Wear-resistance, lubricity, and adhesion of femtosecond pulsed laser deposited AlMgB14-based thin films

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Wear-resistance, lubricity, and adhesion of femtosecond pulsed laser deposited AlMgB\textsubscript{14}-based thin films

by

Austin Harold Shaw

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
Alan Russell, Major Professor
Scott Beckman
Palaniappa Molian

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Ames, Iowa
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Abstract

Ultrahard, wear-resistant coatings of thin-film AlMgB$_{14}$ coatings could extend the service life of wear-prone components such as cutting tools and hydraulic pump vanes. Previous work with AlMgB$_{14}$ has shown that it can have a hardness up to 46 GPa if alloyed with TiB$_2$, and it can be coated as a thin film using pulsed laser deposition (PLD). These films have already shown promise in various industrial applications. Vane blades coated with AlMgB$_{14}$ films via magnetron sputtering have significantly reduced the wear rate of the pump blades. Some research has been done on production of these films using nanosecond laser PLD, but this project was the first to use femtosecond pulsed laser deposition of coatings.

In this work, research was conducted into methods to optimize the thin films’ wear resistance and lubricity. The addition of 70wt%TiB$_2$ and/or a titanium interlayer was investigated to improve three parameters: wear-resistance, the steady-state coefficient of friction, and adhesion. The addition of TiB$_2$ lowered the adhesion and increased the wear rate of the film. However, the films with the TiB$_2$ addition did decrease the run-in time it took for the films to reach a steady-state coefficient of friction value. Films produced with a titanium interlayer were found to adhere to the M2 steel substrate better than films without the interlayer. The adhesion of the thin films to M2 tool steel substrates, assessed using the Rockwell C indentation adhesion test, was found to be substantially improved by the deposition of a titanium interlayer. The addition of the interlayer also lowered the steady-state coefficient of friction of the films. Ultimately, it was concluded that the film with the best properties was the pure AlMgB$_{14}$ deposited for 20 minutes with a Ti interlayer.
Chapter 1: Introduction

Many engineering components rely not only on their bulk properties, but also on their surface characteristics. This is especially true in wear-resistant components, which often must function in a wide variety of environments. The behavior of a material interacting with other objects is dependent on three major aspects: the surface properties, the surface contact area, and the environment in which the material must operate.

In many cases, a material’s surface properties are inadequate to withstand degradation in its working environment. When this is the case, the material’s performance can be improved either by treating the surface or by coating the surface. Surface treatments can be broken into two subcategories, treatments that alter the microstructure and treatments that alter the chemistry. Surface treatments that cause microstructure changes in the bulk material include heating and cooling/quenching through induction, flame, laser, and electron beam techniques, or mechanical treatments (e.g., cold working). Surface treatments that alter the chemistry of a surface include carburizing, nitriding, carbonitriding, nitrocarburizing, boriding, siliconizing, chromizing, and aluminizing [1].

These treatments harden the surface and are effective methods to improve wear properties. For a given system configuration and loading, the wear rate has been found to be inversely proportional to the hardness of the material in the system [2]. Hard surface layers lower wear by reducing plowing, the depth a counter surface can penetrate into the part’s surface. Reducing the depth of penetration of the counter surface in the material also provides the advantage of reducing the number of contact points between the surfaces, which can reduce the coefficient of friction between the two parts [3]. Increasing wear resistance and
lowering the coefficient of friction between parts are highly beneficial. It increases the working life of parts, and it lowers the amount of energy needed to slide the parts against each other. Because of the improvement to efficiency and service life, surface hardening has been studied intensively.

These surface-hardening methods improve performance, but for some applications the improvements are inadequate to achieve the desired level of wear or friction behavior. The maximum surface hardness achievable in a given material is limited by its chemistry. Steel, for example, can be treated to raise its hardness to 10 GPa [4]. Applying a surface coating, also known as hard facing, is not limited by the material’s chemistry because any coating material can be used to attain a higher surface hardness.

In the simplest analysis, the optimal materials to use as surface coatings would be materials with extremely high hardness. Diamond and cubic boron nitride are the hardest materials known and are obvious choices for coating materials. However, both are metastable materials and must be produced at high pressures and temperatures. This greatly increases their production cost. Other hard materials like tungsten carbide (WC) and alumina (Al₂O₃) are less costly but also have much lower hardness. Most ultra-hard materials are strongly bonded with simple, highly symmetric crystal structures. However, a new family of materials, based on boron icosahedra, has attracted attention as potential coating materials. These new boron-icosahedra-based materials exhibit high hardness, but they have more complex unit cells and lower symmetry than other hard materials. AlMgB₁₄ is one such boride that has been the focus of considerable research in recent years.
The research attention devoted to AlMgB$_{14}$ was motivated primarily by its ultra-hard properties. Single-crystal samples of AlMgB$_{14}$ were first studied in 1969 and reported [5] to have a moderately high hardness, around 28 GPa. Later research discovered that nanocrystalline samples had still higher hardness and that combining AlMgB$_{14}$ with other hard materials in composites further increased the hardness. The hardnesses of nanocrystalline samples of AlMgB$_{14}$ were reported to be 35 GPa, and composites of AlMgB$_{14}$ with TiB$_2$ had hardness as high as 46 GPa [6]. This raised AlMgB$_{14}$ into the realm of ultra-hardness, making it a prime candidate for use as a thin-film coating for engineering parts.

1.1 Crystallography of AlMgB$_{14}$

The structure of AlMgB$_{14}$ was reported when the material was first synthesized in 1969 [6]. In 1983 the structure was refined with more advanced diffraction techniques [7]. These studies determined that AlMgB$_{14}$ has an orthorhombic crystal structure (oI64, space group Imma). Refinement of the x-ray patterns showed that its unit cell dimensions are $a = 0.5848$ nm, $b = 0.8112$ nm, $c = 1.0312$ nm. The unit cell is based on four B$_{12}$ icosahedra centered at (0, 0, 0), (0, 0.5, 0.5), (0.5, 0, 0) and (0.5, 0.5, 0.5). This accounts for the majority of the boron in the structure. The aluminum and magnesium atoms occupy a four-fold position at (0.25, 0.75, 0.25) and (0.25, 0.359, 0), respectively. The eight remaining boron atoms lie outside of the icosahedra, bonding the aluminum and magnesium atoms to the icosahedra.
Initially, the metal atoms in the unit cell were thought to have full occupancy. However, in the later refinement, it was found that the aluminum sites had only 75% occupancy, while the magnesium sites had 78% occupancy [7]. This makes the true composition \( \text{Al}_{0.75}\text{Mg}_{0.78}\text{B}_{14} \).

The icosahedra are arranged in distorted, close-packed layers. The complex interaction within the icosahedra, in combination with the interaction between icosahedra is believed to contribute to the unique properties of \( \text{AlMgB}_{14} \).

1.2 Synthesis of \( \text{AlMgB}_{14} \)

\( \text{AlMgB}_{14} \) was initially discovered during study of a mixture of aluminum borides prepared by heating boron and aluminum to 1000-1400°C. Magnesium was present as an impurity in the boron causing small crystals of \( \text{AlMgB}_{14} \) to form [6]. Later, larger crystals were
grown by heating a mixture of magnesium, boron, and aluminum in a 1:2:14 ratio to 900°C. The excess aluminum served as a crystal growth flux material. After being held at 900°C for six hours, the mixture was cooled to room temperature, and hydrochloric acid was applied to dissolve the excess aluminum, leaving small black crystals whose composition approximated AlMgB_{14}. Later groups improved the process by using an inert atmosphere [7] or metal salts to reduce the reactivity and volatility of the pure metals [8]. This approach produced excellent crystal specimens for testing the structure and some properties, but it was impractical for producing large amounts of AlMgB_{14}.

Later research efforts addressed production of fine-grained bulk samples of AlMgB_{14}. The first attempts to produce larger AlMgB_{14} bulk samples used direct reaction synthesis of the elemental powders. This process involved mixing the powders, then isostatically hot pressing the materials around 1400-1500°C. However, the process yielded a low fraction of AlMgB_{14} [9]. However, if the powders were first mechanically alloyed, the HIP’d compact had a higher yield of AlMgB_{14}. The mechanical alloying of the elemental precursors reduced particle size and created a more homogenous powder that reacted more readily to form AlMgB_{14} [10].

Three milling methods were used to produce the alloyed powder: vibratory, planetary, or Zoz mill. While each produces a good precursor powder to form AlMgB_{14}, the sample sizes differ greatly. Vibratory milling is a high-energy milling technique that produces three to five grams of powder. Planetary milling is a much lower energy process, but it can produce up to 25 grams of powder per charge. However the lower energy of planetary milling necessitates longer milling times and produces a coarser particle size. Zoz milling is a high-energy milling technique...
comparable to vibratory milling [11]; however, Zoz mills can produce a much higher volume of powder, 0.25 to 900 liters of material.

Mechanical alloying of the powders has the unfortunate side effect of introducing impurities. Iron and oxygen are incorporated into the powder during the milling process. Iron comes from wear of the steel milling media and vial. The high-energy impacts of the media abrade both the vial’s inner wall and the media [9]. Higher energy mills, such as Zoz and vibratory mills, introduce more iron than lower energy mills (e.g., planetary mills). Planetary milling introduces 1-2% iron, whereas vibratory milling introduces as much as 10-15% [12]. One benefit to the iron, however, is that it acts as a sintering aid for the AlMgB14. Oxygen impurities come from the atmosphere, which form oxides within the powder both before and during milling. Most of the oxygen reacts with the aluminum and magnesium to form spinel, Al2MgO4; the remainder forms Fe3O4 [13]. Each of these impurities degrades the properties of AlMgB14. Impurities can be minimized by using lower energy mills and handling the powders in an inert atmosphere. Lower impurity contents produce tougher and harder compacts.

Milled powders have been shown to be easily reacted and sintered by hot uniaxial pressing in graphite dies [14]. As previously stated, simply sintering the powders does not produce dense fully formed AlMgB14. It is necessary to hot press the alloyed powder at pressures around 100MPa to produce fully dense AlMgB14 compacts. The pressing temperature also affects the density of the hot-pressed compacts. Samples pressed at 1300°C or lower, even with pressures as high as 100 MPa were found to be porous. However, samples pressed at 1400°C have nearly 100% of the theoretical density with extremely fine grains and an even grain size distribution [15].
1.3 Properties of AlMgB$_{14}$

When AlMgB$_{14}$ was first discovered in 1969, only the crystal structure was reported [6]. Aside from Higashi’s structure refinement in 1983 [7], AlMgB$_{14}$ received little attention until twenty years later. However, since 2000 AlMgB$_{14}$ has piqued extensive interest due to its high micro-hardness in bulk samples.

The hardness of a single crystal of AlMgB$_{14}$ has been measured to be 28 GPa [10]. Bulk powder-processed samples were found to have the same hardness. It was soon apparent that if thin films of AlMgB$_{14}$ could be produced having this same hardness, the material could be used as a protective coating. If used to surface harden steels, it would be the highest hardness surface treatment for steel. M2 tool steel has a hardness of 9 GPa; adding a surface coating of AlMgB$_{14}$ would more than triple the surface hardness.

Table 1.1: Some hard materials and selected properties of those materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{(}$Diamond$)</td>
<td>3.52</td>
<td>70</td>
</tr>
<tr>
<td>BN$_{(}$Cubic$)</td>
<td>3.48</td>
<td>45 - 50</td>
</tr>
<tr>
<td>AlMgB$_{14}$ + TiB$_2$</td>
<td>3.14</td>
<td>30 - 46</td>
</tr>
<tr>
<td>B$_2$C</td>
<td>2.52</td>
<td>38 - 44</td>
</tr>
<tr>
<td>AlMgB$_{14}$</td>
<td>2.66</td>
<td>25 - 35</td>
</tr>
<tr>
<td>TiB$_2$</td>
<td>4.50</td>
<td>30 - 33</td>
</tr>
<tr>
<td>WC</td>
<td>15.77</td>
<td>23 - 30</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.98</td>
<td>21 - 22</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>3.44</td>
<td>17 - 21</td>
</tr>
<tr>
<td>FeB</td>
<td>7.15</td>
<td>11 - 15</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>4.25</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Al$_2$MgO$_4$</td>
<td>3.58</td>
<td>12 - 15</td>
</tr>
</tbody>
</table>
As previously stated, the iron and oxygen impurities drastically reduce the hardness of bulk AlMgB\(_{14}\) [15] by forming softer phases within the material, particularly FeB, Fe\(_3\)O\(_4\), and Al\(_2\)MgO\(_4\), all of which have a much lower hardness (Table 1.1) than that of AlMgB\(_{14}\).[13]

However, the effect of these impurities on thin films of AlMgB\(_{14}\) has not been systematically studied.

Another important property of any thin film is its coefficient of thermal expansion (CTE). The CTE of any coating material must be closely matched to the substrate material’s CTE to avoid large residual stresses. AlMgB\(_{14}\) has a higher CTE than other ultra-hard coating materials such as diamond-like carbon and cubic BN. The CTE of AlMgB\(_{14}\) is 9\((10^{-6})\)K\(^{-1}\) [16], which is close to the CTE’s of steel and titanium, 11\((10^{-6})\)K\(^{-1}\) and 8.6\((10^{-6})\)K\(^{-1}\), respectively. Diamond has an extraordinarily low CTE, only 0.7\((10^{-6})\)K\(^{-1}\) and cubic BN has a low CTE of 1.2\((10^{-6})\)K\(^{-1}\). Therefore, the stresses that develop in AlMgB\(_{14}\) thin films on steel will be much less than those of diamond-like carbon or cubic BN coated on steel. The lower residual stresses between film and substrate allow better adherence to steel substrates. This is a substantial advantage, making AlMgB\(_{14}\) a strong candidate for use as a thin-film coating, especially for parts exposed to both abrasion and changing temperatures.

Chemical inertness and moderate cost both favor selection of AlMgB\(_{14}\) for thin film coatings. Titanium metal is highly reactive with many standard coatings and cutting materials, but AlMgB\(_{14}\) shows little reactivity with titanium. Experiments have shown that juxtaposed layers of Ti and AlMgB\(_{14}\) have minimal interdiffusion at 1200\(^{\circ}\)C temperature [14]. The cost of AlMgB\(_{14}\) is much lower than that of diamond. Depending on particle size and grade, diamond and cubic boron nitride powders cost from $2000 to $15000 per kilogram. The principal cost in
AlMgB$_{14}$ is the boron, which costs $200 to $1500 per kilogram, depending on purity [17]. Including the other elements, milling, consolidation and sintering makes the cost of AlMgB$_{14}$ approximately $400 to $2000 per kilogram. AlMgB$_{14}$-based materials’ moderate cost, high thermal stability, high hardness, and chemical inertness all combine to make them appealing coating materials for various engineering applications.

Pulsed Laser Deposition: An Overview

1.4 Summary of PLD Process

There are many different methods to deposit wear-resistant thin films, but all fall into one of two general categories: chemical vapor deposition (CVD) and physical vapor deposition (PVD). CVD processes involve reacting a gas phase on the surface of the substrate to produce the desired coating. Si$_3$N$_4$ coatings, for example, are produced by reacting ammonia (NH$_3$), and silane (SiH$_4$) at the surface to be coated. CVD processes work with films with relatively simple compositions that can be formed from the reaction of gases. PVD, however, vaporizes solid or liquid targets that can have much more complex compositions. PVD processes work by condensing vaporized material from the target onto the substrate. In some cases the material is reacted during transfer to produce oxides, carbides, and nitrides. For example, wear-resistant films of TiC$_x$N$_{1-x}$ have been produced by ablating titanium targets in an atmosphere of nitrogen and acetylene [18]. Some PVD processes, such as magnetron sputtering and evaporation, cannot reproduce the bulk chemistry of complex targets. This is largely due to differences in vapor pressures of the cationic species in complex targets. If this occurs, the deposited film would have a higher concentration of the more volatile species.
In pulsed laser deposition (PLD) this uneven ablation does not typically occur because PLD transfers enough energy into the material to cause congruent evaporation. Since all of the individual elements in the target are removed and deposited simultaneously, the chemistry of the target material tends to be completely reproduced in the film. PLD’s ability to congruently ablate material suggests that it could reproduce the more complex chemistry of ultra-hard boride materials, such as AlMgB$_{14}$, as thin films.

PLD is also relatively simple and easy to use. All that is needed is to focus a pulsed high-energy laser on to a target within a vacuum and place a substrate near the target to catch the plasma ejected from the target by the laser. Most PLD systems use lasers with short pulse widths, varying from tens of nanoseconds to hundreds of femtoseconds [19, 20]. When the laser is hitting the target, most of the energy of the laser is being absorbed into the target material. If the pulse has sufficient energy, the target material will undergo a phase change, either melting or vaporizing a small volume near the surface. The resulting vapor contains ionized species, neutral species, and possibly some clusters of atoms [21]. The amounts of each depend on the parameters of the laser used.

The vaporized material rapidly moves away from the target normal to the target surface forming a plume. If the substrate is placed in the path of the plume, the material will be deposited on to the substrate. Continued ablation of the same spot has been found to cause a progressive and substantial decrease in material removal rate. In order to maintain the deposition rate, the target should be rotated about its center or the laser should be rastered across the target so different spots are struck by successive laser pulses [22]. This movement
has an added benefit of maintaining a high efficiency of material deposition since deep grooves or holes in the target material block the ejected vapor.

Figure 1.2: Schematic of a pulsed laser deposition chamber

1.5 How material is removed during PLD

During pulsed laser deposition (PLD), the many interactions between the laser and the target material and within the target material itself determine how much of the material and what material will be deposited. These interactions include the absorption of energy from the laser by the material and removal of material from the target through equilibrium and nonequilibrium processes [23]. The mechanisms that govern the absorption of light by the material are similar regardless of the laser pulse duration. However, further processes occurring within the material that involve the transfer of energy from the electrons to the lattice depend heavily on the time scale of the laser pulse [21]. Because these later steps are responsible for the
removal of material from the target, differences in the final chemistry and the surface quality arise between nanosecond-pulse lasers and femtosecond-pulse lasers.

The first step in removal of material from the target is the absorption of the laser light. The efficiency of the ablation is based on the ability of the target to absorb light. If a wavelength of light that is strongly absorbed by the material is used, lower light intensity is required than for a wavelength that is not as easily absorbed. This can cause a problem if the target is a multi-phase material. Past work ablating AlMgB\textsubscript{14} using PLD showed that using an 800nm wavelength laser caused a large amount of spinel (Al\textsubscript{2}MgO\textsubscript{4}) to form in the deposited coating. This was attributed to the stronger absorption of 800nm light by spinel than by AlMgB\textsubscript{14}, causing more spinel to be ablated \cite{24}.

The incident laser light can be absorbed in many ways. Photons with sufficiently high energy can induce electronic transitions in the material in which an electron absorbs a photon, exciting the electron to a higher energy state. Lower energy photons can excite phonons and cause the material to transition between vibrational states \cite{25}. Both methods involve the absorption of a single photon. However, depending on the laser properties, non-linear absorption mechanisms, such as multi-photon absorption, can dominate the process \cite{22}.

At much higher laser fluences, the high density of available photons dramatically increases the odds of photon absorption, even in materials where the photon energy is less than the band gap, via the process of multiple photon absorption \cite{23}. In this case, several photons interact with the same electron at the same time allowing all to be absorbed at once. For this to occur, the combined energies of the photons must be large enough to excite the
electron across the band gap of the material. This process is much less likely to occur than the single-photon excitation process.

In AlMgB$_{14}$ the band gap was measured to be 0.5eV, which is smaller than the energy per photon used in most PLD processes [26]. Near infrared radiation at 800nm has an energy of 1.55eV per photon. This is more than enough to excite an electron across the band gap. Therefore, most of the laser absorption occurs by single photon excitation of electrons across the band gap. Additional energy can be absorbed if the electrons transition to a higher energy state or ionize.

The removal of material depends strongly on the pulse duration of the laser. The energy that is absorbed by the electrons is transferred to the lattice, creating phonons, when the electrons decay back to ground state. This transition occurs over a time period of several picoseconds and causes rapid heating of the material that is absorbing photons from the laser. An excimer laser can increase the surface temperature of the target at a rate of $10^{10}$K/s [22]. Once the material is heated, it melts rapidly. It can sublimate from the solid, but the amount of material removed this way is small. Removal of material by evaporation is much more efficient. However, if the evaporation is too rapid, the surface will cool and contract compared to the bulk, and droplets of materials can be ejected from the surface. Droplets can also form from asperities on the surface of the target due to surface tension and interaction between the surface and bulk. Both the vapor and droplets accelerate away in a nearly normal direction from the surface. As material initially leaves the target, the vapor is further ionized and heated by the laser, forming a plasma. In general, this process could cause the plasma to become a very good absorber of laser light, particularly of visible or IR radiation, but short wavelengths
are poorly absorbed by the plasma [22]. The vapor, neutral or ionized, and droplets are deposited on the substrate causing the film to accumulate.

The pulse duration determines which mechanism dominates material removal. A laser pulse of hundreds of femtoseconds uses a different mechanism to remove material than that of a nanosecond-pulse laser. In the nanosecond regime, there is enough time between pulses for the excited electrons to decay into phonons and heat the material. This process takes several picoseconds [21]. Once this energy enters the lattice, the material melts and evaporates, leaving the surface. However, using a femtosecond laser, the electrons do not have time to decay, and material is removed in a non-equilibrium process.

There are three mechanisms by which material is removed during PLD: thermal ablation (evaporation), nonthermal ablation, and electrostatic ablation. Thermal ablation occurs after the pulse ends when conditions in the target and in the vapor are close to those in equilibrium. This removal process is slow and removes little material per pulse. The vapor produced from evaporation can form droplets due to the previously mentioned difference in temperature between the bulk and the surface of the material.

Nonthermal ablation also occurs between the pulses. In order for this to occur, three criteria must be met. First, the energy absorbed from the electrons must be transferred to the ions. Second, the ion-ion collisions must establish an equilibrium distribution, which occurs after many collisions. And lastly, the ion ablation rate must be lower than the thermal velocity of the ions [21]. If these conditions are met, the rate at which the solid is transferred into vapor is higher than the rate of evaporation. This means the material has not had time to reach equilibrium, and evaporation proceeds in a nonequilibrium process.
Electrostatic ablation can occur during the pulse, unlike thermal and nonthermal ablation. Electrostatic ablation occurs when the electrons in the surface layer of the material gain enough energy to exceed the threshold energy required to leave the target. This is only seen with ultra-short pulses. The ultrafast energy pulses impart enough energy into the electrons that the electrons escape the solid and create a strong electric field due to charge separation. If enough electrons are removed from the surface that the force of the electric field is greater than the binding energy of the lattice, ions will be removed from the surface and form a plasma. If the electric field is too weak to remove the ions from the lattice, the electrons will be attracted back into the lattice. This process takes about 40 femtoseconds [27]. Because the process is so quick, there is insufficient time to transfer thermal energy from the electrons to the ions. Therefore, the bulk material will remain cold, and there will be no thermal or nonthermal ablation.
Figure 1.3: SEM images of the surface morphology of AlMgB₁₄ film made by PLD using a nano-second (top) and femto-second PLD film (bottom)

Since the surface and bulk materials do not heat during electrostatic ablation, no droplets will be formed. However, nanoparticles do form within the plume during electrostatic ablation. Many experiments have shown that using laser pulse widths less than a few picoseconds create films that are not smooth [28]. The films are composed of nanoparticles stacked on top of each other [29]. These particles are less than 1 micron in diameter. This makes them too small to be formed from droplets being ejected from the surface, which have diameters greater than 1 micron. These particles are smaller in size, have a smooth surface and are much more abundant than the particles formed by nanosecond lasers. This suggests that these nanoparticles are being condensed from the material after removal [28].

Formation of nanoparticles can degrade the film’s compositional uniformity. The composition of these particles would not be identical to the target material. For example, pure metal particles could react with the atmosphere and oxidize in transit. The plasma plume is made of individual ions which could react with each other in flight to create other compositions, also degrading the film quality. Other researchers have shown when depositing
BaTiO$_3$ that if the laser is nearly normal to the target more titanium is seen in the films, whereas at oblique incident angles more barium accumulates [28]. For this reason, it is key to optimize the laser’s power and incident angle in order to minimize the production of particles and ensure congruent ablation while using pulsed laser deposition.
Chapter 2: Experimental Procedure

Two targets were made, one AlMgB$_{14}$ and one AlMgB$_{14}$ with 70wt% TiB$_2$. The AlMgB$_{14}$ target was made by Zoz milling the elemental powders. The boron was 95% pure boron purchased from SB Boron Corp., which was then vacuum outgassed at 800°C to reduce oxygen and moisture impurities. The aluminum was produced in Ames Laboratory’s Materials Processing Center by gas atomization rapid solidification (GARS). The GARS process passivates the surface to minimize oxygen contamination. The GARS aluminum was -140 mesh, 99.9% pure. The magnesium was -325 mesh 99.5% pure from Alfa Aesar. The Zoz mill was run for four hours at various speeds to ensure homogeneity, using stainless steel milling media. The mixed powder was then retrieved and loaded into a one-inch diameter graphite die for hot pressing. The graphite die was coated with hexagonal-BN and graphfoil to enhance lubrication and to protect the die. Consolidation was performed in a Centorr vacuum hot press under 106 MPa pressure for 1 hour at 1400°C. The AlMgB$_{14}$+70wt%TiB$_2$ target was produced using a proprietary powder from NewTech Ceramics. The powder was then uniaxially hot pressed at 1500°C and a pressure of 35 MPa pressure to produce a four-inch diameter compact. From this a smaller target was fashioned to give an approximately 0.75-inch diameter target. X-ray diffraction (XRD) was performed on the targets, and that showed that both targets contain some oxygen impurity in the form of spinel, Al$_2$MgO$_4$. The substrates upon which the boride composite was deposited were M2 steel vane blades.

PLD experiments were performed in a turbopumped vacuum chamber (<5x10$^{-6}$ Torr) using a Ti: sapphire laser with a pulse duration of 100 femtoseconds. The femtosecond laser was operated at a frequency of 1 kHz with a pulse energy of 2.0 mJ per pulse. The substrate was
heated to 500°C and held at that temperature during deposition of all coatings and interlayers, using an electric heater built into the substrate holder. Titanium interlayers were deposited on half of the samples. The deposition times and coating thicknesses are presented in Table 2.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition Time (min)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlMgB$_{14}$</td>
<td>10</td>
<td>0.32</td>
</tr>
<tr>
<td>AlMgB$_{14}$ + TiB$_2$</td>
<td>10</td>
<td>0.99</td>
</tr>
<tr>
<td>AlMgB$_{14}$ + TiB$_2$</td>
<td>20</td>
<td>1.30</td>
</tr>
<tr>
<td>AlMgB$_{14}$ + TiB$_2$</td>
<td>20</td>
<td>0.72</td>
</tr>
<tr>
<td>Ti interlayer</td>
<td>5</td>
<td>0.31</td>
</tr>
<tr>
<td>Ti interlayer</td>
<td>5</td>
<td>-</td>
</tr>
</tbody>
</table>

*Total thickness, different layers not distinguishable

The microstructure of pure AlMgB$_{14}$ and pure TiB$_2$ was examined with a Philips CM30 transmission electron microscope. XRD data were collected using Cu Kα radiation with a Panalytical X-ray diffractometer. Tribological data were collected using a pin-on-disk tester. The pin-on-disk testing parameters were: load=10 N, sliding speed=0.5 m/s, sliding distance=32000 meters. The testing was lubricant starved; two drops of DTE-24 oil were placed under the ball at the start of the test, and no further lubrication was added for the duration of the test.

The film thickness was measured using ball cratering. This process works by using a rotating sphere with a known diameter that is pressed on the coating surface with a pre-selected load. Both the position of the sphere relative to the sample and the contact load are constant. After adding abrasive paste to the contact zone, a spherical cap depression is abraded into both the coating and the substrate. Optical inspection of the depression reveals the projected surfaces of the abraded coating and substrate sections. By measuring the diameter of
the crater at the surface and at the interface between the film and the substrate, the thickness of the coating can be calculated by a simple geometrical equation.

A Rockwell-C indentation test was used as a destructive qualitative assessment of coating adhesion. This test method uses a standard Rockwell-C hardness tester to cause damage adjacent to the indentation. The damage to the film was compared with defined adhesion-strength-quality illustrations. This adhesion test is standardized in the VDI\textsuperscript{1} guidelines 3198 (2003), as shown in Fig. 2.1. HF 1 through HF 4 are defined as good adhesion, while HF 5 and HF 6 are defined as poor adhesion and coating failure. After indentation a JEOL JSM-840a scanning electron microscope was used to observe the surface morphology and the damage done by the Rockwell-C indentation for comparison on the HF scale.

![Figure 2.1. The principle of the VDI 3198 indentation test.](image)

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\textsuperscript{1} Verein Deustcher Ingenieure or the Association of German Engineers


Results and Discussion

XRD

Figure 3.1 shows the XRD pattern of femtosecond laser PLD coatings of pure AlMgB$_{14}$, while Figure 3.2 shows the XRD pattern of femtosecond laser PLD coatings AlMgB$_{14}$+70wt% TiB$_2$. Both patterns are similar. Neither shows the major diffraction peaks for the ternary boride structure. Both indicate that the films are largely amorphous, although the mixed-phase sample does show peaks that correspond to crystalline TiB$_2$.

Figure 3.1: XRD Pattern of AlMgB$_{14}$ thin film
Figure 3.2: XRD Pattern of AlMgB$_{14}$+70wt% TiB$_2$ thin film, peaks correspond to TiB$_2$.

TEM

Using a Phillips CM-30 transmission electron microscope, AlMgB$_{14}$- and TiB$_2$-coated copper grids were analyzed. Figure 3.3 shows a plan-view bright field TEM image of deposited AlMgB$_{14}$. The amorphous structure of the film is indicated by the halo ring in the selected area diffraction pattern. Figure 3.4 shows a plan-view bright field TEM image of TiB$_2$, similarly deposited. The crystalline nature of the TiB$_2$ is indicated by the rings and dots in the selected area diffraction pattern. Both films show spherical particles, which is typical of PLD coatings. In order to further understand the PLD coatings, the AlMgB$_{14}$ sample was tilted 0˚ to 40˚ in the TEM sample holder to generate Figures 3.5 and 3.6. This showed that the deposited film contains rounded particles that flattened upon impact with the substrate.
Figure 3.3: Bright field TEM image of AlMgB$_{14}$ deposited by femtosecond laser PLD. Inset shows the selected area diffraction pattern (SADP).

Figure 3.4: Bright field TEM image of TiB$_2$ deposited with femtosecond PLD with SADP (inset).
The AlMgB$_{14}$ TEM sample was also placed on a hot stage to see if the particles would crystallize. However, up to 700°C, the highest temperature attainable on the TEM hot stage, no AlMgB$_{14}$ particles had crystallized. The XRD and TEM results indicate that the AlMgB$_{14}$ + TiB$_2$ PLD films are an amorphous matrix of AlMgB$_{14}$ containing crystalline particles of TiB$_2$.

Figure 3.5: Bright field image of AlMgB$_{14}$ with no stage tilt.
Figure 3.6: Bright field image of AlMgB$_{14}$ with a 40 degree stage tilt. This is the same region of the TEM specimen shown in Figure 3.5. Note how particles in this image appear to have major and minor axes, indicating that the particles flattened somewhat on impact with the substrate.

The samples were also examined using the Tecnai scanning transmission electron microscope (STEM) with an energy dispersive spectrometer (EDS). The STEM provided clearer images of the individual particles, and the compositions of individual particles could be determined by EDS. The AlMgB$_{14}$ sample can be seen in Figures 3.7, 3.8, and 3.10. From the STEM images, it was determined that while the individual particle size varied greatly, the largest particles were only ~200 nm in diameter. In theory the minimum particle size would be a single atom, which could not be resolved using the STEM; however, particles less than 1 nm could be seen. An average particle size would be difficult to determine and would be erroneously large if there are significant numbers of sub-nanometer particles. The EDS spectra obtained are shown in Figures 3.9 and 3.11.
Figure 3.7: STEM image of a coating produced by PLD from an AlMgB$_{14}$ target.
Figure 3.8: STEM image of a coating produced by PLD from an AlMgB\textsubscript{14} target. The region marked by the red circle in the upper left was analyzed by EDS to generate Figure 3.9.
Figure 3.9: EDS Spectra of spot marked in Figure 3.8. Far left peak is associated with boron and carbon.
Figure 3.10: STEM image of a coating produced by PLD from an AlMgB$_{14}$ target. The region marked by the red circle in the upper left was analyzed by EDS to generate Fig. 3.11.
Figure 3.11: EDS Spectra of spot marked in Figure 3.10. Far left peak is associated with boron and carbon. The peak at 1.5 keV is silicon and the 7 keV peak is copper.

The coating produced from a TiB$_2$ target was also analyzed using the STEM and EDS. Figures 3.12 and 3.13 show the STEM image and corresponding EDS spectra. The particles sizes also varied greatly in this specimen. The largest particles found were about 50 nm in diameter, which is only a quarter the size of the largest AlMgB$_{14}$ particles. The average particle size would be similarly difficult to determine for the same reasons as stated for the AlMgB$_{14}$. From the spectra it was concluded that the particles were Al, Mg, and B. The high Cu peak results from the grid being pure Cu. The high Si and O peaks were thought to be a contaminant from the
grid. Analysis of an unused grid (see Figures 3.14 and 3.15) showed that all the grids had Si and O peaks.

Figure 3.12: STEM image of a coating produced by PLD from a TiB$_2$ target. The region marked by the red circle in the left center was analyzed by EDS to generate Fig. 3.13.
Figure 3.13: EDS Spectra of spot marked in Figure 3.12. Far left peak is associated with boron and carbon.
Figure 3.14: STEM image of uncoated Cu TEM grid
Figure 3.15: EDS Spectra of spot marked in Figure 3.14.

**Pin on Disk (POD) Results**

Figures 3.16 and 3.17 show the friction data acquired from pin-on-disk testing of the thin films. Figure 3.16 shows the results from the coating produced from a pure AlMgB$_{14}$ target. The AlMgB$_{14}$ thin films deposited without a Ti interlayer show the same friction profile as the thin films with an interlayer, but the films with a Ti interlayer had a lower steady-state coefficient of friction than the pure AlMgB$_{14}$ film without a Ti interlayer. Figure 3.17 shows the results from the pin-on-disk test for the mixed-phase thin films, with and without an interlayer. The mixed-phase thin film friction results are also very similar in profile. However, the steady-state coefficient of friction of the mixed-phase thin film with a Ti interlayer is 0.02 lower than
the mixed phase without an interlayer. The mixed phase thin films also show an extremely short run-in time. After a sliding distance of 1000 meters, the mixed-phase thin films had reached a steady state, whereas the pure AlMgB\textsubscript{14} thin films had not quite reached a steady-state friction even at the 17,500 meter mark.

Figure 3.16: Results of pin-on-disk tests on AlMgB\textsubscript{14} films. Film deposition time was 10 minutes unless noted otherwise.
The thin films with a longer deposition time showed a much lower wear rate than their thinner counterparts. However, the 20-minute-deposition films did not adhere as well as the 10-minute-deposition films. When compared against each other, the pure AlMgB$_{14}$ thin films showed lower steady-state coefficients of friction, which can be seen in Table 3.1. However, the mixed-phase thin films achieved steady state quite rapidly in comparison to the pure AlMgB$_{14}$ films. While the Ti interlayer did lower the steady-state coefficient of friction in both the pure AlMgB$_{14}$ and mixed-phase films, it improved the mixed-phase films more than the pure AlMgB$_{14}$. Through the introduction of an interlayer, the mixed-phase films achieved nearly the same steady-state coefficient of friction as the pure AlMgB$_{14}$ films.
Table 3.1: Steady-State Coefficient of Friction and Wear Rate of Films and Balls. *(n/m)* indicates mass loss was too small to measure (<0.1x10^-8).

<table>
<thead>
<tr>
<th>Vane Material</th>
<th>Steady-state COF</th>
<th>Wear Rate of vane (mm³/N-m)</th>
<th>Wear Rate of ball (mm³/N-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlMgB₁₄</td>
<td>0.09</td>
<td><em>(n/m)</em></td>
<td>0.01x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄ (#2)</td>
<td>0.06</td>
<td>1.6x10^-⁸</td>
<td>0.7x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄-TiB₂ <em>(coating partially broken)</em></td>
<td>0.10</td>
<td>3.3x10^-⁸</td>
<td>0.3x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄ w/ Ti interlayer</td>
<td>0.06</td>
<td>2.4x10^-⁸</td>
<td>2.3x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄-TiB₂ w/ Ti interlayer</td>
<td>0.07</td>
<td>2.0x10^-⁸</td>
<td>0.08x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄-TiB₂ <em>(20 min deposition)</em> <em>(localized coating broken)</em></td>
<td>0.06</td>
<td>0.4x10^-⁸</td>
<td>0.05x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄ <em>(20 min deposition)</em> <em>(coating totally removed)</em></td>
<td>0.04</td>
<td>0.3x10^-⁸</td>
<td>0.3x10^-⁸</td>
</tr>
<tr>
<td>AlMgB₁₄-TiB₂ w/ Ti interlayer <em>(20 min deposition)</em> <em>(coating totally removed)</em></td>
<td>0.10</td>
<td>6.7x10^-⁸</td>
<td>1.0x10^-⁸</td>
</tr>
</tbody>
</table>
Rockwell C Adhesion Test

Optical micrographs of the indents made on the films are shown in Figure 3.18. All of the films passed the DIN adhesion test. Table 3.2 lists the evaluations for each film. The interlayer improved the adhesion in both the AlMgB$_{14}$ films as well as the mixed-phase films. In the pure AlMgB$_{14}$ films, minimal radial cracking around the edge of the indent occurred in the films without an interlayer. The pure AlMgB$_{14}$ films with an interlayer showed no signs of radial cracking. The mixed phase films showed the same improvement. There is some radial cracking in the mixed-phase film, which is reduced with the addition of an interlayer.

![Figure 3.18: Optical microscope image array of Rockwell C indents: a) Pure AlMgB$_{14}$ b) Mixed Phase c) Pure AlMgB$_{14}$ with interlayer d) Mixed Phase with interlayer](image)
Table 3.2: VDI Adhesion Test Results for PLD films

<table>
<thead>
<tr>
<th>Coating Material</th>
<th>Deposition Time (minutes)</th>
<th>VDI Adhesion Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coating</td>
<td>Interlayer</td>
</tr>
<tr>
<td>AlMgB(_{14})</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14})</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14})</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) w/ Ti interlayer(^2)</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) w/ Ti interlayer</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) w/ Ti interlayer</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2)</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2)</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2)</td>
<td>10</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2) w/ Ti interlayer</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2) w/ Ti interlayer</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2) w/ Ti interlayer</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14})</td>
<td>20</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14})</td>
<td>20</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) w/ Ti interlayer(^2)</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) w/ Ti interlayer</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2)</td>
<td>20</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2)</td>
<td>20</td>
<td>N/A</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2) w/ Ti interlayer</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>AlMgB(_{14}) + TiB(_2) w/ Ti interlayer</td>
<td>20</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^2\)Substrate oxidized, coating’s adhesion is poor

The Rockwell C indentation test was also applied to the longer deposition length mixed-phase films. In this case SEM images (Fig. 3.19) were taken rather than optical images. Figure 3.19a shows the full indentation crater, while Figure 3.19b and Figure 3.19c give a higher
magnification view of the delamination and cracking of the film. The longer deposition mixed-phase film without an interlayer showed many of the signs of a poorly adhering film, such as large radial cracks and delamination. This is expected of thicker films because the internal stresses produced in a deforming film increase with film thickness and are thus more likely to exceed the yield strength of the film, causing fracture. Even though the film separated from the surface, the coating was not removed.

Figure 3.20 shows the longer deposition time mixed-phase film with a Ti interlayer. The delamination and radial cracking are drastically reduced, which can be seen in Figure 3.20a and 20b. Upon closer inspection of the film (Figure 3.20c), microcracks are visible all around the edge of the indent. The film without an interlayer would rate an HF4 DIN rating; whereas, the film with an interlayer would score as HF2.
Figure 3.19: SEM images of 20-minute mixed-phase deposition without an interlayer
Figure 3.20: SEM images of 20-minute mixed phase deposition with a Ti interlayer
Chapter 4: Conclusions

Pure AlMgB\textsubscript{14} and AlMgB\textsubscript{14} +70wt\%TiB\textsubscript{2} thin film coatings were synthesized by pulsed laser deposition (PLD). These films were analyzed by x-ray diffraction, transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and scanning electron microscopy (SEM). The mechanical wear properties of the AlMgB\textsubscript{14}-based thin films were characterized by pin-on-disk testing, and the film adhesion was characterized using the DIN Rockwell C indentation test, and methods were investigated to improve the adhesion of the thin films.

From the XRD analysis, it was determined that the AlMgB\textsubscript{14} was being deposited as an amorphous thin film. The mixed-phase coatings’ XRD results showed that the TiB\textsubscript{2}, however, was crystalline and not amorphous. The SEM, STEM, and TEM results all confirm this analysis. The STEM and TEM also showed the largest particles were 100 and 50 nanometers at the largest for AlMgB\textsubscript{14} and TiB\textsubscript{2}, respectively. The smallest particles viewed were less than two nanometers in diameter, the resolution limit of the TEM. The TEM showed that the particles were approximately spherical, but they are flattened somewhat, presumably from their impact onto the substrate.

The pin-on-disk wear testing showed that the pure AlMgB\textsubscript{14} thin film deposited for 20 minutes had the lowest steady-state coefficient of friction and the lowest wear rate of the film. The film with the lowest ball wear rate was the 20-minute deposition of the mixed-phase sample. The mixed-phase thin films showed a lower wear rate on the ball than pure AlMgB\textsubscript{14} films, while the pure AlMgB\textsubscript{14} films had a lower wear rate on the vane, with the only exception being the 10-minute films with a titanium interlayer.
Deposition of a titanium interlayer between the steel substrate and the thin film improved adhesion. The interlayer also lowered the steady-state coefficient of friction compared to the films without an interlayer. The wear rate of the mixed-phase coating decreased with the addition of the interlayer, whereas the pure AlMgB$_{14}$ film’s wear rate increased with the addition of the interlayer. The interlayer increased the adhesion more for the thicker 20-minute deposition films than it did for the 10-minute deposition films.

Based on these conclusions, the coating to use for a wear-resistant thin film would be a long-deposition-time, pure AlMgB$_{14}$ with a titanium interlayer. The pure AlMgB$_{14}$ would provide the most wear-resistant coating while the titanium interlayer would improve the adhesion of the coating to the steel substrate surface.
Chapter 5: Future Work

This project focused on the improvement of AlMgB$_{14}$ films for use as a wear-resistant coating, either through the addition of TiB$_2$, a titanium interlayer, or both. The 20-minute-deposition pure AlMgB$_{14}$ with a titanium interlayer showed the best properties in this study, but it may not be the optimum configuration. Some questions were not addressed in this project. First, optimal film and interlayer thickness should be investigated. As seen in this project, the films with longer deposition times performed better. However, the thickness of the interlayer was unchanged. Second, materials other than Ti could be tested as an interlayer, although Ti has oxygen absorption properties that make it a particularly effective interlayer.

Minimization of particles in the material plume should also be investigated. If the particle size could be reduced, the film surface would become smoother and the wear properties should improve. More films should also be tested for wear-resistance. Not all the films made in this project were tested, and the additional data may lead to a better understanding of the films.

Microhardness or nanohardness of the amorphous AlMgB$_{14}$ and crystalline TiB$_2$ composite should be investigated. If TiB$_2$ is added to crystalline AlMgB$_{14}$, the hardness increases up to 46 GPa. However, the pin-on-disk results show that the films’ wear resistance is lowered by the addition of TiB$_2$. This could be because the microhardness was measured on bulk, fully crystalline specimens, and the bonding between the AlMgB$_{14}$ and TiB$_2$ phases in crystalline form is probably stronger than the bonding between the amorphous AlMgB$_{14}$ and crystalline TiB$_2$ present in the thin films.
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