-carbon technology.

Firstly, the team decided to focus their treatment on relevant steels and identified the AISI 1045 low carbon steel for the substrate material. The sample preparation (A) mentioned in **Figure 2**a) included polishing and solvent cleaning before the parts could be objected to either the boriding and/or ta-C coating.

The boriding step (B) in **Figure 2**a) was conducted in a molten salt composed of 90% borax and 10% sodium carbonate at a temperature of 950 °C at a current density of 50 mA/cm^2 (2.5 A) 15 min. Detailed descriptions of the boride treatment and equipment can be found in [9–11]. **Figure 2**b) shows the cross section of a borided 1045 steel (St-B), with its typical "boride teeth" for the Fe_2B phase. A homogeneously grown boride layer was achieved with an average thickness of around 58 µm. The process parameters were chosen to suppress the growth of the brittle FeB phase and to promote the preferred Fe_2B growth, which was shown to enhance the adhesion of subsequent coatings [11–13].

The final ta-C layer was deposited (**Figure 2**a) step (C)) by laser pulse controlled cathodic arc (LaserArc) evaporation [14,15], which promotes the formation and stabilization of predominantly diamond-like sp^3 bonds in the deposited carbon films. To ensure proper adhesion and stress relief of the films, the samples were plasma cleaned and a direct current cathodic arc process was used to deposit a chromium-carbon (Cr/C) interlayer about 200 nm thick. The thickness of the deposited ta-C film was 2 µm with a Young's modulus of 320 GPa.

Table 2 gives an overview of the produced samples with the required process steps (see also **Figure 2**a).

After some adjustments in the individual process steps (A), (B) and (C), which included among others the change of cleaning procedures and surface treatment such as polishing, we achieved an acceptable HF1 failure according to VDI 3198 [16] for the duplex treated sample St-B-C (shown in **Figure 3**). This important milestone and go-no-go decision point enabled us to measure duplex layer performance regarding friction, wear, corrosion and fatigue properties.

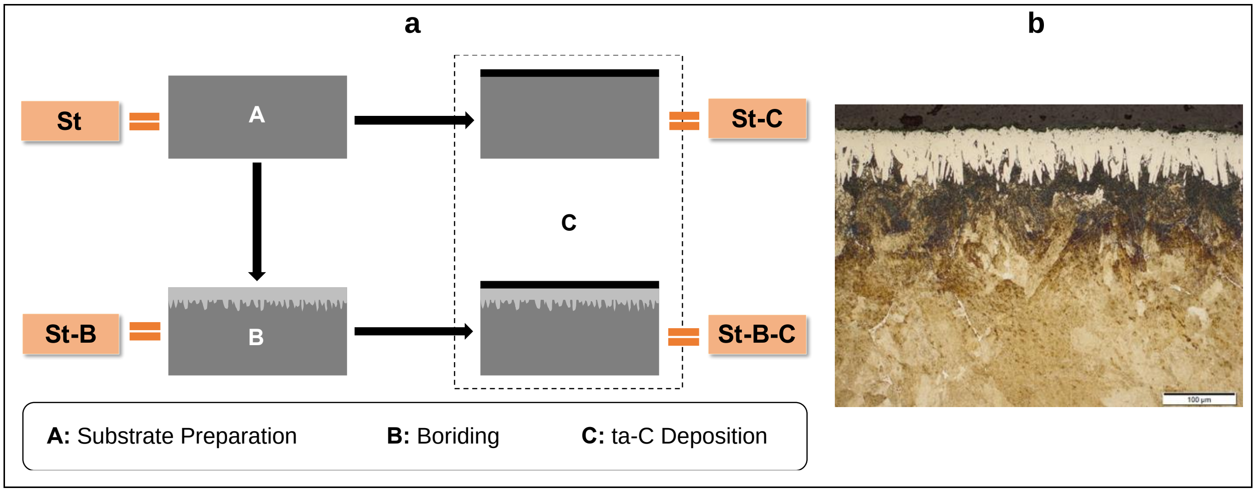

Figure 2. a) Process flow for making the AISI 1045 steel substrate sample (St), borided AISI 1045 substrate sample (St-B), ta-C coated AISI 1045 substrate sample (St-C) and the duplex treated (borided and ta-C coated) AISI 1045 substrate sample (St-B-C). b) Optical microscopy cross section of a borided 1045 steel substrate, etched with Nital (solution of nitric acid and ethanol).

Table 2. Sample overview with the required process steps.

Sample-ID	AISI 1045 steel	Borided	ta-C coating
St	x		
St-B	x	x	
St-C	x		x
St-B-C	x	x	x

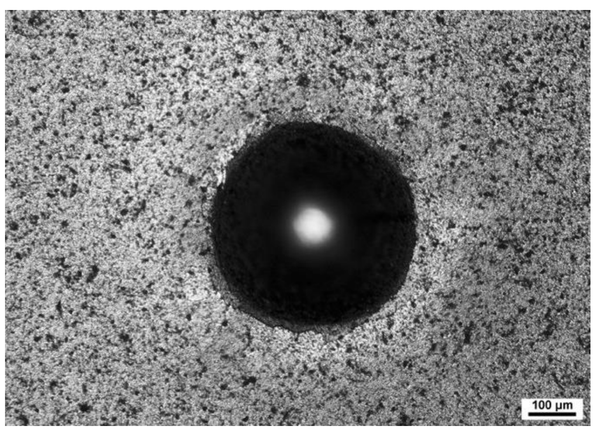

Figure 3. Rockwell-C adhesion test according to VDI 3198 for the duplex treated St-B-C sample.

4.3 Optimization and Performance Tests

To investigate the suitability of the duplex technology for applications under harsh service conditions, certain performance goals have to be achieved. Since this technology is mainly aiming at tribological systems in extreme environments such as corrosive and high load, the layer design has to be optimized to achieve low friction, wear, corrosion, and fatigue resistant coatings. During this project, the team used a finite-element analysis model for the layer optimization and utilized different characterization methodologies that are described in the following section.

4.3.1 Finite-element analysis modeling

Finite-Element Analysis (FEA) software ANSYS was used to model nanoindentation to obtain the mechanical properties of the coating systems. All material combinations (St, St-B, St-C, St-B-C) were modeled with a sample width of 60 µm. Stress and strain data was obtained from literature and converted into true stress and true strain for the data input [17,18]. **Table 3** summarizes the properties of each material used in this model. The material for the indenter was isotropic and elastic while the material for the layers were isotropic and elasto-plastic.

The geometry of the models was constructed and meshed. In order to save computing time, a symmetric plane was assumed. The geometry of the spherical indenter tip was modeled to be a radius of 10 µm sphere.

Two different sets of studies were conducted. Firstly, a constant force of 1.2 mN was applied to analyze the resulting deformation and stresses experienced during indentation. Secondly, a constant deformation of 14 nm was applied to analyze the force that is required to induce that particular deformation.

Figure 4a shows the results for the constant force experiments for all samples. The force applied was selected to just induce plastic deformation in the steel substrate, the coated assemblies are under elastic deformation. As expected, the experienced deformation which is represented here as the maximum indent depth is the lowest for the duplex treated assembly. It should be also noted, that both single layer solutions, St-B and St-C, increase the resistance to indentation compared to the bare steel substrate.

Under the same experienced deformation, similar results are found, as shown in **Figure 4**b. In this case, the duplex treated assembly requires the highest load to enforce the same deformation as the other material systems. Additionally, from the results in **Figure 4**b it is clear, that the borided layer contributes mainly to the increased resistance to deformation, as St-B requires just a slightly smaller force to induce the same amount of deformation compared to St-B-C.

The FEA model is also successful in predicting stress distributions under impact throughout all layers of an assembly. **Figure 5** shows the stress distribution in x- and y-direction resulting from an induced constant deformation of 0.014 µm for all material combinations. Along the x-axis the duplex treated assembly requires the highest induced stress to result in a deformation of 0.014 µm. Additionally, the stress distribution for ta-C coated and hybrid assembly is very similar, which agrees with the theoretical model in **Figure 1**. In y-direction, that behavior is similar: ta-C coated and duplex treatment experience an equivalent stress distribution. However, the ta-C coated samples experiences slightly lower stress which can be attributed to the softer non-borided substrate.

We can conclude that the FEA model resembles the actual samples and be utilized to predict mechanical behavior under impacts. Based on this model, application-oriented load conditions can be simulated for optimal layer design regarding thickness and mechanical properties. To exemplify, one conclusion that can be drawn from the nanoindentation model is, that for this particular load case boride layer thicknesses of 50 µm are sufficient to effectively support the carbon coating.

Table 3. Material properties used in the FEA model.

Materials	**Thickness (µm)**	**Young's modulus (GPa)**	**Poisson's ratio**
Diamond indenter	-	1140	0.04

ta-C coating	2	300	0.30
Boride layer	50	200	0.17
AISI 1045 substrate on a spring	15	88	0.30

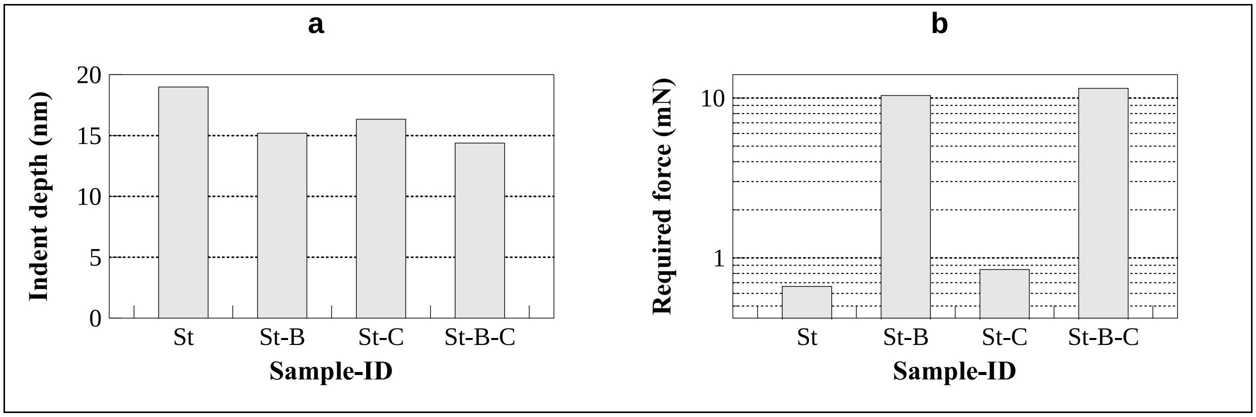

Figure 4. FEA nanoindentation modeling results for a) a constant applied force and the resulting deformation in y-direction and b) a constant deformation in y-direction and the resulting force for all samples.

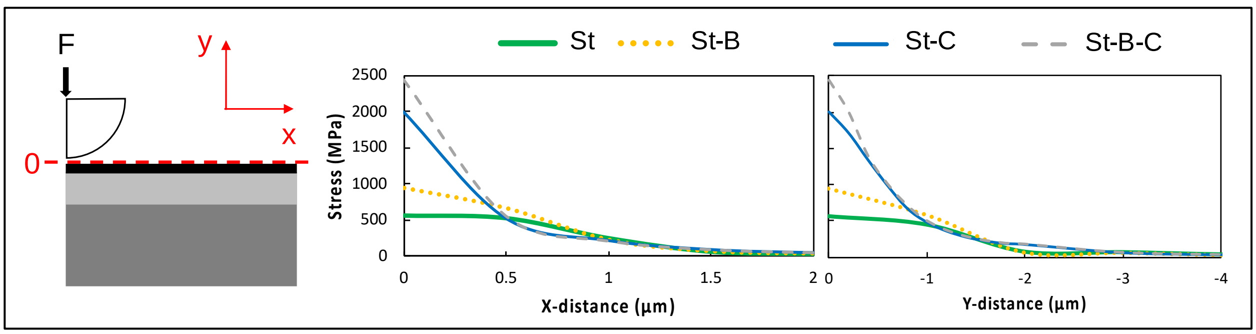

Figure 5. FEA model under a forced deformation of 0.014 µm and the resulting stress distribution in x- and y-direction.

4.3.2 Tribological properties: coefficient of friction and wear resistance

A reciprocating ball-on-disk setup was used to determine the coefficient of friction (COF) and wear rates under dry conditions for samples St, St-B and St-B-C. The counter ball was an uncoated 440C stainless steel (440C SS) ball with a diameter of 6.35 mm. At a sliding speed of 2cm/s and a track length of 8 mm, a sliding distance of 100 m (12,500 cycles) was carried out. The applied load of 5 N resulted in a Hertzian contact pressure of about 1 GPa between the ball and sample. For the sample, the wear volume is calculated by the wear track's depth and width, which was measured with a Veeco Dektak 6M profilometer, multiplied by the overall track length.

The CoF proved to be much lower for the duplex treated St-B-C sample than for the single-layer boride St-B sample as shown in **Figure 6**. The COF for the St-B-C sample reached as low as 0.14, while the COF for the St-B sample is as high as 1.2.

While the wear track for the duplex treated sample was almost undetectable after a running-in distance of 100 m, the borided sample showed significant wear (**Figure 7**). Based on profilometric analysis of the St-B-C wear track, the occurring wear is remarkably lower than on the borided surface (**Figure 7**, center). The wear rates are 6 x 10^{-8} mm^3 N^{-1} m^{-1} for the duplex treatment and 5 x 10^{-5} mm^3 N^{-1} m^{-1} for the borided surface. Wear on the St-B-C sample occurs only in the ta-C coating as determined by the wear track depth of about 180 nm.

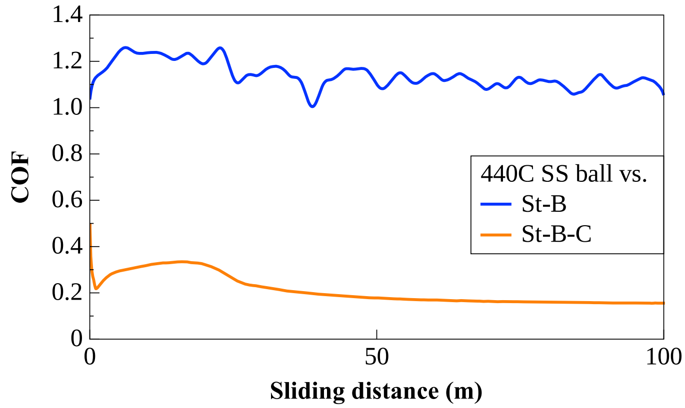

Figure 6. Coefficient of friction (COF) as a function of the sliding distance for samples St-B and St-B-C.

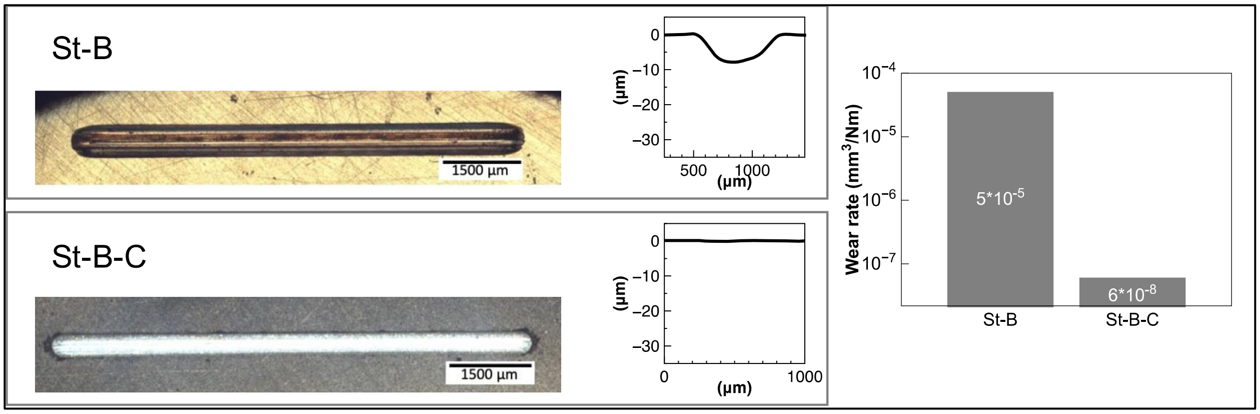

Figure 7. Comparison of wear tracks (left), cross sectional profiles (center) and wear rates (right) for samples St-B and St-B-C.

4.3.3 Corrosion resistance

To investigate the corrosion protection of the substrate by the boride layer for the hybrid system, samples St-C and St-B-C undergo corrosion tests. The specimens were submerged in 15% hydrochloric acid (HCl) for 3 hours and then rinsed in deionized water. After drying in pure nitrogen, the surface morphologies and elemental composition were analyzed in a Scanning Electron Microscope (SEM, tungsten emitter, JEOL JSM-6610 Series) with an attached Electron Dispersive X-ray Spectroscopy (EDS, Oxford) unit.

Preliminary tests revealed, that exposing samples St-C and St-B-C to 15% HCl acid for 3 hours resulted in delamination of the carbon coating in both cases. While delamination for the St-C sample was expected due to pinhole corrosion, the St-B-C samples was anticipated to withstand the exposure because the corrosion resistant boride layer should prevent any corrosion products from forming on the substrate's surface under the coating.

It was revealed through SEM and EDS analysis that the delamination occurred at the interface between the boride and Cr interlayer. To proof that the Cr interlayer is attacked by the solution, **Figure 8** shows the SEM image with EDS analysis of a single Cr coated steel substrate which was partially exposed to the 15% HCl solution for 3 hours. From the comparative EDS analysis of the untreated and exposed surface area, it can be concluded that the Cr coating cannot withstand the 15% HCl and is most likely causing the delamination of the top carbon coating in the St-B-C sample. As a result, the team prepared samples without the Cr interlayer, St-noCr-C and St-B-noCr-C, to evaluate the corrosion resistance of the duplex treatment.

Pinhole corrosion for sample St-noCr-C resulted in typical corrosion products in form of pits on the steel surface as shown in **Figure 9** as well as the delamination of the ta-C coating. EDS analysis in area A (**Figure 9**b) confirmed the existence of corrosion products with an elemental composition of 67% Fe, 22% O, 8% C and 3% Cl, whereas area B in **Figure 9**b) only consists of Fe, C and small traces of O.

Figure 10 shows the surface morphology of the St-B-noCr-C sample before (**Figure 10**b) and after (**Figure 10**c) exposure to the HCl solution. Comparing the overall appearance of St-noCr-C in **Figure 9**a) and St-B-noCr-C in **Figure 10**a), it is obvious that St-B-noCr-C shows no coating delamination and corrosion products. The surface composition and morphology before and after exposure of St-B-noCr-C, show no significant differences with the surface mainly consisting of carbon and some traces of oxygen.

The results of the corrosion studies revealed that the borided layer will protect the substrate from corrosion under a 15% HCl solution environment despite the fact that pinholes might be present in the ta-C coating. However, this is only the case if a Cr interlayer is neglected and the ta-C layer is deposited directly on the Fe_2B interface.

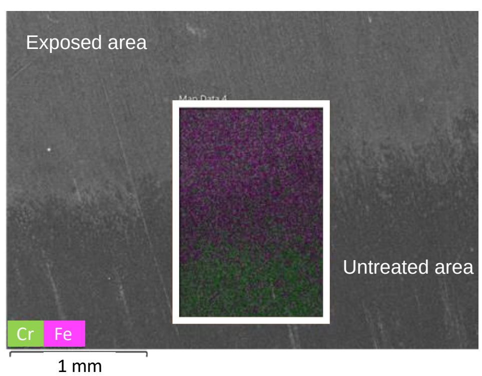

Figure 8. SEM surface image of the Cr coated sample with an exposed and untreated area to 15% HCl for 3 hours and corresponding EDS analysis (Cr indicated in green, Fe indicated in magenta).

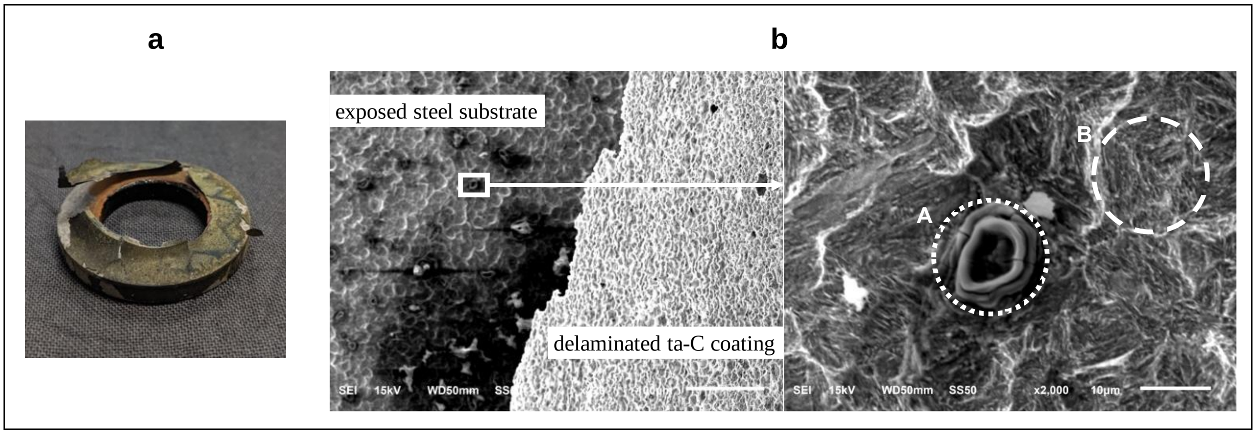

Figure 9. St-noCr-C sample's a) overall appearance and b) SEM images after the exposure to 15% HCl for 3 hours. Delamination of the ta-C coating exposes corrosion pits on the underlying steel surface (left). The magnification of a corrosion pit is shown on the right. EDS analysis was conducted in the areas A and B.

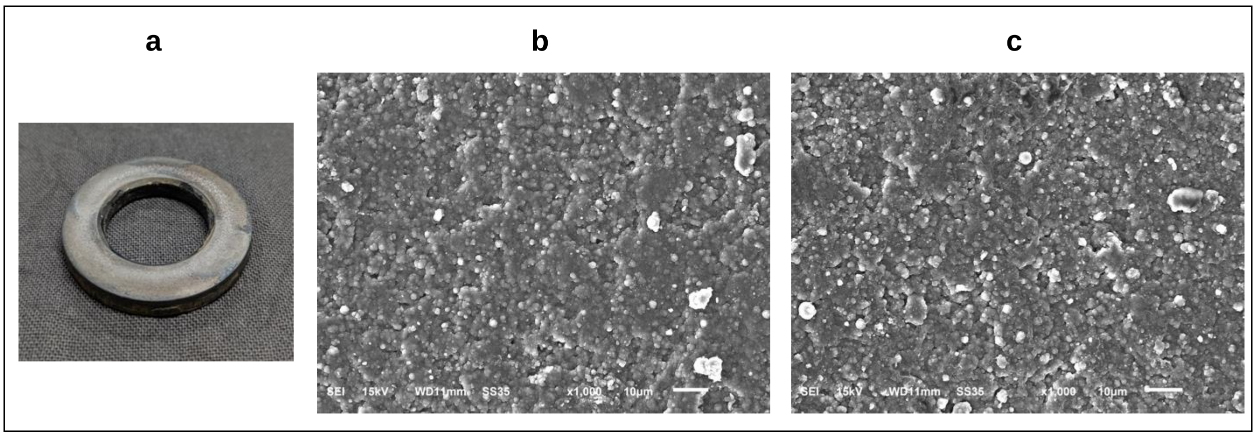

Figure 10. St-B-noCr-C sample's a) overall appearance after exposure to 15% HCl for 3 hours and surface morphologies b) before and c) after exposure.

4.3.4 Fatigue performance

An impact tester (Tricor System Inc.) was used to execute the fatigue performance analysis. All experiments were conducted with a spring-loaded spherical steel indenter (ø 1/8"). For the first set of experiments, all material combinations (St, St-B, St-C, St-B-C) were subjected to a load of 50 psi for 3,600 cycles. The second set of experiments only sampled St-C and St-B-C specimens, which underwent 10,000 cycles at a lower force of 10 psi.

The purpose of the first set of experiments was to compare the failure behavior and resistance to impacts of all materials under high loads and a lower cycle number. The second set of experiments was to evaluate the performance of the hybrid technology for applications under harsh long-term conditions.

The impact marks for the first set of experiments is shown in **Figure 11**. Sample St shows the largest indentation mark with a diameter of 1062 ± 99 µm (**Figure 11**a). St-B (**Figure 11**b) and St-C (**Figure 11**c) show a reduced diameter of 1026 ± 52 µm and 975 ± 24 µm, respectively, which indicates an increased resistance to impact force. The duplex treated sample (St-B-C, **Figure 11**d) was found to have to smallest indentation mark with 828 ± 20 µm. As a result, the size of the indentation mark decreased by 20% from St to St-B-C (**Figure 11**f).

In addition, the bare steel substrate experiences cracking under the described conditions, as shown in **Figure 11**e. No cracking was observed for any other sample. This shows that the yield strength of the substrate material is exceeded, while the other materials do not experience plastic deformation under those conditions. The light spot in the center of the St-C indentation mark in **Figure 11**c is residue from the steel ball, which was verified by EDS and should not be seen as ta-C coating delamination.

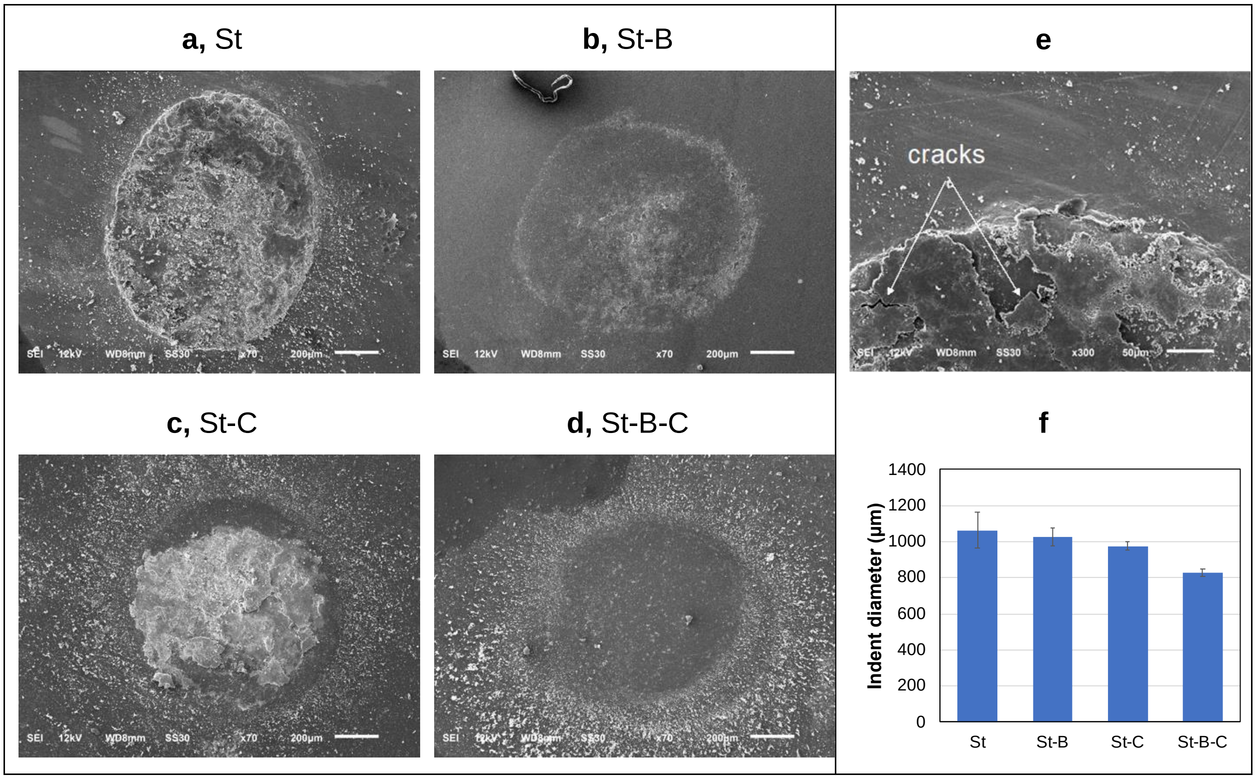

Figure 11. Impact test indentation marks subjected to 3,600 cycles at 50 psi for samples a) St, b) St-B, c) St-C and d) St-B-C. e) Surface cracks on the St sample. f) Indentation mark diameters for all materials.

The results from the second set of experiments is shown in **Figure 12**. In both cases, St-C and St-B-C, no cracking or coating delamination can be observed.

All the test results indicate that the hybrid coating has led to at least 3X increase in the fatigue strength of the steel substrate, which exceeds the target performance of 30% improvement.

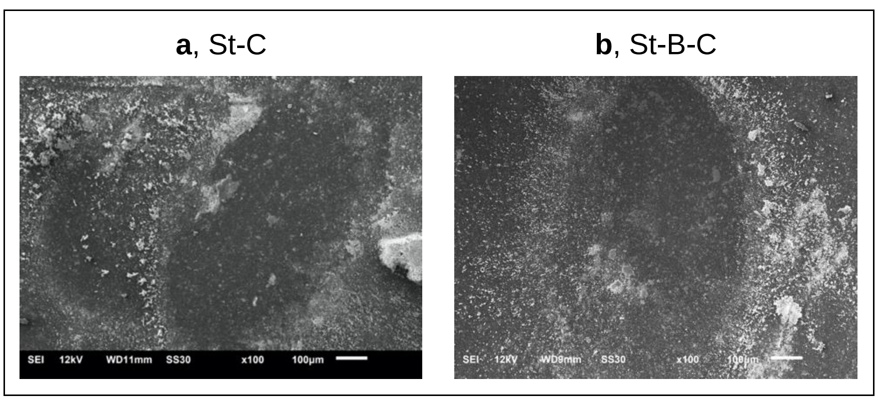

Figure 12. Surface images for a) St-C and b) St-B-C after applying 10 psi for 10,000 cycles.

5 Benefits Assessment

Bearings, especially wind turbine bearings (see details in section 6) have been identified as one potential application for the boride-carbon hybrid technology. **Table 4** summarizes the performance benefits and costs of the boride-carbon hybrid technology for wind turbine bearing applications in comparison to currently employed surface technologies in the field. The main take from this qualitative analysis is, that even though the initial costs of applying this technology are higher due to mostly more process steps, the performance benefits lead to an increased life time of treated parts, which will lower the costs in the long-term. This is mainly due to less maintenance and replacement costs.

Table 4. Qualitative benefit analysis, comparing the hybrid technology to currently employed technologies for bearing applications.

	Boride-carbon (Fe_2B + ta-C)	**Amorphous carbon (a-C:H:Me)** [19]	**Hardened bearing steel**
Base material	AISI 1045	AISI 52100	AISI 52100
Heat treatment of base material	Boriding and quenching replaces hardening	Hardening	Hardening
Coating type	Tetrahedrally amorphous carbon (ta-C)	Hydrogenated, metal-doped amorphous carbon (a-C:H:Me)	N/A
Coating synthesis	Physical vapor deposition	Physical vapor deposition	N/A
Coating treatment time	1.5 h/2 µm	2.0 h/2 µm	N/A
Coating adhesion to substrate	* * * * *	* * * *	N/A
Typical hardness	30 – 70 GPa	12 GPa	8 GPa (64 HRC)
Relative wear resistance	* * * * *	* * * *	* *
Coefficient of friction	0.10 – 0.15	0.20	0.60 – 1.00
Relative corrosion resistance	* * * * *	* *	*
Relative fatigue resistance	* * * * *	* * *	* *
Relative costs	**$ $ $**	**$ $**	**$**

6 Commercialization

We have identified typical applications of the St-B-C duplex coatings. An example is bearing for windmill. Bearings, especially wind turbine bearings (main shaft bearing, see **Figure 13**), have been identified as one potential application for the boride-carbon hybrid technology. Bearing rollers and balls are tribological components that experience high loads and specifically in off-shore installations are exposed to a corrosive environment. Additionally, repair costs for tribological failures are extremely high, which affects the overall generating costs per kW-hour and therefore the competitiveness of wind energy in the overall energy market [20].

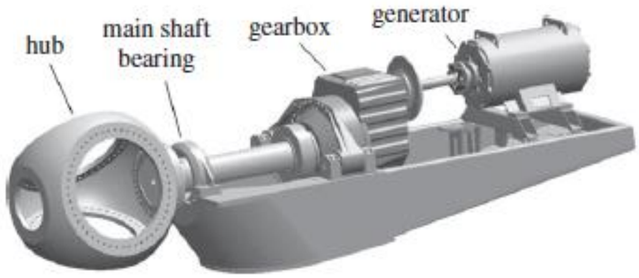

Figure 13. Mechanical assembly of a wind turbine [20]. The main shaft bearing is the bearing of interest.

To investigate the coating performance of the duplex treatment for typical load conditions in wind turbine bearings, our team has engaged with a team at Argonne National Laboratory (ANL) to investigate the process of white etching crack initiation in bearing steels. For that, Fraunhofer USA, Inc. coated test specimens as shown in **Figure 14**a with ta-C which will be tested in the PCS Instruments' micro-pitting rig at ANL (**Figure 14**b).

Since this cooperation with ANL was established during the last month of the project, the team was not able to apply the full hybrid coating to the test specimens. But since the top ta-C coating determines the tribological performance, this test will confirm if it's worth investigating this application further.

It should be also mentioned, that this work is not being conducted under the current DOE contract. Hence, this performance measure is important for future potential customer engagement and the commercialization of the technology.

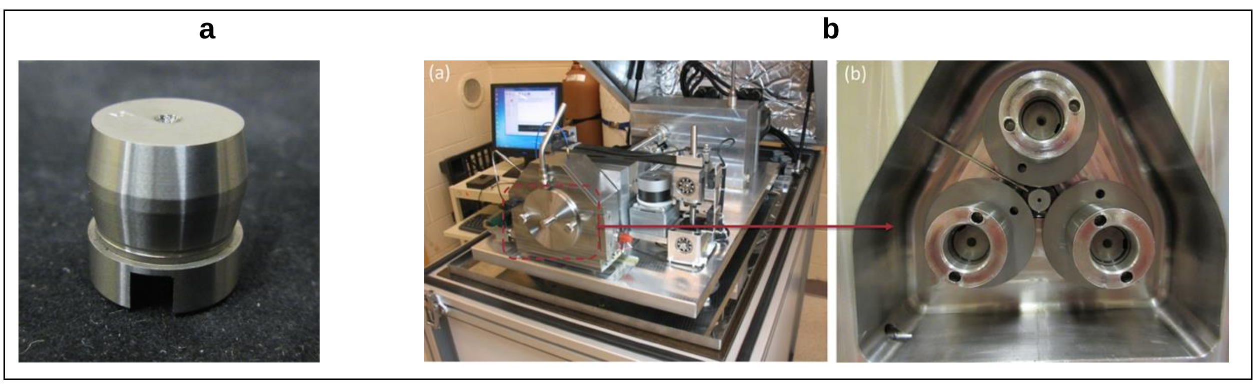

Figure 14. PCS Instruments' micro-pitting rig, a) test specimen and b) test setup [21].

7 Accomplishments

The first part of this project focused on the demonstration of technical performance on laboratory scale, which mainly included the preparation and iterative optimization of the duplex layer design to accomplish the targeted performance on test samples. We achieved the following performance goals which make this technology promising for applications in harsh service conditions:

- Carbon-on-boride achieved with HF1 adhesion
- FEA model of the technology's layer structure
- Coefficient of friction below 0.2 with a wear rate of 6*10-8 $mm^3 N^{-1} m^{-1}$
- Corrosion resistance to 15% hydrochloric acid for a specified time of 3 hours
- Increase in fatigue strength by a factor of 3.

Additionally, the team showed the potential of the duplex technology for windmill bearing applications and presented a benefit analysis based on that specific real-world application. Beyond the project goals, the team engaged with a team at ANL that specializes on the characterization of windmill bearing materials to further back up the technology for this potential application.

A manuscript that is summarizing the results is under preparation.

8 Conclusions

This project is successfully completed through close collaborations among Michigan State University, Fraunhofer USA Center for Coatings and Diamond Technologies, and Argonne National Laboratory. The team has achieved the planned milestones specified in by the project SOPO.

The team has validated the excellent wear- and corrosion-resistance of the boride-carbon duplex coatings under harsh conditions, such as strong acid and large impact loads over extended periods.

Modeling has proven effective in predicting the coatings structures required for specific loadings.

There are numerous potential applications of the boride-carbon hybrid technology. A representative application is bearing shaft coatings for off-shore windmill. Tests are still underway.

9 Recommendations

This project successfully validated that the boride-carbon hybrid-technology can withstand harsh conditions. A possible approach to commercialization is to transfer the technology to a startup or an existing coatings company.

10 References

[1] Earth Overshoot Day 2016, (n.d.). https://en.wikipedia.org/wiki/Earth_Overshoot_Day.

[2] W. Musial, S. Butterfield, B. Mcniff, Improving wind turbine gearbox reliability, in: Eur. Wind Energy Conf. Exhib. 2007, EWEC 2007, 2007: pp. 1770–1779. http://www.osti.gov/bridge (accessed November 5, 2020).

[3] Status and Applications of Diamond and Diamond-Like Materials : An Emerging Technology, Committee on Superhard Materials, Commission on Engineering and Technical Systems, National Reserach Council, 1990.

[4] C. Donnet, A. Erdemir, eds., Tribology of Diamond-like Carbon Films, Springer Science, 2008. doi:10.1016/s1369-7021(08)70060-9.

[5] V.S. Veerasamy, H.A. Luten, R.H. Petrmichl, S. V. Thomsen, Diamond-like amorphous carbon coatings for large areas of glass, in: Thin Solid Films, 2003: pp. 1–10. doi:10.1016/S0040-6090(03)00929-5.

[6] A. Inspektor, E.J. Oles, C.E. Bauer, Theory and practice in diamond coated metal-cutting tools, Int. J. Refract. Met. Hard Mater. 15 (1997) 49–56. doi:10.1016/S0263-4368(96)00045-5.

[7] C.P.O. Treutler, Industrial use of plasma-deposited coatings for components of automotive fuel injection systems, Surf. Coatings Technol. 200 (2005) 1969–1975. doi:10.1016/j.surfcoat.2005.08.012.

[8] S. Hoppe, T. Kantola, DuroGlide® - New Generation Piston Ring Coating for Fuel-Efficient Commercial Vehicle Engines, SAE Tech. Pap. 2014-January (2014). doi:10.4271/2014-01-2323.

[9] A. Erdemir, O. Eryilmaz, V. Sista, Ultra-fast Boriding for Improved Energy Efficiency and Reduced Emissions in Materials Processing, 2008. www.anl.gov. (accessed August 13, 2020).

[10] G. Kartal, O.L. Eryilmaz, G. Krumdick, A. Erdemir, S. Timur, Kinetics of electrochemical boriding of low carbon steel, Appl. Surf. Sci. 257 (2011) 6928–6934. doi:10.1016/j.apsusc.2011.03.034.

[11] G. Kartal, S. Timur, O.L. Eryilmaz, A. Erdemir, Influence of process duration on structure and chemistry of borided low carbon steel, Surf. Coatings Technol. 205 (2010) 1578–1583. doi:10.1016/j.surfcoat.2010.08.050.

[12] G. Kartal, O. Kahvecioglu, S. Timur, Investigating the morphology and corrosion behavior of electrochemically borided steel, Surf. Coatings Technol. 200 (2006) 3590–3593. doi:10.1016/j.surfcoat.2005.02.210.

[13] G. Kartal, S. Timur, V. Sista, O.L. Eryilmaz, A. Erdemir, The growth of single Fe2B phase on low carbon steel via phase homogenization in electrochemical boriding (PHEB), Surf. Coatings Technol. 206 (2011) 2005–2011. doi:10.1016/j.surfcoat.2011.08.049.

[14] H.J. Scheibe, B. Schultrich, D. Drescher, Laser-induced vacuum arc (Laser Arc) and its application for deposition of hard amorphous carbon films, Surf. Coatings Technol. 74–75 (1995) 813–818. doi:10.1016/0257-8972(95)08280-8.

[15] H.J. Scheibe, D. Drescher, B. Schultrich, M. Falz, G. Leonhardt, R. Wilberg, The laser-arc: A new industrial technology for effective deposition of hard amorphous carbon films, Surf. Coatings Technol. 85 (1996) 209–214. doi:10.1016/0257-8972(95)02648-7.

[16] N. Vidakis, A. Antoniadis, N. Bilalis, The VDI 3198 indentation test evaluation of a reliable qualitative control for layered compounds, in: J. Mater. Process. Technol., Elsevier, 2003: pp. 481–485. doi:10.1016/S0924-0136(03)00300-5.

[17] Z. Hu, K.J. Lynne, S.P. Markondapatnaikuni, F. Delfanian, Material elastic-plastic property characterization by nanoindentation testing coupled with computer modeling, Mater. Sci. Eng. A. 587 (2013) 268–282. doi:10.1016/j.msea.2013.08.071.

[18] E.E. Cabezas, D.J. Celentano, Experimental and numerical analysis of the tensile test using sheet specimens, Finite Elem. Anal. Des. 40 (2004) 555–575. doi:10.1016/S0168-874X(03)00096-9.

[19] D. de Garavilla, X. Zhou, Extending Bearing Life in Wind Turbine Mainshafts | Power Engineering, (2019). https://www.windpowerengineering.com/extending-main-shaft-bearing-life-in-wind-turbines/ (accessed November 12, 2020).

[20] M.N. Kotzalas, G.L. Doll, Tribological advancements for reliable wind turbine performance, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 368 (2010) 4829–4850. doi:10.1098/rsta.2010.0194.

[21] B. Gould, A. Greco, Investigating the Process of White Etching Crack Initiation in Bearing Steel, Tribol. Lett. 62 (2016) 1–14. doi:10.1007/s11249-016-0673-z.