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Ultracoatings: Enabling Energy and Power Solutions in High Contact Stress Environments through next-generation Nanocoatings

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Abbreviations and Acronyms

AFM	Atomic Force Microscopy
ASTM	American Society for Testing Materials
at.	Atomic
BAM	AlMgB ₁₄ -based material
BAMC	AlMgB ₁₄ -TiB ₂ +C coating
BTU	British thermal unit(s)
CVD	Chemical Vapor Deposition
deg	Degree(s)
DOE	Department of Energy
DSP	Dry Solids Pump
EDS	Electron dispersion spectroscopy
GPM	Gallon(s) per Minute
h	Hour(s)
HT	High Temperature
Hz	Hertz
IC	Innovation Center (Eaton)
IPR	Inch(es) per Revolution
in	Inch(es)
K-WATT	Kilowatts
kW	Kilowatts
LOC	Length of Cut
L	Liters
lbF	Pounds-Force
LT	Low Temperature
MTBF	Mean Time between Failures
min	Minute(s)
N	Newton(s)
NDA	Non-Disclosure Agreement
ORNL	Oak Ridge National Laboratory
PLD	Pulsed Laser Deposition
Psi	Pounds per Square Inch
PVD	Physical Vapor Deposition
REV	Revolution(s)
RPM	Revolution(s) per Minute
sec	Second(s)
SEM	Scanning electron microscopy
SFM	Surface Foot per Minute
TEM	Transmission electron microscopy
TRL	Technology Readiness Level
TZB	(Ti, Zr)B ₂ material or coating
wt.	Weight
XRD	X-ray diffraction

1.0 Executive Summary

This report summarizes the work performed by an Eaton-led project team under a 1-year DOE-ITP Grand Challenge sponsored project titled, “Ultracoatings – Enabling Energy and Power Solutions in High Contact Stress Environments through next-generation Nanocoatings.” The Report serves as the project deliverable for the Grant # DE-EE0003490.

1.1 Project Objective

The primary objective of this project was the development of thin film nanocoatings derived to address improved durability and performance in high contact stress (1 GPa and above) environments. A review of commercially available, industrial-grade, low friction coatings showed that, prior to the development of nanocomposite materials like $\text{AlMgB}_{14}\text{-TiB}_2$, interfacial contact pressures nearing 1GPa (~150ksi) inherently limit surface engineering solutions like WC, TiN, TiAlN, and so forth. Previous work on AlMgB_{14} composites and their vapor-deposited coating derivatives led the way to additional research on a variety of novel compositions, including, but not limited to $(\text{Ti, Zr})\text{B}_2$, a single phase composite shown to exhibit extreme wear resistance. Other materials explored by Ames Laboratory included $\text{AlMgB}_{14}\text{-IrB}$, $\text{AlMgB}_{14}\text{-HfB}_2$, $\text{AlB}_{12}\text{-CrB}_2$, and $\text{Al}_4\text{SiC}_4\text{-TiC}$. In each composite, the constituent phases were selected because of their similar surface energies, intrinsic wetting characteristics, and potential for high strength. The key focus of the project is to transfer the benefits of these materials to industrial scale applications and enable operation and sustained performance in extreme environments. The Ultracoatings technology, as it was titled, would be capable of sustaining higher load-carrying capacity than current state-of-the-art coating compositions, while maintaining low friction. Examples of applications benefiting from such technological advancements would include transmission gears, heavy-duty clutches, aerospace pump components and conveyance systems, hydraulics, automotive supercharger components, engine timing chains, and components used in Pratt & Whitney Rocketdyne’s coal gasifier. In each of the respective industrial application spaces, energy savings would be realized through the reduction of wear and, subsequently, eliminating re-work or replacement of components during their expected field service.

1.2 Purpose

While a variety of novel materials were considered for possible exploration at the onset of the project, the one year timeframe and available resources served to limit the research focus to $(\text{Ti, Zr})\text{B}_2$ and to a lesser extent, Al_4SiC_4 . To accomplish the objective noted above, the following approach was developed:

The primary focus of the program was to evaluate and screen the performance of the selected Ultracoatings compositions and identify end-use application spaces offering the potential for maximum energy savings. This process included friction and wear testing on both sample coupons designed to mimic production-intent materials, surfaces, and environmental conditions as well as end-use prototype components. The main project deliverables used to gage the project’s adherence to its objective were:

- Development of a coating/substrate pairing that exhibits wear rate of 0.1 mg/hour or lower at a 1GPa contact pressure, while achieving a maximum coating cost of \$0.10/cm².

- Demonstrate the aforementioned wear rate in both lubricated and starved lubrication conditions.

1.3 Results

The key results from the work are discussed below.

1.3.1 Characterization

Characterization of the (Ti,Zr)B₂ (TZB) deposited films revealed that it can be deposited as a single phase structure using pulsed laser deposition processing (PLD). The physical vapor deposition (PVD) coatings obtained from a commercial sputtering target were observed to be multi-phased in nature because of the target manufacturing process. Further characterization of the PVD-deposited TZB films revealed that they are capable of sustaining high contact stress (greater than 1 GPa) performance and, accordingly, have demonstrated coefficients of frictions as low as 0.09.

1.3.2 Functional Testing

Several applications were considered for immediate implementation of the Ultracoatings technology, including a shaft that drives an aerospace fuel pump. For this particular product, the contact pressures were known to exceed 2 GPa, and so it was unclear if a coated TZB shaft would survive the product durability testing plan. Upon completion of over 200 hours of low lubrication testing with minimal wear to the shaft, however, it was evident that the coating had enabled a level of performance not previously seen. As of the completion of this report, the shaft has gone on to pass an additional 1000 hours of durability testing with minimal wear.

For the engine timing chain application, the immediate benefits of the coating were not realized in the single evaluation test performed. A prime consideration to the mixed performance is that the multi-phase coating deposited by Eaton, using PVD methods, may not be producing the synergistic level of wear resistance observed for the single phase TZB, which was produced by PLD methods at Ames National Lab.

1.4 Conclusions

This project demonstrated that application of the TZB Ultracoatings technology to industrial materials will enhance their wear resistance.

Highlights of the coating research throughout the project include the following:

- Development of PLD processing techniques to deposit (Ti,Zr)B₂ to industrial-scale components and substrates
- Although the specific composition of the coating was not tailored for low friction performance, friction and wear evaluations of the material demonstrated a coefficient of sliding friction as low as 0.09. This suggests that varying the percentage of TiB₂ present in the composite could enhance the materials' performance in water-based lubricants.
- PVD-TZB applied to an industrial drive shaft for a production-intent aerospace fuel pump survived over 200 hours of low-lubrication testing, with contact pressures exceeding 2

GPa (again, the original plan for the material was to demonstrate limited wear at contact pressures exceeding only 1 GPa).

- The TZB material as a PVD-sputtered coating was shown to exhibit high wear resistance (0.06 mg/hour) at high contact pressures (+1 GPa), well beyond the performance of previously-developed AlMgB₁₄-TiB₂-based coatings.

Full implementation of the technology into the targeted markets equates to a U.S.-based energy savings potential of over 100 trillion BTU per year by 2030. This exceeds the original projection of 60 TBTU/year by 2030.

1.5 Recommendations

There are many unanswered questions regarding the nature of the TZB coating and the differences in performance between single-phase and multi-phase depositions. Further R&D work would help define how far this particular material system can be advanced in terms of low friction, wear resistance, and durability enhancement.

1.6 Commercialization

Based upon the performance enhancements observed in laboratory-level testing and successful completion of the low-lubricity, high contact stress fuel pump testing at Eaton, the following commercialization steps are being taken:

1.6.1 Aerospace Components

The fuel pump system that is the lead application for the Ultracoatings technology is currently positioned at a technology readiness level (TRL) of 6. This level indicates that the system has been shown to perform in functional testing. Through application of the Ultracoatings technology, the system passed cyclic loading, the low-lubrication, and a 1000 hour durability schedule. Next steps planned are the completion of a system-level design review with Eaton's executive management team, discussion on the performance characteristics to a selected end customer, and the external sourcing of the PVD coating process for this application.

1.6.2 Engine Timing Components

Borg Warner Morse TEC plans to assess the performance of the Ultracoatings technology in other, severe service environments beyond those originally targeted for the project. Work is planned to evaluate the Ultracoatings technology in direct injection and diesel engine conditions.

1.6.3 Coal Gasifier Components

The dry solids pump and other elements of the PWR gasification system are currently in the development phase. Discussions continue on the application of the Ultracoatings technology for those specific components. Expectations are for a Demonstration Plant to be commissioned in 2013.

The reader is referred to Section 6.0 (Commercialization) for specific details regarding the commercialization pathways for these coatings.

2.0 Introduction

In many industrial application spaces that involve high interface contact stresses, increased wear and reduced durability are simply tolerated and the associated components are replaced or retrofitted. In spite of the measurable benefits observed in thin-film coatings, including those at the leading edge of technology like Diamond-Like Carbon (DLC), and advanced processing technologies such as High Power Pulsed Plasma Magnetron Sputtering (HiPPMS), Plasma Assisted Physical Vapor Deposition (PAPVD), and Plasma Assisted Chemical Vapor Deposition (PACVD), these coatings cannot sustain contact stress levels in the 200 to 300 ksi range. Thus there is a unique opportunity to “push the envelope” with recent advances in surface engineering technologies that are currently under development at the laboratory level. The development of functionally-graded coating compositions may offer enhanced lubricity (even beyond that of “tailored” nano-level compositions like AlMgB₁₄-TiB₂) with high wear resistance.

The industrial partners of this project, Eaton Corporation, Borg-Warner Morse TEC, and Pratt & Whitney Rocketdyne (PWR), propose transformational development of new coatings that are designed from the individual constituent phases to withstand higher contact stresses that far exceed that of any current surface engineered technology. While the new wear resistant compositions have not yet been proven amenable to deposition as a thin film coating, this concern is mitigated by several factors: functionally graded compositions are considered a proven technology^[1], bulk material properties of nanocomposite materials have, in fact, been transferred to the resultant thin film coatings^[2,3,4] and the assembled partners have a wide breadth of experience with the development of novel, wear-resistant materials.

Given the large volume of components and systems that are regularly replaced in severe service environments, the need to accelerate and transfer the benefits associated with the Ultracoatings proposed has never been greater. What has made this project immediately beneficial to the targeted application spaces is, first and foremost, a substantial reduction in energy intensity of industrial processing. Secondly, given the diverse product portfolio under each industrial partner, the opportunities associated with cross-implementation of the technology are even greater. Thirdly, the expected learning curve(s) to develop the materials in question is/are expected to be minimal. Lastly, previous experience has shown that multi-party contracts benefit from the input of all partners, and that technical challenges can be mitigated in an expeditious manner.

To ensure greater market acceptance and adoptance, the project was guided by a net-zero cost implementation approach. In other words, any performance enhancements or gains in durability would be achieved by using alternative, less costly substrate materials. As an example from previous research, in certain applications 52100 steel can be substituted for heat-treated M2 steel when a wear-resistant nanocoating is applied. As the relative cost differential between M2 and 52100 is a factor of 13, any incurred cost add associated with sourcing the coating or adding capital to an existing manufacturing site would be negligible or nearly negligible. In some cases, implementation of the coatings technology would even result in an end-use cost savings (adding the benefits of components and systems that fundamentally last longer than their non-coated counterparts).

Although many potential applications exist for wear resistant materials, the following application spaces were selected as key initial opportunities for development in this project:

- 1) Aerospace hydraulic and fuel system components to enhance the wear resistance in low lubricity environments. In many cases, these products utilize non-flammable lubricants that do not lend themselves to mixed or elastohydrodynamic lubrication regimes.. Accordingly, any coatings developed for these markets will need to survive in metal-on-metal or boundary lubrication conditions
- 2) Engine timing components are exposed to a variety of temperature extremes and the constituent components see contact pressures ranging from below 1GPa to in excess of 2GPa. Any wear incurred on the chains leads to reduced engine efficiency and, if left unattended, can present a safety concern to vehicle operation.
- 3) coal gasifiers that include the use of a dry solids pump, the immediate need is for a surface that can withstand an abrasive material consisting of coal and other hard, potentially abrasive particles.

At the beginning of the project, the goal was set to establish a coating/substrate pairing that could withstand a pressure * velocity product ($P*V$) of 70,000 MPa*m/s. This goal was subsequently updated to reflect use of SMART project objectives (specific, measurable, achievable, realistic, and timely).

The best representation of the modified goal is as such:

Development of a coating/substrate pairing that exhibits an erosive wear rate of $0.2\text{mm}^3/\text{kg}$ or lower and capable of withstanding a 1GPa contact pressure, while achieving a maximum coating cost of $\$0.10/\text{cm}^2$.

The scope of the project included development of two coating deposition methods – pulse laser deposition (PLD) and physical vapor deposition (PVD). Scale up and quality control were important considerations.

3.0 Background

3.1 Current State of Industrial Coatings

Given the potential number of applications that would benefit from a coating capable of surviving high contact stresses, it is important to first review a selection of the many compositions currently available. A review of literature and market data shows that there are many variants of surface treatments. None have proven satisfactory for the 1GPa levels desired. Given this, the ultracoatings that were the focus of this project would need to demonstrate an advantage in performance beyond that which is available today.

3.1.1 Cr or Ni-Cr electroplating

Electroplating Cr or Ni-Cr alloy onto components has long been used to harden component's surfaces and to improve efficiency and wear resistance. These coatings can be applied without the need for a vacuum chamber, which imposes size limitations on PVD coatings and raises cost. Unfortunately, the Cr in these coatings must be applied using hexavalent (Cr^{+6}) salts in the electrolytic bath. Cr^{+6} is highly toxic and poses a threat to both workers and the environment^[5]. For these reasons, use of Cr electroplating has declined sharply in recent years, and many organizations are striving to eliminate electroplated Cr from their products all together^[6].

Even when Cr electroplating is used, the application procedure is complex and costly, requiring multiple baths to first clean the component (usually steel), then apply a thin strike/bond coating of Cu and/or Ni to assure adhesion to the substrate. It is worth noting that Cr is brittle and has a much lower coefficient of thermal expansion than steel^[7], and so the Cr coating usually contains a microscopic network of cracks, which do not survive high stress applications. Pack coating and gas coating techniques exist to apply Cr coatings without the use of Cr^{+6} , but these processes require high temperatures (900°C or higher) that ruin the impact of the prior heat treatment. The outcome is a rough, dull finish that has a much higher coefficient of sliding friction than the Cr electroplating process.

3.1.2 TiN

Titanium nitride (TiN) is widely used to make a hard, conductive coating on cutting tools, medical implants, and electronic assemblies. It is typically applied via physical vapor deposition or chemical vapor deposition and leaves coated parts with a distinctive gold color appearance. TiN coatings are electrically conductive, allowing use for specific electronic and switchgear applications. TiN coatings are perhaps best known for extending the service life of specific tool steels that are commonly used for drill bits, mills, and lathes. TiN requires a vacuum chamber for PVD or CVD coating and it has a coefficient of thermal expansion ($9 \times 10^{-6}/\text{C}^\circ$) close to those of steel and titanium^[8]. TiN coatings perform well in the machining of steel and cast iron. However, TiN is limited in terms of its ability to survive high contact stresses.

3.1.3 TiAlN

TiAlN is a family of materials similar to TiN, but it possesses greater hardness and oxidation resistance. TiAlN is available in a range of compositions through varying the Ti:Al ratios. Its hardness varies between 26 and 33 GPa^[9], higher than that of TiN and is usually applied to steel cutting tools by physical vapor deposition methods to improve wear resistance.

TiAlN is oxidation resistant up to about 800°C, approximately 300°C higher than TiN^[10]. Above 850°C (approximate), TiAlN begins to segregate into two phases (AlN and TiN). The coefficient of friction (dry) is 0.4^[11] against uncoated steel at room temperature and its coefficient of thermal expansion is approximately $7.5 (10^{-6}) \text{ }^{\circ}\text{C}^{-1}$, extrapolated from TiN and AlN respectively.

3.1.4 Diamond-like Carbon (DLC)

Diamond-like carbon (DLC) coatings have gained wide acceptance in recent years as hard, protective coatings for components as diverse as razor blades, computer hard disk readers, and artificial hearts. DLC coatings are applied in cathodic arc or chemical vapor deposition vacuum chambers and have a wide range of compositions and crystal structures. The coatings containing little or no graphite or hydrogen provide the highest hardness but are the most difficult to produce. DLC coatings may contain cubic, hexagonal, or amorphous diamond, often in nanoscale nodules that nucleate independently from one another during the deposition process and grow until they encounter their neighboring nodules.

DLC coatings can exhibit hardness values as high as that of pure, crystalline diamond (hardness between 40-60 GPa) and have a coefficient of sliding friction of about 0.1, which is lower than that of most metals^[12]. They maintain their low coefficient of friction in vacuum, whereas graphite and boride coatings do not because they require small amounts of water vapor or liquid water to form their lubricious surfaces. As such, DLC coatings are preferred in spacecraft or vacuum system applications.

Diamond-like carbon thin films have two major disadvantages when compared to other compositions. First, they are reactive with Fe and Ti, so they are ill suited to use on steel or titanium alloys in applications involving elevated temperatures. For example, DLC results in poor performance on cutting tools because the carbon dissolves into the Fe work piece at the temperatures normally encountered during machining^[13,14]. This leads to rapid removal of the hard, wear-resistant surface. Second, the coefficient of thermal expansion of diamond is near zero^[15] and may result in a mismatch to steel ($11.5 \times 10^{-6}/^{\circ}\text{C}$) or titanium ($8.4 \times 10^{-6}/^{\circ}\text{C}$). Thus, DLC coatings tend to crack or spall on these metal substrates if exposed to elevated temperatures during service.

3.1.5 TiB₂

TiB₂ is a refractory (Tm.pt. = 3200°C), hard (25 to 30 GPa) material with an unusually high thermal conductivity (96 W/m-K) and low electrical resistivity ($15\mu\Omega\text{-cm}$) for a non-metallic material^[16]. TiB₂ resists oxidation well up to approximately 1000°C and it is sometimes used as a coating on steel or other substrates to improve wear resistance. Bulk TiB₂ is a somewhat difficult material to process into PVD targets, since it requires sintering temperatures above 1750°C to densify. At this elevated temperature, grain growth can progress rapidly, resulting in an undesirably coarse-grained material. The anisotropy of TiB₂'s hexagonal lattice makes coarse-grained specimens vulnerable to cracking during temperature changes because the coefficient of thermal expansion varies from 6.4 to 9.2 ($10^{-6}) \text{ }^{\circ}\text{C}^{-1}$, depending on crystallographic orientation. To reduce this problem, Fe, Cr, or C are sometimes added to TiB₂ powders as sintering aids. The coefficient of friction of non-lubricated TiB₂ is 0.7 to 0.9 at room temperature but drops to as low as 0.25 at 800°C^[17].

3.1.6 Anodizing

Anodizing treatments harden metal surfaces by deliberately thickening the metal's naturally occurring oxide surface layer. As most oxides are harder than their parent metal, surface hardness increases can be achieved, thus enhancing the wear resistance. An anodized surface treatment is achieved by making the part to be anodized the anode in an electrolytic cell of chromic acid (Cr^{+6}), sulfuric acid, or one of several other organic acids. While anodizing does not require a vacuum system and the coating is electrically insulating, the anodized surface is porous unless special processing steps are performed. In addition, the coefficient of friction for oxides are generally greater than 0.1^[18], and their measured hardness is about one half that of boride compositions. Perhaps the greatest drawback of anodizing is that it cannot be used to coat iron or steel components, because the oxide layer does not adhere to iron. (More than 90% of all metal products are steel, stainless steel, or cast iron). Conversely, anodizing does work well on Al, Ti, Mg, Zn, Nb, and Ta. It cannot withstand high contact stresses, which is the goal of this project.

3.1.7 AlMgB₁₄-TiB₂

In a previous Eaton-led DOE project (DE-FG36-06GO16054)^[19], a new family of wear-resistant nanocoatings based on AlMgB₁₄+TiB₂ was developed for industrial applications such as hydraulic pumps and high-performance cutting tools for Ti-based alloys. Through physical vapor deposition processing, the resulting nanocomposite coatings combine the wear resistance characteristic of hard materials (e.g. the AlMgB₁₄) with a regenerating lubricant. Within the top layers (10-20 nm) of the nanocomposite coating, the same TiB₂ phase used to enhance the strength and provide ductility to the otherwise brittle AlMgB₁₄ material reacts with available oxygen to form boron oxide. As the TiB₂ constituent continues to react, layers of boric acid form at the surface. This affords an exceptionally low coefficient of friction (as low as 0.02) to the coating. Physical vapor deposition processing parameters were evaluated and optimized during the project to minimize the difficulties common to transitioning a laboratory-scale process or technology to a salable product. Coating process times and temperatures, process gas flows and ramp rates, and a number of other adjustable parameters were optimized based on the results of testing and coating characterization. The overriding goal of all of these efforts was a repeatable coating process that yields the benefits observed in the laboratory, independent of the intended product or market.

From the perspective of industrial hydraulics, the AlMgB₁₄ nanocoatings technology progressed beyond baseline laboratory efficiency tests into measurable energy savings and enhancements to product durability. Eaton Corporation identified three key markets that would benefit from implementation: industrial vane pumps, orbiting valve-in-star hydraulic motors, and variable displacement piston pumps. In the vane pump application, the overall product efficiency was improved by as much as 11%. Similar results were observed with the hydraulic motors tested, whereby efficiency gains of over 10% were noted. For the variable displacement piston pump line, the overall efficiency was improved by 5%.

In the high-performance tooling sector, the most significant gains in productivity (and, accordingly, the efficiency of the machining process as a whole) were associated with the roughing and finishing of titanium components for aerospace systems. Use of the AlMgB₁₄ nanocoating in customer field tests clearly demonstrated that the coated tools were able to withstand machining rates as high as 500 surface feet per minute (limited only by the substrate material), with relatively low flank wear when compared to other industrial offerings.

Another key enabler to producing viable commercial opportunities associated with the new technologies proposed is the idea of a net-cost implementation strategy. Any costs incurred by additional processing steps (e.g. magnetron sputtering) would be offset by the selection of alternative substrate systems, where possible. In previous work, 52100 steel was considered as a low-cost alternative to heat-treated M2 steel. In that use case, the cost differential between the two materials served as an appropriate means to enhance the attractiveness of the coating in low-cost hydraulic markets. A similar approach was planned for widespread implementation, again where appropriate, for the Ultracoatings.

Full implementation of the nanocoatings technology into the industrial hydraulic and cutting tool markets equates to an energy savings of 46 trillion BTU/year by 2030. U.S.-based GHG emissions associated with the markets identified would fall accordingly, dropping by as much as 50,000 tonnes annually

3.2 Specific Area Being Addressed

Of the materials initially identified for development as Ultracoatings, (Ti, Zr)B₂ was considered as the most near-term opportunity for potential commercial implementation due to its superior erosive wear performance^[20]. The research performed illustrates that (Ti, Zr)B₂ as a material exhibits a steady state erosion rate as low as 0.14 mm³/kg, which compares very favorably with state-of-the-art binderless WC (RocTec 500) that has an erosion rate of 0.2 mm³/kg. For comparison to a previously developed ultra-hard material, the steady-state erosion rate of AlMgB₁₄-TiB₂ composites range from 0.5 mm³/kg to 1.5 mm³/kg, depending on phase size, distribution, and percentage of spinel present. A graphical representation of the erosive wear resistance of the TZB material is illustrated in **Figure 3.2-1**. Note that, in comparison to WC-Co, a known wear-resistant material, the TZB wear rate is an order of magnitude less. During the first 10 minutes of testing the tungsten carbide experienced 3mg of cumulative mass loss associated with erosion. In contrast, the TZB material experienced less than 0.1mg of cumulative mass loss.

Figure 3.2-1. Comparison of steady-state erosive wear rates between conventional cemented carbide (WC/6%Co), wear-resistant binderless WC (RocTec 500), various AlMgB₁₄-TiB₂ compositions, and the down-selected TZB composition.

In addition to the TZB composition, only Al₄SiC₄ was explored in further detail due to the program's condensed one-year time frame.

3.3 Statement of Project Objectives

3.3.1 Project Milestones

The following milestones were established to measure the success of the project upon its completion:

Milestone 1: Demonstration of severe service wear resistance

A key outcome of the project was in the development of one or more composite coating and interlayer combinations that demonstrate excellent adhesion to steel substrates, as determined by Rockwell "C" indentation tests, and that showed improved resistance to diamond scratch testing compared to baseline AlMgB₁₄/TiB₂ composites and other industry leading materials, such as diamond-like carbon (DLC), TiC, and VC. At present, there are many industrial applications where the durability of components is directly affected by coating quality. Any improvements in quality would directly impact the reliability, service uptime, and the amount of energy consumed during repairs.

Note that this milestone was reviewed by the team and modified slightly to reflect the SMART goal methodology. SMART goals are defined as (S)pecific, (M)easurable, (A)chievable, (R)ealistic, and (T)imely. Concerning the focus of the team, the best representation of the modified goal is as such:

Development of a coating/substrate pairing that exhibits an erosive wear rate of 0.2mm³/kg or lower at a 1GPa contact pressure, while achieving a maximum coating cost of \$0.10/cm². A transfer function was utilized to convert the erosion wear data into an equivalent per-hour wear rate, that being a value lower than 0.1mg/hour at a 1GPa (150ksi) contact pressure. Note that

the current state of the art, RocTec 500, exhibits a wear rate of $0.2\text{mm}^3/\text{kg}$, and so our solution was targeted to be at least as wear resistant as the industry best.

Milestone 2: Survival at high contact stresses in a variety of lubrication regimes

A second key outcome of this project was to demonstrate that the Ultracoatings selected can operate under high contact stress levels of 150 to 300 ksi (1-2 GPa) in both lubricated and starved lubrication conditions. There is an immediate need in many energy-consuming markets for components and systems to perform at higher stresses, in spite of any environmental limitations. A coating/substrate system capable of a high level of performance at high contact loads under varying degrees of lubrication would be very impactful.

3.3.2 Tasks

The following tasks were performed to accomplish the project goals and objectives.

Task 1: Research and develop new materials and processes

The recently-discovered, wear resistant compositions, many of which show superior wear behavior in bulk form compared with current-generation $\text{AlMgB}_{14}\text{-TiB}_2$ compositions, were down-selected. The compositions that were synthesized for further testing and analysis include $(\text{Ti, Zr})\text{B}_2$ and AlSiC_4 .

Subtask 1.1: Deposition target synthesis

Synthesis and characterization of fully-dense target materials of the proposed compositions were performed for use in Pulsed Laser Deposition (PLD) and/or Physical Vapor Deposition (PVD). Processing of deposition targets were accomplished either by mechanical milling and hot pressing or by arc melting. Prior to deposition, the targets were validated for correct chemical stoichiometry, phase, and homogeneous microstructure.

Subtask 1.2: Deposition Tests

The proposed coating formulations was deposited through PLD processing onto coupons to assess coating/substrate adhesion behavior (i.e., no spallation, continuous coverage, and application of diamond scratch and Rockwell “C” indentation tests).

Subtask 1.3: Analysis of deposited coating compositions

In order to establish the relationship between the ultracoating composition, nano/microstructure, and functional performance, the team employed a combination of optical microscopy, electron microscopy, surface chemical analysis, and x-ray methods. Surface micro-mechanical properties were also measured using indentation and scratch testing techniques. Results for the ultracoatings were then compared to those for a previously-developed $\text{AlMgB}_{14}\text{-TiB}_2$ nano-composite (ITP-funded Project) and other selected state-of-the-art coatings to assess the relative advantages of ultracoatings in terms of their adhesion, hardness, and resistance to abrasion.

Subtask 1.4: Microscopic analysis of coatings

The new coating formulations were characterized via X-Ray Diffractometry and Scanning Electron Microscopy (SEM) for comparison to baseline $\text{AlMgB}_{14}\text{-TiB}_2$ and other

industry-leading thin films (e.g. Diamond-like Carbon). The objective of this testing was to couple phase and morphology characteristics to wear behavior under high loads with the aim of future optimization.

Subtask 1.5: Lead application determination

Loads/pressures/speeds representative of lead industrial applications were calculated for the development of laboratory-level coupons. The industrial partners identified lead applications based on measurable energy savings, wear performance, and commercialization potential. Current applications reviewed included coal gasifiers, engine timing chains, and on-highway transmission components.

Subtask 1.6: Deposition onto coupons with application-representative substrates

The proposed coating formulations was deposited via PLD/PVD processing onto application-representative substrates for simulative wear evaluation. The industrial partners derived application-simulative coupons based on real-world contact pressures and speeds and then readied these coupons for wear tests.

Task 2: Evaluate coating/substrate system performance on lead application coupons

Laboratory testing were completed to assess the end-application performance of the new coating compositions with respect to contact stress levels, lubrication regimes, and wear performance.

Subtask 2.1: Laboratory Validation of Frictional Performance and Wear Resistance

One or more laboratory-scale friction and wear tests were selected and employed to measure the lubricity and durability of ultracoatings prepared in Task 1.2. In particular, the contact pressure and velocity of candidate ultracoatings were mapped against their friction and wear response in order to determine the maximum sustainable PV level for safe operation [that is, the product of nominal contact pressure (P) and the sliding velocity (V)]. The PV limit is a key engineering parameter for the operation of bearing surfaces under severe operating conditions, and hence has been chosen as the target quantity for coating performance in the selected applications. Results were compared with the 70,000 MPa-m/s objective and candidates were down-selected accordingly.

Subtask 2.2: Characterization of best performing coating/substrate systems

Coating/substrate systems identified as having performed well in the laboratory-scale friction and wear evaluation trials were further evaluated in application-scale coupon trials including an aerospace fuel pump, a hydraulics pump, and engine timing chain components. In each of the application spaces, the components selected were identified as critical to operation with a high degree of commercial viability. Post test characterization of the components selected included surface profilometry (to assess wear rate and degree of wear), optical microscopy, scanning electron microscopy, and energy dispersive spectroscopy.

Task 3.0: Potential Benefits Assessment

The project team estimated the potential energy benefits (% reduction in energy intensity, the year in which the savings would begin, total projected savings in TBtu/year in year 2020), economic benefits (\$/year), environmental benefits (reduction in CO₂ emissions, Mlb/yr, other)

and market benefits (US economy) that can be realized in year 2020, assuming successful development and commercialization of the technology being developed.

Subtask 3.1: Initial calculations of potential benefits associated with the technology

The potential benefits of the technology were calculated at the front end of the project and subsequently reported in the initial quarterly reports.

Subtask 3.2: Determination of the technology's impact to lead application markets

Basic calculations to assess the impact that the technology would have on lead markets were computed over the project length. These were then used to compute the commercialization potential and likelihood of market penetration associated. A proposed outcome of this activity was expressed by the following term:

$$\frac{\text{energy savings (BTU) associated with technology}}{\text{likelihood of commercialization (\%) market acceptance in end units delivered}}$$

Subtask 3.3: Final calculations of potential benefits associated with the technology

The final assessment and a discussion on the differences between the initial and final assessment are included in this report.

Task 4.0: Project Management and Reporting

For project management and reporting, the Principal Investigator held bi-weekly project status conference calls and issued quarterly progress reports to inform the Dept. of Energy program office on the status. In the case of quarterly reports, these were submitted within 30 days of the end of each project quarter. The reports covered items such as technical progress, tracking of tasks, deliverables and milestones. Any program costs or expenses were included in the quarterly for the industrial partners and National Labs.

3.4 Technical Approach and Hypothesis

The research, development, and commercialization plan was largely focused on improving materials' resistance to degradation in a unique array of industrial applications: vehicle systems, industrial hydraulic components operating in severe environments, aerospace actuation and fuel delivery components, vehicle timing chains for diesel, gasoline, and direct injection, and coal gasifiers. These applications were well suited for fundamental technology development and eventual technology transfer because many previous efforts to improve durability and enhance wear performance have been marginalized by both high stresses and challenging lubrication regimes.

The focus of the current project was to "push the envelope" in surface-engineering technologies, and so the key hypothesis to be tested was development of a coating/substrate pairing that exhibits a wear rate of 0.2mm³/kg or lower and is capable of surviving a 1GPa contact pressure, while achieving a maximum coating cost of \$0.10/cm².

This milestone pertaining to the wear rate of the proposed coating/substrate is specific in that there was an established wear rate in mind. Note that the current state of the art, RocTec 500, exhibits a wear rate of $0.2\text{mm}^3/\text{kg}$, and so any of the proposed solutions would have to be at least as wear resistant as the industry best. Moreover, when one considers that, of the commercially available thin films today, none of those researched can withstand contact pressures in excess of 1GPa. Hence, the challenges associated with technical development and the associated potential benefit were that much more significant. Given the aggressive goal to develop at least one solution that could withstand the proposed coating pressures within a single year's time, it is first worth noting the fundamental and practical considerations for materials engineers when selecting coatings for use in severe-duty applications. These include (but are not limited to):

- Suitability of the coating to resist the particular type of wear that occurs in the application (e.g., abrasive wear, sliding, impact, fretting, etc.)
- Adhesion to the substrate
- Compatibility with the substrate, including matched coefficients of thermal expansion and the avoidance of 'anvil effects' and low inter-diffusion rate with the substrate
- Ability to produce the same quality of coating consistently in a production environment
- Sufficient toughness to avoid brittle fracture, delamination, and spalling
- Lubricity over the range of operating conditions
- Compatibility with any lubricants that may also be used
- Compatibility with anticipated operating temperatures
- Toxicity and environmental impact
- Added cost of the constituent materials and processing (cost-benefit)
- Availability of constituent materials

3.5 Initial Energy Savings Calculations

As previously discussed, existing materials and commercially available coating technology are simply incapable of extending the life of components that have interfacial contact stresses exceeding 1GPa. Consequently, a solution for such application spaces has enormous potential for energy savings and also for the reduction of greenhouse gas emissions into the atmosphere. According to MECS data (Manufacturing Energy Consumption Survey) from 2002, energy losses due to industrial equipment inefficiency (motors, mechanical drive, waste heat) amount to 2,838 trillion BTU (TBtu) (2.8 Quad) per year ^[21]. Frictional losses in industrial machinery result in increased energy consumption by generating heat, which requires more energy input to operate the machinery. Considering examples specific to this proposal, in a typical multi-stage gear transmission, energy losses can amount to 80% ^[22]. Furthermore, parasitic losses in Class 3-8 on-highway trucks can exceed 60%.

Eaton, as a diversified power management company, produces in excess of 20 million carburized gears annually, which results in over 500,000 tons of CO₂ emitted into the atmosphere each year.

As related to engine timing components, there are currently two distinct applications for this technology: gasoline engines utilizing direct injection lean-burn technologies, and diesel engines. Chain products, notably those coated with existing wear-resistant coatings such as vanadium or chromium carbides, experience reduced efficiencies because of engine oil contamination and soot. Furthermore, many chains fail to meet their operating service lives, as wear leads to elongation of the chain (typically 0.4 to 0.7% of its original length). This is especially critical in applications using turbochargers, where increased power density is accomplished while maintaining low emissions.

Table 3.5-1 illustrates the potential for this technology in the areas of energy/fuel savings and reduction of greenhouse gas emissions in just the aforementioned vehicle markets.

Table 3.5-1. Annual greenhouse gas emission reductions associated with Ultracoatings

Participant	Annual Emissions Reduction (metric tonnes)				
	CO	SO ₂	NO _x	CO ₂ e	Particulates
Eaton	3,900	49,000	32,000		1,000
Borg Warner Morse TEC				40,000 ^[23]	

CO₂e: (CO₂ equivalent including CO, SO_x, NO_x, etc.)

In addition to providing energy and fuel savings as described above, application of ultracoatings to support environmentally-benign alternative energy sources, such as coal gasification, broadens the economic benefit achieved with the proposed technology developments. The coal gasification process currently in development at Pratt & Whitney Rocketdyne is an oxygen-blown, dry-feed, plug-flow entrained reactor capable of achieving carbon conversions approaching 100%. Preliminary analysis for the Integrated Gasification Combined Cycle (IGCC) using an Illinois #6 coal at \$1.5/MMBTU fuel cost has shown that near term Compact Gasification Program (CGP) technology implementation could reduce cost of electricity by 15 – 20% relative to current gasifier technologies, while achieving a >10% reduction in plant capital cost per kW and a 50% reduction in gasifier capital cost (**Table 3.5-2**).

Table 3.5-2. Comparison of Rocketdyne Advanced Gasifier with an Existing Single Stage Quench Gasifier for Single Train IGCC Application

Application	Existing Gasifier	Rocketdyne Gasifier	Improvement
Plant Capital Cost (\$/kWe)	1517	1297	14.5%
Cost of Electricity (\$/MWh)	49.3	40.2	18.5%
Plant Efficiency (HHV, %)	39.8%	43.1%	3.3 pts
Plant Availability (%)	85%	94%	9 pts

Successful demonstration and implementation of the Rocketdyne coal gasification process demands long-life, including extended life of components exposed to the erosive wear of coal particulates. The combination of surface erosion and frictional heating induced by sliding of the coal on critical wear surfaces is an issue of concern with respect to achieving a key operational target of >1 year (>8000 hrs) mean time between overhaul (MTBO) of gasifier components.

3.6 Key project participants

Eaton Corporation:

Clifton Higdon: Provided project management for the Ultracoatings effort. Also provided sample test coupons and the physical vapor deposition (PVD) system for depositing coatings on test coupons and for testing coated pump components in their in-house instrumented systems. Higdon established all of the Eaton energy savings models resulting from commercial implementation of the technology. Higdon also actively investigated additional applications for Ultracoatings within Eaton's diverse product portfolio.

Ames Laboratory:

Bruce Cook, Alan Russell, and Joel Harringa: Conducted research on pulsed laser deposition (PLD) coatings process development. Further characterized the crystallographic differences between single-phase and multi-phase (Ti, Zr)B₂ coatings. Ames Laboratory provided coated coupons used for friction and wear testing at both Eaton and Oak Ridge National Laboratory. Ames also provided the team with detailed surface morphology analysis of coatings before and after laboratory testing, and ongoing technical support.

Oak Ridge National Laboratory:

Peter Blau and Jun Qu: Designed and conducted tribological tests of coated coupons and provided mechanistic understanding of the superior performance via wear modeling. The laboratory testing of friction and wear of coated coupons required modification to existing instrumentation and infrastructure.

Pratt and Whitney Rocketdyne:

Colin Swingler: His role as lead materials and process engineer on the Dry Solids Pump design team provided the insight required to identify opportunities for implementation of new wear control technologies and advise the Ultracoatings project on the DSP design constraints and performance goals.

Borg Warner Morse TEC:

Yumin Wang: Lead activities pertaining to the application of Ultracoatings on engine timing chains for Borg Warner Morse TEC. Provided accurate wear modeling data and production-intent coupons to the various team members for deposition trials and friction and wear evaluation. Responsible for estimated fuel savings associated with implementation of the technology in passenger vehicle markets.

4.0 Results/Discussion

Over the course of the project, the project participants focused on a deeper understanding of the fundamental material properties of the (Ti,Zr)B₂ nanocomposite that lead to improved wear resistance, product performance under high loading, and enhanced durability. A key project deliverable was a down-selected coating/substrate pairing that could withstand interfacial stresses of greater than 1 GPa, all while exhibiting low erosion and/or wear rates. Prior to the project's start, Eaton Corporation had identified aerospace hydraulic and fuel systems as lead application space opportunities. Borg Warner Morse TEC had identified engine timing chain components (links and pins) as a strong opportunity to validate the coating's performance. Lastly, Pratt and Whitney Rocketdyne identified their dry solids pump and components therein as hardware benefiting from the use of a wear resistance surface coating. To that end, the results included within this section of the report aim to address the fundamental research that has guided the progress of technology development.

4.1 Development and Characterization of (Ti,Zr)B₂ PLD and PVD Films

Prior to the development of (Ti,Zr)B₂ sputtering tiles for adhesion tests, friction and wear testing of coupons, or the processing of prototype hardware for functional testing, the project team sought to evaluate and assess the benefits associated with processing the material through pulsed laser deposition equipment. Some of the background work discussed in Section 3.2 had shown that the (Ti, Zr)B₂ composite in bulk form was capable of extremely low erosion rates, approximately 10x lower than cobalt stabilized WC in solid form. Translating this promising performance into coating required significant modification to existing PLD processing capabilities at Ames Laboratory, as well as an understanding of the desired outcome. Several M2 vane segments were polished to 100 nm in preparation for deposition of TZB in the PLD system. The metallurgical polishing sequence was necessary in order to remove any prior coating material down to the base substrate.

Several preliminary depositions were performed in order to establish a baseline for the friction and wear behavior of this material. Depositions were performed for 10 and 20 minutes with a substrate temperature of 500°C, leading to coating thicknesses of 500 and 1000 nm, respectively. Coating thickness values were determined by profilometry on selectively masked substrates. Two coated substrates were sent to ORNL for pin-on-disk (POD) testing. A 9.525 mm dia. AISI 52100 steel ball was used as the slider at a speed of 0.5 m/s with a 10 N load. The testing was performed at room temperature with 3 drops of Mobil DTE-24 lubricant added prior to the start of the test. The test had a duration of 6 hours, corresponding to a distance of 10,800 m (6.7 miles). Friction behavior is shown in **Figure 4.1-1**, in which both coatings are seen to exhibit a steady-state COF of about 0.1. The slight difference between the 10 and 20 minute coatings is not considered significant.

Figure 4.1-1. Friction behavior of two early PLD-coated TZB M2 substrates.

Since TiB_2 was found in the AlMgB_{14} - TiB_2 composite system to contribute a surface layer of boric acid, $\text{B}(\text{OH})_3$, which results in ultra-low friction, it was curious that the TZB coating, which is a single phase composite of ZrB_2 and TiB_2 exhibited a substantially higher COF. It is possible that the presence of Zr within the phase structure inhibits formation of boric acid. Assuming that the formation of boric acid is inhibited with the introduction of zirconium, it may be possible to form a composite composition consisting of TZB with a distinct TiB_2 phase to enhance low friction. This avenue was not explored as part of the project, largely because the PLD coating wear rates were high enough that a self-effacing coating may not be considered durable enough for the applications identified.

Wear rates for the ball were calculated from the length and width of the wear scar, and for the disk based on the average depth and width of the wear track. Results are summarized in **Table 4.1-1**.

Table 4.1-1. Wear Rates of Preliminary TZB Deposition on M2

Test ID	Sample ID	Ball wear rate ($\text{mm}^3/\text{N-m}$)	Disk wear rate ($\text{mm}^3/\text{N-m}$)
ST1_PB_100	TZB on M2 500C 10 min	3.17E-9	1.40E-8
ST1_PB_101	TZB on M2 500C 20 min	4.48E-9	2.14E-8

The 10 minute deposition exhibited better wear behavior than the 20 minute coating, presumably because of the periodic delamination in the thicker coating, as seen in **Figure 4.1-2**.

The periodic delaminations could be the result of surface contamination on the M2 substrate that was not completely removed prior to deposition, or to the increased thickness

without sufficient relief of residual stresses generated during deposition. The removal of particles during the test results in 3-body wear and a corresponding increase in the observed wear rate. Even with the delamination in the 20 minute coating, the ball wear rates are comparable to the best values observed in earlier tests with the $\text{AlMgB}_{14}\text{-TiB}_2$ nanocoatings, which is highly encouraging considering this represents the first TZB coatings ever produced on M2, and that the process had not been optimized.

Figure 4.1-2. Ball (left) and disk (right) wear scars for 10 minute (a) and (b) and 20 minute (c) and (d) TZB depositions.

In an effort to increase the deposition area using PLD processing technology, a copper fixture was fabricated to accommodate a standard Falex ring. Previous PLD work had centered on rectangular substrates approximately $2 \times 2 \text{ cm}^2$ in size. By increasing the target-to-substrate distance, it was possible to take advantage of the geometry of the plasma plume as it expands with distance from the target, and thus obtain coverage on larger substrates. However, the intensity (or density) of the plume decreased with distance from the target, meaning a proportionally longer deposition time required for a given coating thickness. In addition, because of the tendency of the vaporized material to condense in-flight, the longer time-of-flight meant larger particulates. The Falex ring adapter is shown in **Figure 4.1-3**. Since the holder was machined from copper, its thermal transfer was excellent, enabling the part to reach the desired temperature easily during deposition. Elevated temperature facilitates coating adhesion and also promotes relief of compressive stresses generated during deposition.

Figure 4.1-3. Photographs of a TZB coated Falex ring and copper holder for use in the PLD system.

The coating morphology of the TZB coated Falex ring was examined by scanning electron microscopy in an effort to assess coating growth, thickness, and surface morphology. The TZB coating displays a granular morphology with larger particulates present (in the 100 to 200 nanometer range), as shown in the top micrograph in **Figure 4.1-4**. A reduced magnification backscattered electron image is shown in the center micrograph. The overall coating appears uniform, with a few large particulates on the surface. Of particular note are the elongated cavities ranging from approximately one to four microns in length. It is believed these cavities are related to pre-existing scratches on the surface of the ring and their presence would be expected to reduce the wear resistance of the coating relative to a defect-free morphology. A secondary electron image of a pore is shown in the bottom micrograph.

Figure 4.1-4 Scanning electron microscope images of TZB coating on steel Falex ring.
Top: secondary electron image showing granular morphology and particle size of the coating. Middle: backscattered electron image showing large particles and cavities in the coating. Bottom: high-magnification secondary electron image of a cavity, which is believed to be related to a pre-existing scratch on the surface.

One of the key focus areas throughout the project was in transitioning the laboratory level PLD work performed at the onset of (Ti, Zr)B₂ bulk solid development to a robust and repeatable process that would yield real performance increases in both of the industrial applications identified. Any developed coatings of this composition, or any composition with novel wear characteristics for that matter, would have to be tested in a variety of configurations to assess the respective material's behavior in severe service. Any positive test outcomes would in turn help to retire the risks associated with introducing a new technology into established markets. Down-selected coatings eventually would be subjected to long-term durability testing as a means to emulate long-term service in harsh environments. Given the length of the project, opportunities for process optimization would be limited and so careful selection of parameters (from both the processing end *and* the testing and characterization side) would have to be kept in careful consideration.

Pursuant to reaching the technical milestones and targets of the project, Eaton Corporation's first activity under the program was to develop a process for deposition of the Ultracoatings technology that could be reliable and repeatable. This was best accomplished by identifying the preferred target material for initial deposition trials, the (Ti, Zr)B₂ material, selection of a suitable target vendor, and specifying the desired composition. Initial testing of the (Ti, Zr)B₂ bulk solids and PLD-deposited thin films illustrated superior abrasive slurry wear resistance when compared to tungsten carbide. Refer to Section 3.2 for the bulk solid testing that served as the motivation for further exploring the TZB composition. Eaton selected a known vendor of novel sputtering materials to process a single 80x200mm PVD tile for application of the TZB material to laboratory level substrates and prototype component trials. First stage evaluation of the PVD coatings would be on Falex rings in a pin on ring/disk orientation. Successful completion of this initial verification of the material's performance would serve to move ahead with component depositions for functional testing. It is worth noting that, as this was the first time such a composition was processed, it was unknown as to whether or not the sputtered films would emulate the bulk solid's superior wear performance.

At nearly the same time that Eaton had received its new (Ti, Zr)B₂ PVD sputtering target, an opportunity arose whereby Innovation Center personnel were contacted to perform simulative tribology testing on an interface within an aerospace piston pump (discussed in Section 4.2.2). This particular product had not met durability targets and so the aim of the study was to assess the impact that Ultracoatings would have on the overall product life (or at least, a best estimate given the coupon configuration and test conditions chosen). The specific interface in question were the cylinder block and valve plate. Testing of this system and subsequent teardown revealed that the sintered bronze applied to the pump's cylinder block was smearing onto the hardened tool steel valve plate component.

As with previous efforts to characterize sputtered thin films, Eaton's Innovation Center includes M2 tool steel vane blades with the PVD processing batch for coating thickness measurement. Representative thickness values for the (Ti, Zr)B₂ coatings over the length of the project are included in **Figures 4.1-5 and 4.1-6**.

Heat-up time: 1 hour, 20 minutes

Etching time: 54 minutes

Coating wattage: 1500W during sputtering

Coating time: 4 hours, 20 minutes of sputtering the (Ti, Zr)B₂

Coating temperature: 162-337°C

Figure 4.1-5 Photomicrograph of M2 vane blade surface from Eaton Innovation Center coating batch #1209. Coating thickness was measured at 2.7 microns.

Figure 4.1-6. Photomicrograph of M2 vane blade surface from Eaton Innovation Center coating batch #1210. Coating thickness was measured at 2.7 microns.

As noted previously, $(\text{Ti,Zr})\text{B}_2$ had not previously been sputtered using a PVD system on the scale of Eaton's. First steps to characterize the nature, phase concentration, and growth morphology(ies) of the TZB material included defining if the Eaton sputtering target was similar in x-ray structure to the material evaluated by Ames and illustrated in Section 3.2. The resulting diffraction pattern from the x-ray structure analysis is shown in **Figure 4.1-7** and reveals a mixture of TiB_2 and ZrB_2 , along with minor amounts of secondary impurity phases. It is clear

from the pattern that this target is not a (Ti, Zr)B₂ solid solution (single phase), although the associated benefits to ZrB₂ and/or TiB₂ may still be present with the material as individual phases. It's worth noting, however, that this mixture of two or more soluble phases will not necessarily exhibit the same wear and friction behavior as a solid solution alloy. Hence, we believe that any issues associated with premature wear of components coated from this target could be attributed to the absence of a solid solution between the two primary phases. The effect(s) of the secondary impurity phases is an additional confounding factor, since they are not easily identified, and hence their effect on the coating properties is difficult to assess.

Figure 4.1-7. X-ray diffraction pattern of (Ti,Zr)B₂ PVD target obtained for Eaton deposition

In comparison, **Figure 4.1-8** shows a similar x-ray diffraction pattern obtained on a piece of arc-melted, fully-alloyed, single phase TZB prepared at Ames. The figure shows 8 diffraction peaks between 10 and 90 degrees (2-theta), consistent with the calculated pattern for a single-phase, hexagonal polymorph (P6/mmm). Also shown in **Figure 4.1-8** is the x-ray diffraction pattern obtained by pulsed laser deposition (PLD) on a quartz substrate. This demonstrates that TZB can be deposited as a phase pure coating.

Figure 4.1-8. X-ray diffraction pattern of arc-melted (Ti,Zr)B₂ target and PLD coating on quartz showing complete solid solution between the two boride phases.

Following the Diffractometry work performed on the composite sputtering target received by Eaton, the associated TZB coatings were evaluated using scanning electron microscopy methods to identify key morphological differences between the PLD applied coatings and those coatings processed with the mixed-phase TZB at Eaton. The TiB₂ – ZrB₂ composite target, discussed above was used to deposit a coating on hardened 440 B 2.7 mm diameter stainless steel pins supplied by Borg-Warner Morse Tec.

The composite coating deposited on the stainless steel pins exhibits a distinctly different morphology, as shown in the series of SEI micrographs in **Figure 4.1-9**. The presence of discrete phases (as opposed to a homogeneous structure) in the coating is evidenced by the backscattered electron component in the signal that shows regions of optical contrast.

Figure 4.1-9. Secondary electron images of $\text{TiB}_2\text{-ZrB}_2$ composite PVD coating on hardened steel pins.

The SEM evaluation of each processing method reveals that the growth mode associated with TZB appears to be mixed mode, with a predominant layered structure. The highlighted region in the bottom (10kx) image shows what appears to be a small, possibly nascent growth column.

4.2 Development of (Ti, Zr) B_2 PVD Coatings for Eaton's Aerospace Applications

At the initiation of the program's period of performance, Eaton identified three distinct applications within its aerospace product portfolio as opportunities for the wear resistant TZB coating. These include, but in a broader sense, are certainly not limited to, an **axial displacement piston pump** experiencing galling and material transference at the valve plate/cylinder block interface, a **high speed radial piston pump** (also experiencing smearing of bronze onto tool steel), and a **variable displacement fuel pump** (wear associated with interface between rotating group and the drive shaft). In each of these respective applications, alternative surface engineering processes have been attempted, though none has provided an acceptable solution to the present wear. Furthermore, the product performance (meaning prior to implementation of any surface enhancement, e.g. Ultracoatings) is inherently limited by the

degree to which friction and/or wear immediately limit the system's longevity in service. In the case of the high speed radial pump and the fuel pump noted, these products have reached a "go/no-go" point, whereby further engineering progress has been halted until a solution is reached.

For the aerospace axial displacement piston pump, the end application calls for a product with improved efficiency and durability, most notably at the interface between the valve plate and the rotating cylinder block. This particular system is intended to be run at nearly 4,000 RPM, with pressures reaching 6,000 psi or greater. In an effort to prove out the system's durability, however, the rotating group may be driven to speeds in excess of 8,000 RPM. Sintered bronze is presently used at the interface to improve the lubrication conditions. However this material reaches its lateral shear strength, temperature limitations, and begins to wear itself adhesively onto the tool steel counterface under these operating conditions.

A key challenge in this particular system is that the bronze galling condition occurs at random intervals – reports from divisional engineering staff have reported that the system successfully runs 90-95 percent of the time without smearing. Hence, if the coated part survives, it still provides no verification that the 10 to 5% rejection rate has been eliminated. A variety of test conditions were derived to produce interface failure 100% of the time, although this, too, proved challenging. An example is dry state testing, whereby no lubricant is applied to the interface. This particular arrangement always yields the smearing condition, though it is not a direct representation of the actual system in field use. The other downside to this testing is that other components in the system fail because of improper lubrication.

The actual testing of this system began with small Falex friction and wear test coupons. Refer to **Figure 4.2-1** for representative images of the samples. As these coupons arrived during the final stages of the previous US Department of Energy-funded "Nanocoatings" program (DE-FCG36-06GO16054), a comparison coating of $\text{AlMgB}_{14}\text{-TiB}_2\text{+C}$ was applied to coupons as well. This would afford the team an opportunity to compare the two compositions for wear resistance. Due to the material grades used in the study, low temperature PVD processing was selected. Two of the six coupons provided were processed using the $\text{AlMgB}_{14}\text{-TiB}_2\text{+C}$ coating and another two samples were coated with a new composition being evaluated, $(\text{Ti, Zr})\text{B}_2$.

Figure 4.2-1. Falex tribology coupons provided to the Eaton Innovation Center for coating and wear trials. The aim of this study was to eliminate the “smearing” that occurs and to minimize the wear to the tool steel ring. The leftmost image represents the “working faces” of the samples. The back-face of each coupon is shown on the right image to illustrate the thermocouple wire placement.

The pressure*velocity (PV) information provided with the coupons indicated that the current point of failure, meaning bronze from the annulus smearing onto the ring through adhesive wear, is approximately 1.5 million psi*sfm. Simple calculations showed that an applied load of 500 lbs. and a rotational speed of 2300 RPM would equate to a similar P*V. Discussions at the Eaton Innovation Center led to the test plan shown in **Figure 4.2-2**.

The lubricant for the selected Falex testing was Skydrol V, a newly developed fluid that is being targeted to replace older formulations such as 500B4 and LD-4. Skydrol 5 offers higher temperature capability than Type IV fluids, the lowest density, and better paint compatibility. The failure point on this graph (identified as the point where measured torque dramatically increases) corresponds to a P*V of approximately 1.35 million psi*sfm. While slightly less than the value provided from the end-use piston pump application, this P*V product indicates that the test setup is very close to simulating the system.

Figure 4.2-2. Graphical representation of the test plan for the aerospace coupons provided. The lubricant for the selected Falex testing was Skydrol V, a newly developed fluid that is being targeted at replacing older formulations such as 500B4 and LD-4. Skydrol 5 offers higher temperature capability than Type IV fluids, the lowest density, and better paint compatibility.

Figure 4.2-3. Falex wear plot illustrating the point of failure identified for the baseline bronze-on-uncoated tool steel sample. The point at which the test was interrupted corresponds to 380 lbs load and 2550 RPM (P*V product of 1.35 million psi*sfm).

The test was repeated for additional coated specimens, including those using Eaton's existing AlMgB₁₄-TiB₂+C nanocoating. The Falex plot for the (Ti, Zr)B₂ composition is included for reference in **Figure 4.2-4**. Note that, in each of the coated sample trials, the testing was interrupted prior to full completion of the test. It is believed that this has more to do with exceeding the shear strength of the bronze on the annulus than any adhesive wear occurring between the two interfaces.

Figure 4.2-4. Comparison of second (Ti,Zr)B₂ coated sample set to baseline. Note that the test was interrupted at a load of 400 lbs and a rotational speed of 2500 RPM. This corresponds to a full-contact P*V product of 1.32 million psi*sfm.

After completion of the test, the samples were photographed to illustrate the degree of wear. As shown, the baseline sample exhibits a high degree of adhesive wear/material transfer. Discoloration of the annulus sample, indicative of localized heating, was also noted. The coated samples, in contrast, exhibit minimal wear and show no signs of bronze material transfer. Refer to **Figure 4.2-5**.

Figure 4.2-5. Comparative photograph of Falex wear samples after testing. For reference, the baseline sample exhibits significant wear and material transfer. The coated samples, in contrast exhibit minimal wear to each annulus and there is no bronze material deposited onto the counterface ring.

Optical profilometry was performed on each of the tested samples as a means to quantify the impact of the material transfer on the baseline sample. Measurements were also performed on the coated samples to assess the ring and annulus wear. Refer to **Figure 4.2-6 through Figure 4.2-8** for profilometry data.

Figure 4.2-7. Post-test optical profilometry data for the (Ti, Zr)B₂ coated ring sample (top) and the bronze annulus (bottom). For reference, the (maximum peak to valley height (PV) value of the ring prior to the Falex wear study was 2 micro-inches. The PV value for the annulus prior to the Falex wear study was micro-inches. As shown, the post test for PV for the ring is micro-inches and the post test PV for the annulus is 52 micro-inches.

Figures 4.2-8. Post-test optical profilometry data for the AlMgB14-TiB₂+C coated ring sample (top) and the bronze annulus (bottom). For reference, the PV value of the ring prior to the Falex wear study was 2 micro-inches. The PV value for the annulus prior to the Falex wear study was 34 micro-inches. As shown, the post-test for PV for the ring is 66 micro-inches and the post-test PV for the annulus is 72 micro-inches.

A summary of all of the results is included in **Table 4.2-1**. For reference, the P*V pressure*velocity calculation for the coated samples was broken down into two terms: the first term represents full contact of the bronze annulus on the coated ring. The second term represents partial contact of the bronze annulus on the coated ring. Through profilometry measurements, it was determined that the wear track widths on the coated rings represent approximately ½ of the full annulus thickness.

Table 4.2-1. Falex test data and post-test observations for Eaton aerospace coupons.

Sample	Speed (RPM)	Force (lbs)	P*V product (psi*sfm)	Sample Condition
Baseline	2550	380	1.28 million	Heavy galling, material transfer
(Ti,Zr)B ₂	2500	400	5.21 million (1.32 million)	Minimal wear to bronze, little to no wear on coated ring

The coupons that were tested were then examined for fine-scale levels of damage and material transfer. SEM imaging and EDS analysis indicated no bronze transfer to the (Ti, Zr)B₂ ring surface. Instead, the surface chemistry exhibits peaks characteristic of the coating constituents; namely Ti, Zr, and faint peaks of B. Refer to **Figures 4.2-9 through 4.2-11** for representative wear scar photomicrographs.

Figure 4.2-9. Wear scar of laboratory Falex coupons that were coated with the Eaton PVD (Ti, Zr)B₂ coating.

Figure 4.2-10. Wear scar of laboratory Falex coupons (coated with (Ti, Zr)B₂ material) tested against a counterface of leaded bronze. Note that the discoloration of this surface is not attributed to coating wear, rather the increased surface temperatures associated with reaching the shear strength of the counterface bronze at high speed/pressure.

Figure 4.2-11. Wear scar of laboratory leaded bronze coupons (run against the ring coated with (Ti, Zr)B₂ material). This particular surface illustrates some surface damage associated with re-deposition of the bronze after exceeding the material's shear strength at the loads and speeds selected for testing. Note that this surface appears to be similar to those of the production-intent components.

The completion of Falex friction and wear testing led the divisional engineering staff to pursue functional testing of end-application hardware. Due to the intermittent nature of the interface failure, however, this testing proved to be somewhat challenging. It was decided collectively that in-service interface conditions would yield (again) intermittent failures and that these test conditions would not conclusively determine an advantage associated with the TZB coating. Conversely, dry friction testing of the interface would be considered too severe and not representative. Eaton's Aerospace group ran the first test on the basic plates trying to induce a smear (material transfer) by running the pump at 8,000 RPM vs. the 3,775 RPM rated speed. This was intended to exceed the recommended PV factor by increasing system velocity (speed). Unfortunately, the baseline pump ran without any reported smearing. Future efforts beyond the timeframe of the project will focus on increased loading, while running the pump at elevated flow rates and speed. The goal again is to establish running conditions that yield repeatable levels of damage to the interface in question. Once the baseline condition has been shown to repeatedly experience damage, the TZB coating will be evaluated for improvements to wear resistance. Successful demonstration that the TZB coating enhances the performance of the system and reduces damage will facilitate implementation of the technology into the existing production architecture.

For the radial piston pump, the components in question mate to a sintered bronze-face plate that is rotating in excess of 10,000 RPM (the preferred speed is greater than 20,000 RPM because this facilitates the removal of transmission gearing used to downspeed the input drive). Under the present conditions, the bronze is smearing itself onto the valve plate component, thus leading to lowered efficiency and a decrease in long-term performance. A 3-dimensional model of the system is included for reference in **Figure 4.2-12**. Current operating conditions result in the pairing that sees relatively low loads (approximately 12lbf), though the high speeds reduce the lubricant film thicknesses along the interface to nearly negligible values. This, in turn, raises the temperatures of the steel-bronze interface and immediately results in the bronze smearing. A photograph of the valve plate component is included in **Figure 4.2-13**.

Figure 4.2-12. 3-Dimensional model of the high speed radial piston pump rotor component that incorporates a sintered bronze valving face at the ends. In the assembled pump, the holes present along the circumference accommodate the pumping pistons.

Figure 4.2-13. High speed radial piston pump valve plate used to pump the fluid through the conveyance to various actuating surfaces in the targeted application.

Post-mortem photography of a radial pump wear test is included for reference in **Figure 4.2-14**. As shown, the sintered bronze along the circumference of the barrel component is heavily smeared. Accordingly, this pump test was interrupted before completion.

Figure 4.2-14. Macrophotograph of the high speed radial piston pump rotor component after testing. Note the smeared bronze along the outer diameter and on the valving face.

Aside from the valve plate/cylinder block interface noted, there is an additional interest in this particular pump centered around the pumping pistons. The high-speed nature of the pump yields high centrifugal forces at the piston/cam ring interface (**Figure 4.2-15**) and high lateral forces between the pumping pistons and the cylinder block itself (**Figure 4.2-16**). In the case of the first interface, contact pressures between the piston and the cam ring are expected to exceed 1GPa, and the relative speed of the pistons to the ring are expected to exceed 15,000 RPM (greater than 180 ft/sec). Within the cylinder block, the pistons rotate about their axes at a maximum velocity of approximately 15,000 RPM. Application of a wear resistance coating to the pistons that reduces friction is of primary concern.

Figure 4.2-15. Graphical representation of the cam-ring interface on the proposed radial piston pump architecture.

Figure 4.2-16. Graphical representation of the piston/cylinder barrel interface on the proposed piston pump architecture.

Falex friction and wear rings were processed through the Eaton PVD system for simulation of the radial piston pump components and interfaces. These samples were part of a broader study run during this project to compare various low friction, wear-resistant materials. Within the test matrix, Eaton considered DLC, the TZB material in question, a Ni_3B coating, and the previous generation Nanocoating. The testing parameters for this evaluation focus on stepped energy, whereby the speed of the test would be kept fixed and the applied load would be increased. A “successful” coupon for this particular test would be one that ran the entire load schedule and exhibited little-to-minimal wear upon completion. Diamond-like carbon films from HEF USA have completed this test with minimal wear observed and are considered the highest performing alternative coatings to the previously developed, Eaton $\text{AlMgB}_{14}\text{-TiB}_2\text{+C}$ nanocoating. As noted in **Figure 4.2-17**, the $(\text{Ti, Zr})\text{B}_2$ coated samples did not complete the test schedule intact. Of note, however, is that the $(\text{Ti, Zr})\text{B}_2$ coated sample exhibited the lowest friction surface recorded of the thin films evaluated. It is believed that the presence of TiB_2 within the multi-phased coating facilitated the formation of boric acid. While this would lead to lowered surface friction coefficients, it would increase the wear rate of the coating under high interfacial contact pressures.

Figure 4.2-17. Falex friction and wear plot illustrating the torque signatures for a variety of coated samples. Note that HEF's DLC coating (red, blue) and UCT's Ni₃B coating (forest green) were the two samples that completed the test. In each case, the surfaces did not exhibit excessive wear or damage. The purple line that terminates at approximately 1 hour, 10 minutes is the (Ti, Zr)B₂+C sample. The light green line is the baseline Eaton (Ti, Zr)B₂ sample.

Additional friction and wear testing was performed by Eaton Innovation Center staff as a continuation study to that shown in **Figure 4.2-17** as a broad(er) comparison of known wear-resistant materials. Whereas the previous Falex friction and wear testing evaluated coatings, this work focused around the following coatings *and* solid materials:

- RocTec 500 binderless tungsten carbide
- Greenleaf WG-100 Al₂O₃ with SiC whiskers
- C17N Ceramic
- H10F Ceramic
- TM10 Ceramic
- Ni₃B Coating
- Al₂O₃-reinforced aluminum-based MMC
- Single-phase, Ames PLD deposit of (Ti,Zr)B₂ on D2 tool steel
- D2 tool steel
- Eaton PVD deposit of AlMgB₁₄-TiB₂ on D2 tool steel

The configuration of the established test was 3-ball on ring (which produces the highest possible contact pressures at the interface of all test arrangements available at Eaton's

Innovation Center), whereby the aforementioned materials were applied to or established as the ring coupon. All of the ball bearings used were Grade 25, D2 tool steel. Test conditions included use of Skydrol 5, with applied loads ranging from 50lbs to 1000lbs at 500rpm. The Falex test conditions are represented graphically below (**Figure 4.2-18**). Individual Falex plots of the materials selected for evaluation are included in **Figures 4.2-19 through 4.2-29**.

Figure 4.2-18. Plot illustrating the Falex testing configuration of load (lbs) and speed (rpm)

Figure 4.2-19. D2 rings coupled with D2 balls. This test was for galling at 1:45. The measured coefficient of friction ranges from 0.11-0.15

Figure 4.2-20. M4 rings coupled with D2 balls. The test was stopped for galling at 2:35. The measured coefficient of friction ranges from 0.10-0.14

Figure 4.2-21. Ni_3B coating coupled with D2 balls. This particular test was interrupted at 2:35 for galling. The measured coefficient of sliding friction ranges from 0.09 to 0.16.

Figure 4.2-22. AIMgB14-TiB2+C coating coupled with the D2 balls. This test was interrupted for galling at 2:30. The minimum coefficient of friction reached was 0.13.

Figure 4.2-23. Single-phase (Ti, Zr)B₂ coating coupled with the D2 balls. This particular test was interrupted for galling at 20 minutes. The minimum coefficient of friction reached was 0.09.

Figure 4.2-24. RocTec500 binderless WC material coupled with D2 balls. This test ran the full schedule. The measured coefficient of friction ranges between 0.13 and 0.14.

Figure 4.2-25. C17N material coupled with D2 balls. This test, like many of the other known carbide materials, completed the entire test up to a load of 1000 lbf. The measured coefficient of friction ranges between 0.12 and 0.16.

Figure 4.2-26. H10F material coupled with D2 balls. This test, like many of the other known carbide materials, completed the entire test up to a load of 1000 lbf. The measured coefficient of friction ranges between 0.13-0.15.

Figure 4.2-27. TM10 material coupled with D2 balls. This test was interrupted for galling at 1:45 and then resumed after inspection. The measured coefficient of friction ranges between 0.11 and 0.15.

Figure 4.2-28. Greenleaf WG-100 material against D2 balls. This coupling ran the entire test with no galling reported. The measured coefficient of friction ranges between 0.10 and 0.15.

Figure 4.2-29. Aluminum MMC paired with D2 tool steel balls. This test was interrupted at 48 minutes into the schedule because of galling. The measured coefficient of friction ranges from 0.07 to 0.12

The testing performance documented in the Falex friction and wear plots indicates that, of the materials evaluated to date, the WG-100 material provided by Greenleaf Corporation (whiskers of SiC in Al₂O₃ matrix) sustained the full 1000lbf load with the least damage to the ring. Accordingly, while there is measurable wear to the three balls, the degree of surface damage on the worn surfaces is minimal. Of all of the materials, the two that experienced immediate damage were the aluminum MMC and the single phase (Ti, Zr)B₂ material. In the case of the aluminum MMC, this damage is expected to have been caused by yielding of the relatively soft matrix. It is proposed that the TZB material experienced galling early on in the testing because of delamination between the substrate and the coating. The other possibility is that the TiB₂ present (as a singular phase amidst the other mixed phases in the coating) led to the formation of boric acid, thus increasing the coating's wear rate. Future work, beyond the scope of this project, is planned to utilize the benefits of a "bond layer" consisting of either Ti or Cr to alleviate the substrate-coating stresses.

Upon completion of each test (or when galling was detected and the test was interrupted to avoid instrumentation damage), each sample set (all three balls and each ring) was collected, photographed, and evaluated for wear. In the case of each Falex ring, the samples were evaluated using Eaton's Zygo optical profilometer. In the case of the three balls, their wear scars were photographed and measured. A sample output of the Zygo is included for reference in **Figure 4.2-30**. A representative photograph documenting the ball wear associated is included in **Figure 4.2-31**. Photographs of the (Ti,Zr)B₂ coated ring and the counterface D2 balls are included with the corresponding Zygo surface profiles in **Figure 4.2-32** through **Figure 4.2-33**. Baseline D2 on D2 Zygo profiles and ball photomicrographs are included in **Figure 4.2-34** through **Figure 4.2-35**.

Figure 4.2-30. Post-test analysis of the RocTec 500 Falex ring after it completed the full test evaluation (1000 lbf). The Zygo surface analysis indicates that minimal wear occurred.

Figure 4.2-31. D2 tool steel ball wear associated with the RocTec 500 pairing.

Figure 4.2-32. Post-test analysis of the $(\text{Ti,Zr})\text{B}_2$ coated Falex ring after the friction and wear evaluation. This pairing did not complete the full 3 hour test. The coated ring was processed at Ames laboratory in their PLD system. The Zygo surface analysis indicates that, while through-coating wear did occur (22 μm), the degree of surface damage is substantially lower than the baseline D2 material.

Figure 4.2-33. D2 tool steel ball wear associated with the $(\text{Ti,Zr})\text{B}_2$ coating applied to the ring. Note the size of the wear scar with respect to the sample paired with RocTec 500 (Figure 4.2-31) and uncoated D2 (4.2-35).

Figure 4.2-34. Post-test analysis of the uncoated D2 tool steel Falex ring after the friction and wear evaluation. This pairing did not complete the full 3 hour test due to galling. The Zygo surface profile data illustrates the degree of adhesive wear that occurred (47 μm).

Figure 4.2-35. D2 tool steel ball wear associated with the uncoated D2 tool steel ring.

The results of all of the friction and wear testing were collected and placed into a tabular format for comparison. Refer to **Table 4.2-2** for these results and **Figures 4.2-36** and **4.2-37** for graphical representations of the data.

Table 4.2-2. Wear measurements at the conclusion of the 3 ball on ring testing performed using Eaton's Falex machine.

Coating Material	TZB	RocTec 500	TM 10	Ni3B	MMC	H10F	D2	C17N	AlMgB14	WG100
Average Ring Wear (microns)	19.05	1.96	0.46	12.88	167.64	1.04	25.6	0.69	0.95	0.51
Average Ball Wear (mm)	2.63	4.92	4.25	2.99	2.72	4.14	3.77	4.31	4.05	3.14

Figure 4.2-36. Graphical summation of the 3-ball on ring testing (ring wear scar depths shown to illustrate the differences of the tested materials).

Figure 4.2-37. Graphical summation of the 3-ball on ring testing (ball wear average area data shown to illustrate the differences associated with tested materials). Note that in the case of the ball bearings, all were D2 tool steel, though the counterface materials ranged from baseline D2 to a variety of wear-resistant materials.

Additional activities beyond the current scope of the project as follow-on work includes a comparison between Eaton's multi-phase (Ti,Zr)B₂ coating on D2 to Ames' single-phase, PLD-deposited material. And, in an effort to assess the impact that material substrate has on the friction/wear performance of the ball-ring coupling, Eaton plans to apply the (Ti,Zr)B₂ multi-phased coating to the WG-100 material (Al₂O₃ with SiC whiskers). It is worth noting here that the PLD deposited TZB material represented the first time that such a large substrate was employed and that this was a "first pass" attempt at bonding the TZB to D2 tool steel. Ranking these materials from best to worst to show how the TZB compares to the other wear resistant materials tested is considered premature; all of the other materials are production-intent, meaning that they are above TRL of 9 (in production). Conversely, the TZB PLD coating represents a technology readiness level of 5-6 at best, and a good degree of optimization is still required. We believe that these results point to the need for improved pre-deposition surface treatment of the substrate and further refinement of the specific PLD coating parameters that impact adhesion. When all of these variables are understood and fine-tuned, the performance of the TZB coating will show a marked improvement. A good case for this reasoning is demonstrated by the AlMgB₁₄ coating, applied via PVD processing. As this material and its associated processing parameters were the subject of a multi-year development project, its performance can be considered optimal. And, in relation to the other coated specimen, Ni₃B, the AlMgB₁₄ performance improvement in terms of relative wear is rather significant. Further study of the TZB's wear characteristics is planned as a follow on activity – during which the substrate/coating interaction will be explored in greater depth.

A final application within Eaton's Aerospace product portfolio is a high pressure fuel pump that is derived from a radial ring architecture. Baseline evaluation of the main shaft component in the pump reveals that the stresses encountered exceed 1GPa (**Figure 4.2-38**). The graph illustrates the contact pressures and pressure*velocity products encountered in service for this component. As noted, the pin-shaft Hertzian contact pressures reach values as high as 400,000 psi, nearly equivalent to 2.8GPa.

Figure 4.2-38. Graphical representation of the contact pressures encountered on the pump shaft. The interface that the applied $(\text{Ti,Zr})\text{B}_2$ is meant to improve is the pin to shaft (green line on plot).

A photograph of the key surfaces on the pump's main shaft is included in **Figures 4.2-39 and Figure 4.2-40**. This images document the two T-shaped keyways on one side of the shaft's working surface and an oblong keyway on the other side of the shaft

Figure 4.2-39. Photograph of the fuel pump shaft. The interface of primary interest is the pin-to-shaft contact (green line on plot). The circled areas are T-shaped keyways that are a wear concern for the aerospace group.

Figure 4.2-40. Photograph of the fuel pump shaft. The interface that the applied (Ti,Zr)B₂ is meant to improve is the pin-to-shaft contact (green line on the plot) and the pin-to-sleeve contact (red line on the plot). The circled area is an oblong keyway that is a primary wear concern for the aerospace group.

Prior to any discussions on the application of coating the shaft, the fuel systems division engineering team pursued a number of exotic materials with the hopes that one would provide the desired strength and wear performance. Photographs of previous main shafts (or rather the areas of concern on the main shaft – namely the sleeve keyways) are included in **Figure 4.2-41**. These photographs illustrate that the oblong keyway is very prone to erosive wear and that, provided a coating solution can function at the contact pressures reported, the performance of the product will be enhanced through elimination of this wear.

Figure 4.2-41. Measurable wear noted on previous main shaft tests using a variety of different alloy systems.

The shaft was evaluated by Eaton's divisional engineers after 50 hours of cyclic endurance testing to assess the damage. **Figures 4.2-42 (a and b)** illustrate the differences between the baseline surface, a known wear resistant material (Aermett 100), and the (Ti,Zr)B₂ coating. For reference, the surface shown in **Figure 4.2-43a** was tested for a total of 12 hours, approximately ¼ the time of the surface shown in **Figure 4.2-43b**.

Figure (a)

Figure (b)

Figure 4.2-42. Photographs of the different fuel pump shafts after cyclic endurance testing. The image on the left (a) is that of the baseline shaft without the (Ti,Zr)B₂ coating after 12 hours on the test stand. The image on the right (b) is the (Ti,Zr)B₂ coated shaft after 50 hours of cyclic endurance. The degree of damage on the coated shaft is not-measurable.

Additional photographs were collected of the shaft after it had completed 200 hours of both cyclic endurance evaluation, low-lubrication testing, and cyclic low-lubrication testing. Refer to **Figures 4.3.5.1-3 (a and b)** for representative images.

Figure (a)

Figure (b)

Figure 4.2-43. Photographs of the (Ti,Zr)B₂ coated fuel pump shaft after a total of 200 hours of low lubricity cyclic endurance testing.

The testing performed on the pump shaft illustrates that, at a component level, the coating is capable of withstanding a contact stress of greater than 1GPa. Furthermore, the wear rates of this particular material are within the targeted range conceived as a milestone for technology performance.

4.3 Development of (Ti, Zr)B₂ PVD Coatings for Borg Warner Morse TEC Engine Timing Applications

Current chains products cannot fully meet the needs of automotive OEMs for more efficient and durable DI gasoline and diesel engines on account of chain wear and the elongation that results. In general, a timing chain is considered to fail if the elongation of the chain is over 0.4 to 0.7% depending engine applications. Most of current chains manufactured today, including vanadium carbide-coated pin chains, fail to meet this specification in the more demanding diesel engine and gasoline DI engine applications, especially those using turbochargers to increase power, reduce engine displacements, degrease engine exhaust, and/or consume less fuel.

One of the objectives of the project is for Ultracoated pin chains to meet these needs and result in reduced chain elongation when compared with Borg Warner's present solution of vanadium carbide coated pins chains. It is preferred to test a chain with all pins (about or over 100 pins) coated with the same coating, but it is also feasible to evaluate fewer coated pins (10 to 20) in a chain with the remainder of the chain comprised of standard components.

Simulation of pins sliding on timing chain link plates. A reciprocating test apparatus (**Figure 4.3-1**) was modified to use a cylinder-on-flat surface geometry (**Figure 4.3-2**). The actual contact between the test pin and the chain link side is shown in **Figure 4.3-3** The applied load was 200 N, the average sliding speed was 0.2 m/s (10 cycles/s at a stroke of 10 mm), and the lubricant was Mobil10W40 synthetic motor oil. The tests were conducted for a sliding distance of 400 m in air at room temperature.

Figure 4.3-1. Model TE 77 (Phoenix Tribology, UK) reciprocating friction and wear tester used in time chain link studies.

Figure 4.3-2. Schematic representation of sliding conditions.

Figure 4.3-3. Close-up view of the holder containing a link pin (end of the pin can be seen in the center of the image) resting against a chain link plate specimen of hardened 1050 steel (with holes at each end). The sliding motion of the pin is horizontal in this view.

Using Hertz calculations for a cylinder on a flat [2], the maximum and mean Hertzian contact pressures at the beginning of the test are 727 and 570 MPa, respectively. The max speed is 0.314 m/s at the stroke center. Therefore, the maximum PV is 228 MPa-m/s and the

mean PV, at the stroke center, was 179 MPa-m/s. The instantaneous rates of progression of the wear scar during the test are not known, but we can calculate the mean contact pressure at the stroke center at the end of the test, as shown in **Table 4.3-1**. The hardness and rate of wear of the VC coated pin were by far the best. The flat plates used for counterfaces were all hardened 1050 steel, but the plate used against the nitrided pin had a HV of 4.9 rather than 6.0 GPa for the other three plates.

Table 4.3-1. Results of reciprocating sliding tests.

Pin Material or Coating	Hardness, HV, 100 g (GPa)	Contact Pressure, P (MPa)	PV product (MPa-m/s)	Wear Scar Width, pin (mm)
Hardened 440B stainless steel	6.9	59.7	18.8	335
VC-coated 52100 steel	28.6	250.	78.5	80
(Ti, Zr)B ₂ -coated 52100 steel	17.4	66.7	20.9	300
Nitrided 440B stainless steel	12.7	71.4	22.4	280

The appearances of the worn test pins are shown in **Figure 4.3-4 (a-d)**. The narrow wear scar on the VC coated pin is suggestive of its high hardness and that the surface treatment remained intact. The (Ti, Zr)B₂ coated pin showed signs of wear-through, and the wear scar width is only slightly narrower than that for the hardened 440B pin without treatment.

Figure 4.3-4. Wear markings on test pins used in lubricated reciprocating tests. Note that the nitrided pin (b) was run against a plate specimen of slightly lower hardness than the others. Magnifications are the same for all images.

Figure 4.3-5 shows that the friction coefficients during sliding were about 0.09 to 0.12. This is within the boundary lubrication regime and suggests that there was a measure of material contact. The nitrided steel pin exhibited slightly lower friction at the end of the test, but the reasons were not entirely clear. After a noisy interval between 120 and 180 m of sliding distance, the decrease in friction began, suggesting that the noisy interval indicated abrasive wear, which eventually polished the surface and allowed the friction to begin to drop.

Figure 4.3-5. Friction coefficient versus cumulative sliding distance for various pin materials sliding against hardened 1050 steel.

5.0 Benefits Assessment

Final energy savings calculations for each of the potential application spaces have been determined, based on production-intent hardware tests that show the Ultracoatings technology being capable of withstanding high contact pressures (1 GPa) in low-lubricity environments. Although there are specific examples included that illustrate the energy savings potential of the technology, the opportunities extend well beyond those documented. It is worth noting, however, that additional research and development is required to scale the technology beyond prototype-sized lots into full scale, multi-million component production runs.

The high-speed radial piston pump for Eaton Aerospace's hydraulic systems division, as an example, stands to benefit from the Ultracoatings technology because of its wear performance and low-friction behavior. The current pump system is designed to rotate at speeds exceeding 10,000 RPM, and so the resultant centrifugal forces create a friction/wear coupling that immediately limits several possible material candidates. The high-speed radial piston pump is designed to be a direct, engine-driven hydraulic system and eliminates the current gearbox system used to down speed the input shaft required to drive the pump. Eaton's feedback from end customer interaction is that elimination of the input gearbox will save approximately 79 lbs. per engine-driven, hydraulic piston pump. In typical transport and commercial aircraft, there are two of these pumps per airframe, making the weight savings a total of 158 lbs. per aircraft.

Based upon the Federal Aviation Association's data that identifies economic values associated with FAA investment and regulatory decisions²⁴, the incremental fuel burn per pound of weight carried ranges between .004 and .010 US gallons per flight hour per pound of weight saved. This 158 lbs. savings would then reduce specific fuel consumption between 0.632 - 1.58 gallons of fuel per flight hour on Narrow Body and Wide-Body commercial flights. The associated energy savings with removal of this gearbox ranges between 75,840 and 189,600 BTU per flight hour. Nearly 20 million flight hours were logged in 2010 by commercial aircraft (including passenger aircraft at 15 million hours and worldwide transport aircraft at over 5 million flight hours), and so the projected energy savings attributed to removal of the engine driven pump gearbox would amount to 1.7-4.5 TBTU. Note that the energy savings only applies to replacement of the current system and does not factor in any incremental savings associated with implementation of the Ultracoatings technology in other hydraulic components onboard the aircraft.

Figure 5.0-1. Chart illustrating the number of commercial aviation flight hours per month. Aircraft flight hours have increased at a rate (on average) of 3% per year to current levels of 1.3 million revenue hours per month. Note that this does not account for non-revenue aircraft transport, inter-airport transport, and so forth.²⁵

Continuing on the previous statement's message for additional aerospace opportunities, a standard, axial orientation, aerospace piston pump application would stand to benefit from efficiency improvements associated with the coating's low(er) friction performance (in contrast to baseline materials). Current calculations show a per-engine savings of 1-2 HP, based on the application of coatings to each pump's pistons, valve plate, nutating plate, and wear plate. Previous testing has shown that there is a potential improvement in overall pump efficiency of 5% when the aforementioned components are coated. Current power estimates for the GE CF6-80 engine are 50,000 shaft horsepower, and so application of the coating to the hydraulic pumps onboard would result in a drop in fuel consumption of 0.3lb/hour, equivalent to 86 billion BTU in annual energy savings when Eaton's market share and annual volume are considered. Carbon and/or greenhouse gas emissions associated with the Jet A fuel savings would be reduced by 11,987,000 kg, nearly 12,000 tonnes. Assuming implementation of this technology across the total available market for variable and fixed axial displacement aerospace piston pumps, the energy savings would reach 513 billion BTU/year.

As there are many different systems onboard an airframe that Eaton supplies components and subassemblies to, fuel delivery and conveyance stands as a prime opportunity for a wear-resistant surface technology (given the low lubricity of jet fuel). For a typical domestic flight of 2 hours, there is a confirmed minimum of 1.6 gallons of fuel per engine saved per flight, using Eaton's new fuel pump technology over the current baseline system²⁶. It is worth noting that, based on the internal efficiencies of the pump itself, there is reduced waste heat transferred into the fuel. Therefore, additional fuel must be burned to increase the energy

level of the fuel burned during the combustion process. This reduces the net fuel savings to the 1.6 gallons per engine per flight value reported.

Given the energy density of Jet fuel of approximately 120,000 BTU/Gallon, the associated energy savings accomplished using Eaton's pump technology could be as large as 190,000 BTU/ 2hour flight/engine. A review of commercial flight data (**Table 5.0-1**) leads to the following calculations for energy savings:

97% of all domestic flights (typically narrow body, single aisle, and/or regional jet) on shorthaul use two engines (about 330k hours for three engine airframes in 2010 versus 9.5 million hours for two engines in 2010). For all intents, that equates to an energy savings of 400,000 BTU per flight– not withstanding 2-engine widebody, 4-engine narrow, and 4-engine widebody. Considering the 15.4 million worldwide airborne hours in 2010 logged by commercial aircraft, the breakdown for 2-engine narrow body, domestic shorthaul covers 62% of flights worldwide. Even though there may be a tendency to focus on 4-engine, widebody, longhaul flights, given the number of engines and the perception that fuel burn would be at least double that of a shorthaul flight, their total flight hours with respect to the 15.4 million in total is fairly low.

Assuming the 400,000 BTU per flight hour for the narrow body, shorthaul domestic aircraft segment, one could multiply the value by the 9.6 million airborne flight hours to assess the impact for every two-hour flight. The result is a potential savings of nearly 4 TBTU saved per year associated with application of just this pump technology. Lost in this calculation, unfortunately, are the domestic shorthaul flights that are greater than two hours, non-revenue flight hours, and worldwide transport aircraft that log an approximate 5 million additional hours. Therefore, the nearly 4 TBTU energy savings through the reduction of jet fuel burned is a conservative estimate.

For other, non-aerospace industrial applications, a good example of the associated energy savings can be illustrated through the engine timing chains manufactured by BW Morse TEC. This organization supplies approximately 4,000,000 timing drive chains per year in North America for passenger cars and light trucks. Within these application spaces, the timing drive chain friction accounts for approximately 1% of total vehicle energy use. Newly developed coating technologies, including Ultracoatings, have the potential to reduce total timing drive friction by 20%, maintained over the life of the vehicle. The average passenger vehicle produces 5.2 metric tons of CO₂e (CO₂ equivalent including CO, NO_x, SO_x, etc.) or 1.42 metric tons CE based on mileage and annual miles driven.²⁷

Implementation of a newly developed coating for these timing drive chains could result in a total passenger car and light truck CO₂e reduction of approximately 40,000 metric tons per year (5.2 tons per vehicle x 4,000,000 vehicles x 20% reduction in friction x 1% timing drive contribution). Note, this is for engine chains in North America only and does not include transmission chains and other global markets. Further developments of coatings resulting in greater than 20% reduction in friction would provide even greater reductions.

One gallon of gasoline is assumed to produce 8.8 kg of CO₂ or 9.26 kg CO₂e (= 8.8 x 100/95) based on EPA data, so 40,000 metric tons of CO₂e reduction is the equivalent of 4.31 million gallons of fuel savings. Accordingly, for engine chains sold only to the North American passenger car and light truck markets, an energy savings (based on a BTU-gallon of gasoline

equivalence of 150,000 BTU/gallon) of 0.6 TBTU per year could be expected. This does not account for legacy product, transmission chains, or other global markets.

Yet another application of the technology within vehicle markets is on transmission gears for Class 3-8 on-highway, U.S.-based trucks. The reduction of driveline system parasitic losses in the by 30 to 50 percent will improve fuel economy by 2 to 4 percent. This translates into a diesel fuel savings of 390 to 780 gallons per vehicle per annum, representing an energy savings reaching nearly 100 TBTU when accounting for the conversion between a gallon of diesel fuel and energy. While previous generation thin film coatings have been investigated for this application, the contact pressures are considered an inherent barrier to entry. Additional testing of the Ultracoatings technology for transmission components will be explored further as a continuation activity. A key challenge remaining is that a gear coating needs to be applied to production intent hardware and sustain the nearly 750,000 miles that the transmissions and/or driveline systems are covered under warranty.

Given the diverse nature of the application spaces selected, and the potential for energy savings associated with the Ultracoatings technology, the opportunity to make a significant impact becomes quite substantial. For Eaton's aerospace applications, there is a savings of over 9 TBTU, and this is for only two potential applications. Coupling these values with the projected savings for on-highway truck transmission systems (pending further technology development) yields a cumulative benefit of 100 TBTU, beyond the original projection of 60 TBTU in the project proposal.

6.0 Commercialization

While a significant portion of this project was focused on the development of the base technology and application to possible candidate components, there were market opportunities identified that represent significant energy savings and greenhouse gas reduction potential. Future commercialization activities will start with ensuring that the performance characteristics of the coating are repeatable through round robin testing and multiple sample evaluations. Process optimization and scale up is expected to follow. The second stage of commercialization testing will be in application of the coating technology to customer prototypes for field trials. Final activities will center on the development of marketing material(s), identification of a production supply source, and first-stage product release. In cost-sensitive markets, additional steps will be taken to ensure that alternative substrate materials are selected and sourced.

6.1 Aerospace Components

The successful completion of production-intent hardware testing at Eaton's aerospace facility has provided an opportunity for the technology to move into a commercial aviation application. As with previous thin film development, efforts to capitalize on fuel and energy savings hinge on end-market acceptance and product integration. Eaton's lead application for the technology is currently positioned at a TRL of 6 (technology demonstration). The next steps planned are completion of a system-level design review, presentation of data to end customers, and then product re-validation. Once customer acceptance/interest is established, engineering specifications will be created and the external sourcing process will begin.

6.2 Engine Timing Components

While initial Ultracoatings bench tests on engine timing chain pins did not show an immediate performance or life advantage over the baseline vanadium carbide coating currently used by Borg Warner Morse TEC, additional activities are planned that could lead to commercialization of the technology. Borg Warner's experience is that the bench tests do not always correlate well with the performance of in-field chain application. In the Oak Ridge National Laboratory bench tests, as an example, the nitrided stainless steel pins did not perform as well as the supplied vanadium carbide pins. In recent studies, however, Borg Warner Morse TEC found that the nitrided stainless steel pins outperformed equivalent vanadium carbide pins in corrosive and dirty conditions like those found in diesel engines. So to assess the performance of the Ultracoatings technology in other, severe service environments, work is planned to evaluate these materials in direct injection and diesel engine conditions. If the results of this study are positive, there would be a great opportunity for commercialization of the coating in timing chain applications for direct injection gasoline and diesel engines.

7.0 Conclusions

Given the diverse nature of the industries selected for implementation and the accelerated progress of the project, there are several conclusions that can be drawn. The functional performance testing on production-intent prototype components demonstrates that there is a significant improvement in product durability through enhanced wear resistance. This will, in turn, result in a significant energy savings opportunity through product implementation.

As an example:

- Application of the TZB coating to the aerospace fuel pump resulted in the product completing over 200 hours of low-lubricity testing. Prior to this, none of the proposed solutions had completed even 24 hours of testing without a significant reduction in performance
- An additional 1000 hours of durability testing were completed on the fuel pump noted above, thus enabling the product to advance towards commercialization. Next steps for this product include customer review, development of engineering specifications, process development, supplier selection, and market release.
- Friction and wear testing performed showed that the Ultracoatings technology exhibited 80% less wear than comparable AlMgB₁₄-TiB₂-C coated samples.
- Successful demonstration that a (Ti,Zr)B₂ coating/Aermet 100 substrate pairing could sustain contact pressures greater than 1 GPa in clay filtered Stoddard calibration fluid with a wear rate lower than 0.1mg/hour.
- The TZB coating researched does exhibit a growth pattern like that of the previously-investigated AlMgB₁₄-based nanocomposite coatings. Unlike the classic columnar growth columns that retain lubricant and gradually wear down, the TZB films appears to be mixed mode, with a predominant layered structure.
- Implementation of the severe service Ultracoatings technology into U.S.-based hydraulic, vehicle, aerospace, and gasifier markets identified would account for over 100 TBTU/year in energy savings by 2030, greater than the approximate 60 TBTU/year originally calculated using the GPRA analysis.

8.0 Recommendations

Clearly a “one size fits all” approach to composition and coating deposition will not address all application spaces within high contract stress environments. Additional development work is needed to define the best overall combination of composition, use of a coating interlayer, or bond coat (akin to the deposition of Ti, or Cr for DLC coating adhesion), and deposition method to achieve optimal performance for the applications targeted, e.g. fuel or hydraulic pump components, vehicle engine timing chain hardware, or compaction components for coal gasification. The following recommendations are made for further development and implementation of this technology:

1. Further development is recommended on characterizing the differences between single phase (Ti, Zr)B₂ and multi-phase (Ti, Zr)B₂. The wear resistance of the multi-phase coating on the production-intent aerospace fuel pump suggests that even the multi-phase coating is capable of sustaining extreme contact pressures. If the single-phase coating is developed and proves to be more wear resistant than the multi-phase composition, this could further enhance the performance of selected components and systems.
2. The single-phase (Ti, Zr)B₂ PLD coating process stands to benefit from additional process development. Initial wear testing results showed that the material is capable of low-friction, wear-resistant performance, though it may benefit from its own research effort to focus on adding a bonding layer like Ti or Cr.
3. As the aerospace fuel pump results suggest a significant performance enhancement associated with the Ultracoatings technology, the process towards commercialization will reveal [it is expected] many opportunities for process optimization.
4. The other materials originally conceived as part of this project may yield benefits beyond that of the (Ti, Zr)B₂ or the Al₄SiC₄. As with the TZB, these materials may be enhanced further by increasing the current density of states through substitutional replacement or the addition of tertiary phases.

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