Comparative wear in titanium diboride coatings on steel using high energy density processes

Arvind Agarwal, Narendra B. Dahotre*

Department of Materials Science and Engineering, Center for Laser Applications, University of Tennessee Space Institute, B.H. Goethert Parkway, Tullahoma, TN 37388, USA

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Abstract

A comparison between the tribological properties of titanium diboride (TiB$_2$) deposited using high energy density processes such as Pulse Electrode Surfacing (PES) and Laser Surface Engineering (LSE) has been made. The wear resistance of TiB$_2$ coated surface is higher than AISI 1010 steel. The wear resistance of the LSE coated TiB$_2$ coating is even better than that of the PES deposited TiB$_2$ coating. Coefficient of friction values for LSE coated TiB$_2$ coating ($\mu = 0.6$) are lower than PES deposited TiB$_2$ coating ($\mu = 0.7$). Wear occurs in PES deposited TiB$_2$ coating by brittle fracture and attrition type mechanisms whereas mixed adhesive–abrasive wear in LSE deposited TiB$_2$ coating occurs by localized plastic deformation of the soft matrix phase Fe from a “composite” layer on the surface.

Keywords: TiB$_2$ coating; Pulse Electrode Surfacing (PES); Laser Surface Engineering (LSE); Wear resistance; Coefficient of friction

1. Introduction

Tribological properties of ceramic coatings depend upon several factors such as hardness and thickness of the coating, coating material, type of the substrate, operating conditions and coating process. Based on these variables, several wear mechanisms have been proposed for different coating-substrate system, viz. ploughing, flake formation, micropolishing, cohesive failure or fragmentation, spalling, plastic deformation, removal of hard particle phase and attrition [1]. In the present study, wear and friction characteristics of titanium diboride (TiB$_2$) coating has been investigated.

TiB$_2$ is a transition metal based refractory ceramic, which has unique properties of extremely high hardness, high melting point, wear resistance, corrosion resistance and electrical conductivity [2]. It also has excellent corrosion resistance against metallic aluminum and cryolite, which makes it suitable candidate as a coating material for inert cathode used in Hall–Heroult cell for aluminum electrolysis [3,4]. Conventionally, TiB$_2$ ceramics are processed by hot-pressing and sintering which are very expensive, as it requires high temperature processing [5]. Moreover, near net shape forming is also impossible. However, surface engineering seems to be an alternate way to modify the surface properties similar to that of TiB$_2$ without altering the bulk properties of the engineering component or structure. In the present study, TiB$_2$ has been deposited on plain carbon steel using high energy density processes, Pulse Electrode Surfacing (PES) and Laser Surface Engineering (LSE) techniques. A comparative study of wear and friction behavior of TiB$_2$ coating deposited by these two processes is presented. For a better understanding of the comparative wear mechanisms, it is essential to understand the main features of the two coating processes. The detailed comparison of the two coating processes and the resulting coating morphology has been presented elsewhere [6–9].

1.1. PES

PES technique utilizes a high current, short duration pulse via a discharge capacitance and voltage circuit, which results in melting the electrode and depositing the material on the substrate [10–13]. This process is very similar to arc-welding process with the exception of little
total heat input. Hence, PES process is also referred as micro-welding process. The main advantage of this process stems from the fact that metallurgically bonded coatings with an adherent interface can be produced with little heat input to the substrate at ambient temperature [14]. Since the bulk material remains near ambient temperature and acts as heat sink, heat is rapidly dissipated leading to rapid solidification of the molten pool which in turn results in an extremely fine grained coating of high density, hardness and strength. Furthermore, PES process obviates the need of expensive environmental chambers required in several types of other coating processes. The primary requirement and the limitation for the PES process are that electrode material should be electrically conductive and thus capable of melting in an electric arc.

1.2. LSE

LSE is one of the surface modification processes where preplaced ceramic powder precursor is melted along with a thin layer of the substrate to produce a laser melt zone of desired composition [8]. The most important advantage stems from the fact that laser surface modification is a non-equilibrium synthesis. Laser surface modification involves high cooling rates (10\(^3\) to 10\(^5\) K/s), which produces metastable phases by exceeding the solid solubility limit beyond equilibrium phase diagram [15]. This leads to development of wide variety of microstructures with novel properties, which cannot be produced by any conventional processing technique. Moreover, these coatings are metallurgically bonded providing a sound and adherent interface between the coating and substrate. The surface structure can be tailored to the surface requirement of the application by varying process variables such as laser traverse speed, power, beam size and type and composition of the precursor [16]. Also, laser beam has an excellent spatial resolution that makes it ideal for depositing coating on miniature size components such as electronic sensors for high temperature applications. Another advantage of laser surface modification comes from the fact that laser beam can be transported to any remote location through fiber optics. This allows deposition of coatings on components or parts that are complex in shape and remotely located.

2. Experimental procedures

2.1. PES coating procedure

Coupons of AISI 1018 steel of dimensions 25 mm \(\times\) 10 mm \(\times\) 3 mm were mechanically polished on emery paper of grit 240 and then rinsed with acetone. A sintered electrode of TiB\(_2\) containing Ni in the range of 1–3 wt.% as binder was used to deposit coating on these steel coupons. Deposition was done using a hand held gun in air at room temperature. Pulsed electrode deposition was carried out at 50 V and spark duration of 10 \(\mu\)s. The discharge capacitance used for the PES process was 450 \(\mu\)F with a current of 50 A. Such processing parameters provide an input energy of 0.10 MW/m\(^2\).

2.2. LSE coating procedure

Commercially available TiB\(_2\) and Ti powders obtained from CERAC, Milwaukee, WI were used as precursor material for this study. Both powders had a purity of 99.5%. The average particle size range was 5.5 ± 1 \(\mu\)m. Thin plates of AISI 1010 steel of size 75 mm \(\times\) 150 mm \(\times\) 3 mm were cleaned using sand blasting. The precursor of a powder mixture of 2 wt.% Ti and 98 wt.% TiB\(_2\) composition in a water-based organic vehicle was sprayed on these coupons using a paint spray gun. The average preplaced powder bed had a thickness of 150 ± 15 \(\mu\)m. Sprayed coupons were dried at 70°C for 1 h prior to laser processing. The addition of 2 wt.% Ti to TiB\(_2\) was made on the assumption that Ti increases the wettability in the melt zone [17]. It was also anticipated that additional Ti would recombine with any boron, which may disassociate during laser processing. A 2.5 kW Hobart HLP 3000 continuous wave Nd:YAG laser (1.06 \(\mu\)m wavelength) equipped with a fiber optic beam delivery system was employed for synthesis of laser assisted TiB\(_2\) coatings. In order to provide a large sweeping coverage (i.e. rapid processing speed) and to reduce and/or to eliminate overlap between the successive laser passes, laser optics were configured to provide a 3.5-mm-long line beam in spatial distribution (TEM\(_{00}\)) onto the sample surface. The processing parameters were optimized in accordance with earlier reported literature [8,16]. In the present study, laser beam power and laser traverse speed were kept constant at 1.5 kW and 33 mm/s, respectively. Thus, the energy density input for LSE is 15 MW/m\(^2\), which is couple of orders of magnitude higher than PES process.

2.3. Microstructural characterization

Coating morphology and wear surface topography was studied using a ISI Super III-A scanning electron microscope (SEM) coupled with EDAX. Metallographic samples for scanning electron microscopy were prepared by polishing on Buehler TEXMET 2000 cloth during initial stages of polishing. The etchant used for TiB\(_2\) coated steel sample was Nital. Laser-treated samples required longer etching time as compared to PES samples. Such behavior could be explained by the nature of the coatings obtained in the two processes. Structural characterization for phase(s) identification was carried out on a Philips Norelco X-ray diffractometer with CuK\(_\alpha\) radiation (1.54 Å) operating at 40 kV and 20 mA. Surface roughness of the wear surface was examined using a WYKO VISION RST 500 optical profilometer.
2.4. Tribological characterization

Tribological properties of the TiB₂ coating were measured using a block-on-disk tribometer. Coated coupons of dimension 25 mm × 25 mm × 3 mm were tested for dry sliding wear against a hardened steel ring rotating at a linear speed of 4.4 m/s. Weight loss measurements were made after successive 2 min. The dry sliding wear test was conducted for a total of 20-min duration with an applied normal load of 2 kg. Coefficient of friction (µ) was also recorded for a 10-min period by an interfaced computer, which acquired data in the form of electrical output power of the motor.

3. Results and discussion

3.1. Coating morphology

Coating morphology and surface roughness play a crucial role in influencing the tribological properties of the coating. Fig. 1(a) shows the topographical features of the top surface of TiB₂ deposited on the steel substrate using PES technique. The surface is rough and irregular with several islands of globular shape and a splash appearance. This is a characteristic feature of the PES technique. In the present study, PES process was conducted in air, which supports globular mass transfer mechanism. This is attributed to the fact that dissociable gases like nitrogen and air form a plasma of high thermal conductivity, which promotes globular mass transfer [13]. A molten globular droplet forms at the TiB₂ electrode tip and impinges on the steel substrate. This produces a splash appearance on the top surface. The corresponding surface profile of the coated surface is illustrated in Fig. 1(b). The surface is very rough in nature with several peaks and valleys. The average surface roughness, Rₐ, for PES coating is high 16.91 μm in tune with its topographical features observed in Fig. 1. The surface topography of the laser-engineered surface is shown in Fig. 2(a). The surface is relatively smooth, flat and free from cracks. The profile of the LSE deposited TiB₂ surface is illustrated in Fig. 2(b). The average surface roughness, Rₐ, for LSE coating is low (6.39 μm) in comparison to PES surface. The importance of the surface roughness in wear phenomena will be elucidated in the following sections. Fig. 3 presents the SEM micrographs of the cross-sectional views of the TiB₂ coated steel using PES and LSE processes. It can be seen in Fig. 3(a) that PES deposited TiB₂ coating is homogeneous, dense, adherent and free of defects like cracks. However, the coating thickness is not very uniform throughout the cross-section. This is in accordance with the nature of PES process as described above and as earlier observed in the topo-
3.2. Tribological properties of TiB₂ coating

3.2.1. Weight loss analysis

Wear test results are presented in Fig. 4, which shows the weight loss over a 20-min period. It can be easily observed that LSE coated surface shows least weight loss in comparison to the PES coated surface and AISI 1010 steel substrate. The wear rate (g/min) of the PES coated surface has reduced by almost a factor of 3 whereas for LSE surface, wear rate has decreased by a factor of 15 in comparison to the uncoated AISI 1010 steel substrate. Moreover, the wear rate for LSE coated surface tends to stabilize after an initial period of 4 min, suggesting the smoothening and/or breaking off of hard asperities, thereby providing a flat contact with the “composite” composition. The worn surfaces of PES and LSE coated samples were subjected to topographic observations in SEM. Fig. 5(a) shows a low magnification SEM micrograph of the worn region in PES deposited TiB₂ sample. Elemental X-ray maps corresponding to Ti and Fe distribution in Fig. 5(a) are presented in Fig. 5(b) and (c), respectively. The wear mechanism in PES deposited TiB₂ coating is essentially brittle in nature. Because of the inherent brittleness of the ceramic material, wear can occur by chipping. Surface and subsurface cracks form, join and
release small chips of material. These chipped off particles are further crushed into finer particles leading to formation of wear debris [18]. Such wear mechanism has been termed as attrition type of wear. A combination of brittle fracture and attrition wear mechanism is observed in PES coated TiB$_2$ sample. As observed earlier, PES surface is very rough in nature, showing peaks and valleys in the TiB$_2$ coating (Fig. 1). Under sliding conditions of wear, peaks of TiB$_2$ coating act as asperities and regions of high stress concentration. The interfacial strength between two successive droplets of a refractory ceramic like TiB$_2$ is not high and prone to crack formation. These small cracks tend to join, leading to the formation of a major crack. Such phenomenon is clearly evident in Fig. 6, which shows small and thin cracks merging together to form a wide crack. Such wide crack formation results in chipping of TiB$_2$ coating as particles from the steel substrate. Chipping of TiB$_2$ particles suggest a high wear rate, which is evident in Fig. 4. Fig. 5(a) shows denuded steel substrate after the chipping of particles of TiB$_2$ coating. Some of these chipped off particles are further crushed and form wear debris, which is indicated by the presence of Ti over the denuded steel substrate (Fig. 5(b)), while bare regions with loss of TiB$_2$ coating on steel substrate are also visible (Fig. 5(c)). Chipping of TiB$_2$ particles is further corroborated by the surface profile of the worn surface shown in Fig. 7. TiB$_2$ coating have chipped off at several locations, which is indicated by the deep craters formed on the surface. The average surface roughness, $R_a$, of the worn surface reduced from 16.91 µm (as coated) to 6.27 µm, which is attributed to the flattening of the surface after sliding wear during the 20-min period.

The wear phenomenon in LSE coated sample is significantly different from the PES coated sample. As stated earlier, LSE deposited TiB$_2$ coating is "composite" in
nature. Wear mechanism in such multiphase composite materials is very complex, depending upon several factors such as volume fraction, distribution and morphology of the ceramic particles [19]. Under ideal conditions, monolithic ceramic such as TiB₂ is expected to fail in a brittle manner [2]. However, the presence of the softer matrix phase Fe between hard ceramic particles alters the nature of wear mechanism. It has been mentioned earlier that Fe acts as an excellent binder for Ti-based refractory ceramics [7, 20]. This prevents debonding at TiB₂ particle/Fe matrix interface [9]. Under such conditions, Fe-based matrix phase(s) deforms plastically to accommodate the high stresses experienced by TiB₂ particles. This prevents brittle fracture and fragmentation of TiB₂ ceramic particles. Hence, chipping is prevented and no loose debris is observed. A composite layer containing hard TiB₂ particles and soft Fe phase(s) covers the entire substrate, which assists in reducing the wear rate. Such microstructural features are elucidated in Fig. 8, showing TiB₂ particles embedded in Fe matrix. There is no crack formation observed. Wear occurs gradually by mixed adhesive–abr-

Fig. 9. Surface roughness profile of the wear surface for the LSE sample.

Fig. 10. X-ray diffraction spectra before (B) and after (A) wear of TiB₂-deposited (a) PES and (b) LSE steel coupons.
sive mode due to the localized plastic deformation of the softer matrix, Fe (Fig. 4). Fig. 9 is the surface roughness profile of the worn surface of the LSE coated sample. The wear surface clearly exhibits the depressions or gradual wear plastic deformation caused by the rotating disk of the tribometer and relatively small change in the average surface roughness $R_a$ from 6.39 $\mu$m (as coated) to 4.56 $\mu$m.

The X-ray diffraction spectrum of the LSE coated surfaces before and after wear is shown in Fig. 10. Within the limits of resolution of the X-ray diffractometer, the spectrum does not indicate evolution of any new phase(s) during the wear process, indicating that wear in LSE coated sample is essentially physical in nature. Such new phase(s), if formed, could influence the wear behavior of the coatings.

3.2.1.1. Coefficient of friction measurement. In the present work, the coefficient of friction is calculated by measuring the changes in voltage and current in the electrical circuit of the motor driving the block-on-ring tribometer during loading [21]. Based on the principle of energy conservation, the frictional energy ($W_f$) equals the change in the electrical work during loading, given by Eq. (1):

$$W_f = \text{Voltage}(\Delta V) \times \text{Current}(\Delta I)$$

From the friction theory, it is known that

$$W_f = \mu N v$$

where $N$ is normal load, $v$ is the linear speed of the disk and $\mu$ is the coefficient of friction. By equating the above two equations, the coefficient of friction is computed.

The computed coefficient of friction for TiB$_2$ coating has been plotted for the entire test time of 10 min (Figs. 11 and 12). For PES process, the fluctuations in coefficient of friction are higher in comparison to the LSE process. The best-fit line shows coefficient of friction to be about 0.7 for PES process and 0.6 for LSE process. Such difference in the friction behavior can be attributed to the coating morphology and prevailing wear mechanisms in two coatings. In PES process, the surface is inherently rough with peaks and valleys due to the nature of the process yielding a higher friction value. Moreover, fluctuations in coefficient of friction values for PES process are higher, insinuating chipping off TiB$_2$ particles (Fig. 11). Such fluctuations are larger for the first 2 min of the test. The degree of fluctuation decreases with time, which is attributed to the relative smoothening of the surface. In LSE process, the coated surface is inherently smoother than the PES surface, which may explain the lower coefficient of friction value (Fig. 12). The lower degree of fluctuations in friction value for LSE coated sample is accounted by the formation of a smooth ‘‘composite’’ layer on the entire surface. A comparison between the coatings produced by two processes.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Summary of the TiB$_2$ coatings and their tribological characteristics deposited by PES and LSE processes</th>
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</thead>
<tbody>
<tr>
<td>Features</td>
<td>PES process</td>
</tr>
<tr>
<td>Energy density input (MW/m$^2$)</td>
<td>0.10</td>
</tr>
<tr>
<td>Nature of the coating</td>
<td>Thin (35–40 $\mu$m), homogeneous, dense and very fine grained (2–3 $\mu$m)</td>
</tr>
<tr>
<td>Surface roughness, $R_a$ (before wear)</td>
<td>16.91 $\mu$m</td>
</tr>
<tr>
<td>Surface roughness, $R_a$ (after wear)</td>
<td>6.27 $\mu$m</td>
</tr>
<tr>
<td>Wear rate (g/min)</td>
<td>0.0005</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>0.7</td>
</tr>
<tr>
<td>Wear mechanism</td>
<td>Brittle failure in addition to attrition</td>
</tr>
</tbody>
</table>
and their tribological characteristics has been summarized in Table 1.

The wear behavior of the “composite” coating is very complex, which could be explained by a model that elucidates frictional behavior of multiphase and/or composite materials [19]. This model predicts that friction behavior of a composite/multiphase material is influenced by the relative amounts and friction coefficients of the constituent phases. Also, it is affected by the wear resistance of the individual constituent. In most wear situations, the more wear resistant phase(s) carry a disproportionately larger load and hence have a larger influence on the friction of the composite. Hence, the friction coefficient of the composite generally does not follow a linear rule of mixture, but is dominated by the friction coefficient of the most wear resistant constituent. It is well understood that a refractory ceramic like TiB2 has a high wear resistance as compared to plain carbon steel. Hence, according to the model discussed above, TiB2 particles in the coating tend to carry a larger load than Fe and contribute largely to the coefficient of friction of the “composite” coating. However, in the present study, no such mathematical modeling has been done for this particular materials system.

4. Conclusions

1. The wear resistance of TiB2 coated surface is higher than that of AISI 1010 steel. The wear resistance of the LSE coated TiB2 coating is even better than PES deposited TiB2 coating.

2. The coefficient of friction values for LSE coated TiB2 coating (μ = 0.59) is lower than for PES deposited TiB2 coating (μ = 0.68).

3. Wear occurs in PES deposited TiB2 coating by brittle fracture and attrition type failure mechanisms.

4. Wear in LSE deposited TiB2 coating occurs by plastic deformation and gradual wear (mixed adhesive-abrasive mode) of the soft matrix phase Fe from a “composite” layer on the surface.

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References


Arvind Agarwal earned his PhD degree in Materials Science and Engineering from the University of Tennessee in 1999. He earned his B.Tech and MTech degrees in Materials and Metallurgical Engineering from the Indian Institute of Technology, Kanpur, India. He is currently working as a Materials Scientist at Plasma Processes, Huntsville, AL. He is a member of TMS, ASM, American Ceramic Society and AIAA.

Narendra B. Dahotre earned his MS and PhD degrees in Materials Science and Engineering from the Michigan State University. He is currently a Professor of Materials Science and Engineering at the University of Tennessee Space Institute. He is a member of TMS, ASM and SME.