Materials Research Express

Surface structural features and wear analysis of a multilayer Ti6Al4V-B₄C thin film coated AISI 1040 steel

R Malkiya Rasalin Prince, N Selvakumar, D Arulkirubakaran, S Christopher Ezhill Singh, T Ramkumar and R Monish Kumar

1 Department of Mechanical Engineering, Karunya Institute of Technology and Sciences, Coimbatore—641114, Tamil Nadu, India
2 Department of Mechanical Engineering, Meenatchi College of Engineering, Sivakasi 626 005, Tamil Nadu, India
3 Department of Mechanical Engineering, Vimal Jyothi Engineering College, Chemperi, Kannur 670632, Kerala, India
4 Department of Mechanical Engineering, Dr Mahalingam College of Engineering and Technology, Pollachi-642003, Tamil Nadu, India
5 UG Student, Department of Mechanical Engineering, Karunya Institute of Technology and Sciences, Coimbatore—641114, Tamil Nadu, India
6 Author to whom any correspondence should be addressed.

E-mail: malkiya@karunya.edu, nselva@mepcoeng.ac.in, arulkirubakaran@karunya.edu, edbertefren0420@gmail.com, ramkimech89@gmail.com and kumarmonish741@gmail.com

Keywords: Ti-6Al-4V-4B₄C films, surface roughness, nanoindentation, thermogravimetric analysis, wear and friction

Abstract

The deprived wear resistance of AISI 1040 steel often results in higher wear rates. The best ways to upgrade their wear resistance are to introduce hard particle reinforcement to produce a metal matrix composite which can be used as a coating. In the present study Ti-6Al-4V-4B₄C metal matrix composite coatings were coated on AISI 1040 steel using the magnetron sputtering process and their dry sliding wear behavior was studied at room temperature. The coating morphology was explored by SEM, XRD, FT-IR, and AFM. The constant coating thicknesses of 80 nm and 115 nm were achieved for 0.5 h and 1 h coating duration, respectively. The effects of introducing B₄C on the hardness, thermal behavior, wear, and friction characteristics were studied. The nano hardness and elastic modulus were attained by AFM nanoindentation technique which showed a maximum of 21.7 GPa and 218.4 GPa, respectively. It was proven that the adding of B₄C increases the thermal stability of Ti-6Al-4V-4B₄C coatings as well as modifies the oxidation mechanism. It is expected that the addition of B₄C will improve the thermal behavior of thin film coatings for their practical application. Wear tests were executed by ball-on-disc wear tester with E-52100 sphere as the counterface at a sliding velocity of 2 m s⁻¹ with 3 N load. Wear rate and coefficient of friction (CoF) reduced with an increase in load and sliding distances also composite coatings exhibited higher wear resistance within entire loading conditions, hereafter suggesting that it could be a favorable substitute to other hard coatings.

1. Introduction

Physical vapor deposition (PVD) was one of the oldest techniques used for the preparation of hard coatings [1]. Thin film coatings are the most common technique used for tribological purposes since no post-deposition processing is required [2]. According to the literature, it is mentioned that carbide and nitride coatings upgrade the wear resistance, high strength with a better hardness of products explained by Huiying et al [3]. In such a way that AlCrN coatings give better wear resistance, high abrasion resistance, good oxidation resistance and reasonable thermal stability [4]. Also, metal carbides and nitrides with high hardness play an important role in the surface engineering field as discussed by Robinson and Jackson [5]. Moreover, the hardest metal carbide coated stainless steel components show outstanding properties as described by Chiccoa et al [6]. However, the nanoindentation technique is an assessable method to appraise the mechanical properties of the coated thin films. The XRD, SEM, and AFM applied to characterize the surface morphology of thin-film coatings were explored in [7, 8]. The surface roughness of the thin film coating has been investigated by using AFM image analysis explained by Ozmetin and Sahin [9].
The thermal behavior of thin-film coatings was studied through high sensitive TG/DTA analysis. The thermal stability of the thin film coatings was improved by the addition of aluminum as explored by Irina et al [10]. Among them, mass loss of Al-TiC nanocomposite occurred during the decomposition of nanoparticles and the conversion of enthalpy affects the particle size of TiC. DSC analysis shows the weight gain at 825 °C with micron size particle as revealed by Selvakumar and Sivaraj [11]. Moreover, nanosized aluminum powder produces high thermal energy and the thermal behavior of nanoparticles was superior as compared to the micron-sized particles as described by Azhagurajan et al [12]. In general wear resistance of the metals can be improved with hard nitride and carbide coating, which exhibits better wear resistance, low frictional coefficient and improved hardness [13, 14]. Similarly, wear behavior of CrCN coating exhibits lower coefficient of friction and better wear resistance as investigated by Hu Pengfei [15]. Besides, DLC coated 6150 steel substrates shows high nano hardness ranging from 18–19 GPa, due to its coating adhesion on the 6150 steel as studied by Silva et al [16]. Especially TiB2 films were deposited using magnetron sputtering revealed that higher nanohardness (48–77 GPa) as explored by Nils Nedfors et al [17].

In this study, the microstructure, wear resistance also mechanical properties of DC magnetron sputtered AISI 1040 steel from a Ti-6Al-4V-4B4C target were taken into consideration. The films were characterized by X-ray diffraction (XRD), Atomic force microscopy (AFM), Fourier Transform Infrared (FT-IR) and Scanning electron microscope (SEM). Further mechanical as well as tribological properties were analyzed by nanoindentation and ball-on-disc apparatus, respectively.

### Table 1. AISI 1040 Steel Chemical composition (wt%)

|     | C    | Si | Mn | S  | P   | Fe  |
|-----|------|----|----|----|-----|-----|
|     | 0.35–0.44 | 0.20 | 0.75 | 0.05 | 0.04 | Balance |

The thermal behavior of thin-film coatings was studied through high sensitive TG/DTA analysis. The thermal stability of the thin film coatings was improved by the addition of aluminum as explored by Irina et al [10]. Among them, mass loss of Al-TiC nanocomposite occurred during the decomposition of nanoparticles and the conversion of enthalpy affects the particle size of TiC. DSC analysis shows the weight gain at 825 °C with micron size particle as revealed by Selvakumar and Sivaraj [11]. Moreover, nanosized aluminum powder produces high thermal energy and the thermal behavior of nanoparticles was superior as compared to the micron-sized particles as described by Azhagurajan et al [12]. In general wear resistance of the metals can be improved with hard nitride and carbide coating, which exhibits better wear resistance, low frictional coefficient and improved hardness [13, 14]. Similarly, wear behavior of CrCN coating exhibits lower coefficient of friction and better wear resistance as investigated by Hu Pengfei [15]. Besides, DLC coated 6150 steel substrates shows high nano hardness ranging from 18–19 GPa, due to its coating adhesion on the 6150 steel as studied by Silva et al [16]. Especially TiB2 films were deposited using magnetron sputtering revealed that higher nanohardness (48–77 GPa) as explored by Nils Nedfors et al [17].

In this study, the microstructure, wear resistance also mechanical properties of DC magnetron sputtered AISI 1040 steel from a Ti-6Al-4V-4B4C target were taken into consideration. The films were characterized by X-ray diffraction (XRD), Atomic force microscopy (AFM), Fourier Transform Infrared (FT-IR) and Scanning electron microscope (SEM). Further mechanical as well as tribological properties were analyzed by nanoindentation and ball-on-disc apparatus, respectively.

## 2. Experimental

### 2.1. Materials

Titanium alloy Ti-6Al-4V has better mechanical properties and has a low interstitial content that can be offered for particular applications, which demands superior ductility and fracture toughness. Boron Carbide is the very hardest ceramic material and standing third among the hard materials. General applications of Boron Carbide include the usage in tank armour, bulletproof vests, ceramic tooling dies, precision tool parts as well as various industrial applications [18]. Table 1 shows the chemical composition of AISI 1040 steel.

### 2.2. Substrate and target preparation

The uncoated surface of AISI 1040 steel was characterized using SEM and the homogeneity of the raw AISI 1040 steel surface structure is exposed in figure 1(a). A solid Ti-6Al-4V-4B4C target was prepared from Ti, Al, V, and B4C raw powders. The target with a 50 mm diameter and 3 mm thickness was used for coating. SEM image of the pre-compacted Ti, Al, V and B4C raw powders are shown in figure 1(b). Moreover, raw powders exhibit an angular, uneven shape as well as rough surfaces. The ti-6al-4v-4b4c coating was deposited on polished AISI 1040 steel flat specimens with dimensions of 60 mm diameter with 3 mm thickness. The substrate was made ready by way of waterproof 350 grit SiC wheels followed by 60, 80, 120, 220, 320 grade Al2O3 waterproof papers.
Moreover, n-propanol and acetone were used to remove organic impurities. The cleaned substrates were used for coating. Before the coating, the residual contaminant was removed by argon ion bombardment for 30 min. Various elements in the Ti-6Al-4V-4B4C target are validated by Energy Dispersive Spectrum (EDS) analysis. Figure 2 indicates the EDS analysis of the Ti-6Al-4V-4B4C target. The existence of Ti, Al, V, B as well as C is confirmed by EDS analysis. Ti was distinguished as the most important peak by way of high intensity among these elements. Furthermore, other elements are distinguished by way of minor peaks such as Al, V, B, and C in the EDS analysis. The purity of the Ti-6Al-4V-4B4C target is validated through EDS analysis subsequently no oxide peak was detected.

2.3. Ti-Al-V-B4C thin film coating technique

Surface engineering is a multidisciplinary action to modify the properties of the surfaces of engineering components so that their utility and serviceability can be enhanced. DC magnetron sputtering is a physical vapour deposition process for formulating thin films with high purity. In this, the concerned material is released from a target (Ti-6Al-4V-4B4C) and deposited onto a substrate (AISI 1040). Figure 3 indicates the representation of a magnetron sputtering system. The purity of the sputtering target material was around (99.9%) and the purity of the sputtering gas (Ar) was 99.99%. At the time of the deposition process, the coating chamber was evacuated down to $1 \times 10^{-5}$ bar; a mixture of argon (Ar) and nitrogen (N2) gases were introduced in addition to the substrates were blasted by argon-ion (Ar+). The temperature of the substrate during the coating was maintained around 100 ± 20 °C with 0.5 h and 1 h coating duration.
2.4. Characterization

2.4.1. AFM analysis
Atomic force microscope technique is advisable for attaining three-dimensional topographic statistics of thin-film coatings. AFM nanoindentation measurement was executed to examine the mechanical properties of the coatings by way of different loads by using AFM XE-70, Park Systems – S. Korea. The quality of the Ti-6Al-4V-4B4C coated surface and roughness have been obtained by statistical analysis of the AFM images. Z-scale of the AFM image shows the maximum and minimum heights of the features on the scanned area. Nano hardness of the Ti-6Al-4V-4B4C thin film coating was calculated by carrying out force measurements on the underlying AISI 1040 steel substrate at a minor load to ensure slight indentation.

2.4.2. XRD analysis
The crystalline structure of the Ti-6Al-4V-4B4C coated AISI 1040 was assessed by using an XPERT-PRO diffractometer with Cu Kα radiation \((k = 1.54060 \text{ Å})\), operating at 30 kV and 30 mA over the range of \(2\theta = 20–80^\circ\) with a step size of 0.0170 and a step time of 3.1750 s. Peaks of the Ti-6Al-4V-4B4C coatings were identified by using the X’Pert data viewer software [19].

2.4.3. FT-IR analysis
Fourier Transform Infrared (FT-IR) spectra are mounted up for Ti-6Al-4V-4B4C coated AISI 1040 steel, utilizing a Bruker Optics GmbH FTIR spectrometer, (Model: ALPHA, Germany). The functional groups of thin films were recorded and spectra are picked up at 4 cm\(^{-1}\) resolution, with 24 numbers of shots on an average.

2.5. Wear test
After the coating of Ti-6Al-4V-4B4C on the AISI 1040 substrate, wear test has been conducted as per the ASTM: G99 procedure with Ball-on-Disc (DUCOM, Model: TR20LE, India) wear tester in addition to the schematic diagram shown in figure 4. The 10 mm diameter E-52100 steel ball with 450 VHN hardness value has been used as a counter body for the wear test. Table 2 demonstrates the chemical composition of E-52100 steel. Wear loss of the coated disc was assessed after each wear employing a precise electronic balance with an accuracy of \(\pm 0.01 \text{ mg}\) further weight loss was converted into volume loss. The frictional force was measured directly from the documented graph obtained for the duration of wear test. The wear rate, specific wear rate as well as the coefficient of friction was calculated based on the subsequent equations (1)–(4) [20].

\[
\text{Wear volume} = \frac{\text{Wear loss}}{\text{Density}}. \quad (1)
\]

| C        | Cr         | Mn        | Si      | S        | P         | Fe         |
|----------|------------|-----------|---------|----------|-----------|------------|
| 0.98–1.10| 1.30–1.60  | 0.25–0.45 | 0.15–0.30| 0.025 max| 0.025     | Balance    |

Figure 4. Schematic representation of ball-on-disc wear tester.

Table 2. E-52100 Steel Chemical composition (wt%)
3. Results and discussion

3.1. Surface morphology

The surface morphology of Ti-6Al-4V-4B₄C coating was analyzed using Scanning Electron Microscopy (SEM) (SU510 Hitachi, Japan). AFM technique is suitable for obtaining surface morphology of thin-film coatings in three-dimension for structural analysis on the nanoscale. Figure 6 represents the SEM images and atomic force microscopy images of AISI 1040 steel substrate coated with Ti-6Al-4V-4B₄C thin films at various time durations. AFM measurement gives the value of root mean square (RMS) roughness as well as film thickness. Figures 5(a), (c) shows the SEM images of Ti-6Al-4V-4B₄C coated AISI 1040 steel disc with 0.5 h and 1 h coating time. The intensity strip is shown in figures 5(b), (d) point out the depth as well as height along the z-axis. It is clearly shown that the thickness of the Ti-6Al-4V-4B₄C film is increased with the deposition time. AFM images acknowledge that the number of grains located on the film surface which indicates that the grain size is progressively smaller. The addition of B₄C in coating causes a significant reduction of surface roughness. It is noted that these thin films were uniform, regular, homogeneous structures as well as do not have any cracks.

Figure 5(b) shows the surface morphology of Ti-6Al-4V-4B₄C films with a 0.5 h coating duration. From the AFM image, the root means square roughness ($R_q$) value, surface roughness ($R_a$), coating thickness values, the

\[
\text{Wear rate} = \frac{\text{Wear volume}}{\text{Sliding distance}}
\]

\[
\text{Specific wear rate} = \frac{\text{Wear volume}}{\text{Load} \times \text{Sliding distance}}
\]

\[
\text{Coefficient of friction} = \frac{\text{Frictional force}}{\text{Applied load}}
\]
average distance among the highest and lowest peak ($R_z$) were measured. It seems that the coating thickness nature of the prepared film seems much thinner with a thickness of 80 nm. We obtained average surface roughness value from AFM image as 6.692 nm and average mean square value as 8.703 nm. The root means square of the Ti-6Al-4V-4B$_4$C coating and thickness of the film were investigated from the AFM image. The three-dimensional AFM image displays the surface roughness of Ti-6Al-4V-4B$_4$C film with different grain sizes and shapes.

AFM image of the 1 h coated Ti-6Al-4V-4B$_4$C is shown in figure 5(d). The thickness of the coating was obtained at 115 nm. The surface roughness ($R_a$) of the coating was obtained as 6.064 nm, root means square roughness ($R_q$) was achieved as 9.892 nm and the average distance between the highest as well as lowest peak ($R_z$) was measured as 36.343 nm. The surface roughness, defects, amorphous as well as crystalline phases, and nucleation in addition to growth modes of the thin film can be evaluated from three-dimensional AFM image.

### 3.2. XRD analysis of nanocomposite

Figure 6 demonstrates the XRD of Ti-6Al-4V with 4% of B$_4$C with corresponding peaks. XRD study confirms the elemental presence in addition to Ti peaks with 2θ values of 35.1°, 40.2°, 62.9°, 70.6°, 76.1° and 77.9° belong to the crystal planes of (1 0 0), (1 0 1), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) respectively confirm with JCPDS 89-2762. Aluminum was identified by way of 2θ values of 38.4°, 44.8° and 78.3° with (1 1 1), (2 0 0) and (3 1 1) planes confirms through JCPDS file no 89-4037. JCPDS file no 65-6689 confirmed the presence of vanadium peak in the plane of (1 1 0) with a 2θ value of 41.2°. The presence of boron carbide peaks in the plane of (0 0 0), (2 1 4) and (0 2 7) with 2θ values of 53.4°, 58.8°, and 65.1°. The results match very well with the JCPDS file No 75-0424. Not at all any oxide peak is ascertained within the XRD analysis. It was ascertained that all the peaks were wider. Particle size is mainly related to peak width thus it confirms all particles in the coatings are in nano size. XRD patterns authenticate the existence of B$_4$C within the coating. In the XRD pattern, the peak d001 corresponds to the d-spacing of the structure of Ti-6Al-4V-4B$_4$C, which can be calculated from Bragg’s Law [21].
3.3. FT-IR spectroscopic analysis
Infrared spectroscopy is used to measure the vibrations of atoms as well as to define the functional groups. The vibrational frequencies of Ti-6Al-4V-4B4C coating are recorded by the FT-IR spectrometer and shown in figure 7. The spikes come from the substrate. It can be seen that the presence of B4C in the coating confirmed by FT-IR spectra, shows a strong and broad peak at 1058.83 cm⁻¹. Two strong absorption peaks of B4C have been noted on the FT-IR spectra one located at 1058.83 cm⁻¹ and the other at 1511.87 cm⁻¹. The above peaks are attributed to the presence of B4C in the coating [22]. Thus, FTIR images confirmed the presence of B4C in the coatings performed using a magnetron sputtering process. Further, it confirms the purity of Ti, Al and V metals in figure 6, since it does not show any metal oxide peaks.

3.4. Nano hardness
Nano hardness of the thin film coatings can be evaluated by the AFM nano indentation technique on a very small scale. Nanoindentation method is accomplished by striking a small sinusoidal varying force on top of the coating that controls the motion of the indenter. The penetration depth of the coating has been measured continuously from the movement response of the indenter at the maximum frequency and the phase angle between the force and displacement. The maximum force of 4 nN has been applied to the specimen for indentation.

AFM probe with contact mode AFM can be utilized to acquire the image of the coating. The force-displacement (F-D) curve was obtained at the time of indentation besides nano hardness of the coating has been obtained as of the F-D curve. The elastic displacements were recovered during the unloading time, and the final depth of indentation was obtained. The nano hardness is calculated by the indentation load divided by the
projected contact area [20]. The reduced elastic modulus of the coating has been determined based on the relations explained by Wei Hang [23].

Nanoindentation force-displacement curve of 0.5 as well as 1 h coating time is represented in figures 8(a), (b). The nanohardness as well as elastic modulus value was almost independent of indentation depths. Among these two coatings, maximum nanohardness as well as elastic modulus values are about 21.7 GPa and 218.4 GPa. The nanohardness as well as elastic modulus of 0.5 h and 1 h coating increases gradually according to coating thickness (range from 80 to 115 nm) and coating time. With the increasing coating time, the nanohardness and elastic modulus begin to increase because of substrate effects. It designates a composite property, consisting of a contribution from the Ti-6Al-4V-4B4C coated AISI 1040 steel.

Figure 9 shows the variation in nanohardness and elastic modulus of Ti-6Al-4V-4B4C coating. Unwavering coating temperature as well as higher coating time produces higher coating thickness. It is observed that nanohardness and elastic modulus of the coating increases with the increased coating time. As well, higher deposition time produces a coarse structure which leads to an increase in the nanohardness and elastic modulus. Nanohardness and elastic modulus were upgraded due to higher coating thickness, moreover, it is clearly stated that elastic modulus and nanohardness were enriched with an increase in the amount of B4C reinforcement. Besides, a more dense structure in addition to finer surface morphology as well as homogeneously distribution of nano B4C particles in the coating exposes higher nanohardness and elastic modulus.

Also, the surface and sub-surface after indentation was inspected for investigating the indentation behavior of coatings. Figures 10(a), (b) shows the indentation patterns on the surfaces under 2 N and 3 N load, plastic deformation was detected on all indented areas also radial cracks are arising from the plastic impression of indentation patterns corner and spread out up to plastic zone. The radial crack length of 10 μm was measured for 2 N load and more than 15 μm for 3 N load. Besides, crack length generated under loads of 2 N in were generally longer than those of the 3 N load, presenting confirmation of better fracture toughness for the final. The length of radial cracks for the 3 N load is decreased, intergranular propagation of series ligaments along with the extended radial crack is perceived for the 2 N load. The presence of B4C in the coating, that turns as crack-bridging for stop the additional expansion of the cracks.

3.5. Thermal studies
Figures 11(a), (b) shows the thermal analysis (TG/DTA) of Ti-6Al-4V-4B4C coating. Thermogravimetric and differential thermal analysis (TG/DTA) techniques were applied to measure the thermal stability of the thin films at room temperature under atmospheric air. The weight loss and weight gain of the thin films were also measured. All Ti-6Al-4V-4B4C thin films showed a pure melting point and modest volatility before melting.
Chavin et al stated that pure DLC films were totally demolished over 500 °C, signifying the evaporation of the pure DLC films. However, the Ti-6Al-4V-4B4C films were still stable until heating to 650 °C; on the other hand, the diamond-like carbon coating disappeared during heating up to 600 °C [24]. In the present study, all the thin films were heated to 1000 °C. For both samples, initially weight was stabled up to 500 °C followed by a weight gain. The Ti-6Al-4V-4B4C film comes to be a little volatile, and the weight gain considerably amplified at temperatures greater than 500 °C caused by adsorption, absorption, solid-gas reactions in addition to oxidation reactions. The occurrence of oxidation reaction and the formation of metal oxide is distinguished in equations (5)–(6). Besides, the peak oxidation rate of B4C is because of the carbon content. The oxidation rate of Ti-6Al-4V-4B4C coating is depending on the percentage of B4C in the coating. It is assumed that the weight gain of the films with an increase in temperature may have arisen due to the adsorption of oxygen from the atmospheric air into the film surface during heating [24].

\[
\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2 \quad (5)
\]

\[
\text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3 \quad (6)
\]

The ignition temperature of the Ti-6Al-4V-4B4C thin film increases with the addition of B4C in the coating. Again the addition of B4C in the coating increases the thermal behavior of the coating. The significant thermal reaction peaks of Ti-6Al-4V-4B4C thin film within the DTA curve are noted in figure 11(a). The beginning two exothermal peaks have occurred at 324 °C and 606 °C. The mass gain was disclosed within the TG curve in the middle of 700 °C and 900 °C, presenting the best decomposition phase of Ti-6Al-4V-4B4C films. However, it is
prominent that oxygen concentration will play a vital role in deciding the Ti-6Al-4V-4B4C film’s oxidation behavior.

Figure 11(b) shows four exothermal peaks at 321 °C, 650 °C, 660 °C, and 742 °C. The mass gain has occurred within the TG curve in the middle of 742 °C and 900 °C. B4C has thermal higher stability than that of Al. Thus, the % of B4C presents in the coating grows its initiation of ignition temperature increases. For a second time, the addition of B4C increases the thermal behavior of the coating. Figure 12(b) indicates a slower rate of decomposition of the Ti-6Al-4V-4B4C film. Aluminum may react with the oxygen particles present in the atmospheric and to form an aluminum oxide film that is stable and tightly adhering. But during heating, the aluminum oxide film may decompose. This property becomes modified by the addition of reinforcements [25].

All samples were predicted with a large exothermic peak; the oxidation of Ti-6Al-4V-4B4C thin film creates two overlapping exothermic peaks. Subsequently, the exothermic changes occur slowly, afterward a steep rise in temperature. It is distinguished that the exothermic peak temperature overlaps with the oxidation point within the TG curves, specifying that the peak temperatures match up to the most oxidation rate. The oxidation rate governing step is controlled by mass oxygen transference as well as the energy of activation is that the leading issue to initiate oxidization within the coating. During the initial oxidation stage, thermal energy is adequate to assist outward diffusion of oxygen atoms in the direction of the thin film surface, and consequently generate a Ti-rich region close to the thin film surface in addition to the formation of TiO2 phase due to the introduction of the oxygen close to the thin film surface region. Instantaneously, the diffusion of Ti as well as Al ions towards the outside in addition to atomic oxygen towards the inside will form a (TiO2, Al2O3) layer on the film surface, which might entertain as an active diffusion barrier down the inside diffusion of the oxygen.
3.6. Wear analysis

3.6.1. Dry sliding wear

The wear behavior of Ti-6Al-4V-4B4C thin-film coated AISI 1040 steel against E-52100 steel ball was investigated. The wear test was conducted at normal atmospheric temperature. The sliding speeds are fixed as 0.5235, 0.6544, 0.7854 and 0.9163 m s\(^{-1}\) for wear tests with loads of 2 N and 3 N. The mass loss of coated samples was about 0.2 \(\times 10^{-4}\) g, resulting in a reduced wear rate of about 32% when compared with the mild steel substrate. The reduced wear rate is generally due to higher hardness. Obviously, brittle materials may have greater wear rates as a sign of their inability to practice plastic deformation. Two main stages of wear were noted, the first one is the initial running wear and the next one is steady-state wear. Figure 12 shows the coefficient of friction values. The steady-state coefficient of friction value of 0.44 was obtained, and that explains the nature of wear as a steady-state.

Figure 12 signifies the specific wear rate of 0.5 h coating. The calculated values of a specific wear rate are noted as 0.1013 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) to 0.1737 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) for 2 N load. For 3 N load, the range of specific wear rate as 0.2027 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) to 0.2516 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) has arrived. It is clearly shown that there is no oxidation layer as there is no slitting of the coating during the wear test. The energy released due to the mechanical work leads to an increase in the temperature at the points of impressive contact between counter body and coating. Even though, if the surface temperature rises due to frictional heat, some effects could occur, specifically changes in mechanical properties and oxidation. The authors detected that wear rate of the Ti-6Al-4V-4B4C coatings amplified utilizing increasing applied load as well as sliding distance. As well, wear loss also increased with an increase in applied load as well as sliding distance. Moreover, the presence of B\(_4\)C contents in the coating can reduce the wear rate as well as change the roughness of surfaces, enhancing the hardness and reducing the frictional coefficient.

The wear behavior of Ti-6Al-4V-4B4C coated AISI 1040 steel with 1 h coating time was investigated. The samples were tested against 2 N and 3 N loads. The average frictional coefficient was obtained in the range of 0.1 to 0.44 for all the tests. The transfer of Ti-6Al-4V-4B4C film remains stable at the end of testing. The authors noted that the wear resistance of the coating increases with the addition of B\(_4\)C particles. Figure 13 clarifies the deviation of the specific wear rate with 1 h coating. The specific wear rate for the 2 N load was calculated from 0.1970 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) to 0.3297 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) and 0.3128 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) to 0.4472 \(\times 10^{-5}\) mm\(^3\) N\(^{-1}\) m\(^{-1}\) with 3 N load. The authors report that the wear resistance of the Ti-6Al-4V-4B4C coated AISI 1040 steel improved when compared with pure alloy. It is noted that the lower rate and low value of the frictional coefficient have arrived. The higher coefficient of friction produces crack on the surface of the coating. Based on the whole results, a low coefficient of friction with minimum mass loss has been achieved.

Figure 14 shows the comparison of the specific wear rate with various wear testing time. The specific wear rate of the coating has been increased linearly with the time duration for both 2 and 3 N loads. Under the similar load circumstance, with an increase in time duration the rate of wear increases. As well, no material transfer is witnessed on the worn Ti-6Al-4V-4B4C layers under all test conditions. With the higher sliding time, the average wear rates as well as average wear volumes of AISI 52100 steel balls and Ti-6Al-4V-4B4C coating surfaces raises to the maximum value.
3.6.2. Wear mechanism

Figures 15(a), (b) shows the wear scratch images of the Ti-6Al-4V-4B4C coated AISI 1040 steel disc. Once the load and sliding distance increases; widths of wear tracks as well as wear mark areas were increased gradually. The formation of the oxide layer is generally increased with the increase in sliding distance and load. The oxide layers were well-formed between the Ti-6Al-4V-4B4C coating and E-52100 steel ball; it is perceived that the oxide layer act as a protecting film that diminishes SWR of the coated steel. When the hardness increased, the SWR decreases due to the establishment of oxide layer at the coated steel surfaces. As a result, the degree of oxide layer formation as well as the deviation of hardness should affect the SWR of the coated steel.

To recognize the wear mechanisms, worn surfaces of coatings with 2 N and 3 N load were witnessed using SEM. Figure 15 indicates worn surfaces coatings with 2 N and 3 N loads. The worn surface of the coating with 2 N load witnesses rough surface using mixed regions of delamination as well as micro-abrasive wear; moreover reduced wear as well as delamination with a smoother wear surface for 3 N load. Figure 15 shows the wear track of the Ti-6Al-4V-4B4C coating under 3 N load which exhibits signs of plastic deformation. The higher degree of plastic deformation in addition to a pile-up of material has occurred at 3 N load for the reason that of partial crystallization. It is identified that all wear debris be made up of lager flakes besides finer; which designates micro-abrasion and delamination mechanisms of wear in 2 N loads. Moreover, in the 3 N loading condition; there is minimal micro-abrasion in the wear debris. The delaminated brittle oxide layer comes to be crushed and trapped in the middle of the coating as well as E-52100 steel ball to result in micro-abrasive wear in conjunction with the separation of weaker inter-splat regions. The coating indicates a denser and smooth surface suggesting a stronger inter splat region. On 2 N and 3 N loads decreased splat delamination as well as lower wear losses were observed because of dense structure. Both coatings were exposed to the oxide layer; which is more adherent between mating surfaces hence, restricts micro-abrasive wear. The schematic representation exposed in figure 16 reviews the overall wear mechanisms throughout the dry sliding wear. The micro abrasion as well as the
Figure 15. Wear track of coated samples after wear test (a) 2 N load (b) 3 N load.

Figure 16. Scheme of wear mechanism.
The delamination of the oxide layer in addition to splats is the dominant wear mechanism in the coatings. The dominant wear is severe plastic deformation and delamination of the deformed layer was detected, which is attributed to micro-abrasive wear during sliding.

The Energy Dispersive Spectrum (EDS) analysis of the worn surfaces of Ti-6Al-4V-4B4C coated AISI 1040 steel is made known in figure 17. Through EDS analysis, it is acknowledged that wear tracks mainly be made up of Ti, Al, V, B, Si, Cr, Mn, S, P, O, and Fe. The highest intensity peak was identified as Ti in the EDS analysis. The presence of oxide layers was identified in the wear track; besides confirms through EDS analysis.

3.6.3. Effect of counterface material

The friction and wear of the counter-body (E-52100 steel ball) were counted against Ti-6Al-4V-4B4C coatings. E-52100 steel balls of diameter 10 mm with hardness about 62 Rc. Tests with these balls were conducted at room temperature over a time period of 2 min. Figure 18 shows the variation of frictional coefficient during the test with E-52100 steel ball, sliding against Ti-6Al-4V-4B4C coatings at 2 N and 3 N loads. In general, friction and wear of the counter-body depend upon the load, sliding distances and sliding speed conditions. The value of coefficient of friction started at comparatively low at 0.1, but progressively increased, finally ending with a final coefficient of friction value of about 0.42 and 0.47 for 2 and 3 N loads with 0.5 h coating time. The coefficient of friction increased concerning sliding distance and time. Frictional heat is developed between the coating and counter-body (E-52100 steel ball) during the relative motion was uninterrupted since there was no time to heat dissipation. Moreover, the steady coefficient of friction value for 1 h coating has arrived as 0.40 and 0.44 against
2 N and 3 N load. The high coefficient of friction and noise in the wear test data for the E-52100 steel ball was attributed to a broad transfer of metal from the coated surface, as illustrated in figure 19. The behavior of the friction is the result of both transfers of material from E-52100 steel ball into the coating as well as the wear damage of the coating. It is noted that the value of the coefficient of friction is lower than uncoated steel. Wear rate of the (E-52100 steel ball) counter-body has been increased, due to the improvement of hardness on coating. It acknowledges that comparatively higher nanohardness of the coating over the counter body.

3.6.4. Strengthening mechanism of Ti-6Al-4V-B₄C composite coatings
Nano-particles were clustered into clusters certainly throughout coating because of their smaller size and high surface energy. The B₄C nanoparticles within the coating were clustered into clusters of a few 100 nanometers size for the period of the deposition process. The higher volume of B₄C particles concentration will increase the number of particles suspended in the coating, leading to additional particles amalgamated into the coatings that successively improve the strengthening result by additional phase dispersion. The nano-particles deposited on the substrate surface will perform the part of nucleation sites and managing the grain growth. Thus a decrease within the grain size of the coatings additionally ends up in again refinement strengthening. Conversely, with increasing the number of B₄C within the coating, the trend of particle cluster is additionally intensified. Further B₄C clusters are implanted into the Ti-6Al-4V-4B₄C coating, leading to poor particle distribution results and even porous structure. Consequently, the strengthening result by B₄C particles dispersion is restricted by the competition of the 2 mechanisms. A noble dispersion strengthening and grain refinement will be earned once correct B₄C was added into the coating target, leading to a significant improvement of the mechanical property. Above all, the strengthening mechanism of Ti-6Al-4V-4B₄C coatings may well be principally authorized to parts: grain refinement strengthening and dispersion strengthening. The grain size of Ti-6Al-4V-4B₄C coatings will be refined by adding B₄C particles. Additionally, conferring to the idea of dispersion strengthening, a noble distribution strengthening result will be recognized by a highly dispersed additional phase microstructure. Resulting in a highly dispersed microstructure is the significant improvement of nanohardness. According to the concept offered by Musil, when the grain size of the particles in the coating was reduced, the more grain boundaries in the coating surfaces which caused the hardening of coatings [26].

4. Conclusions
In the present work, nano hardness, elastic modulus, thermal analysis, and wear analysis of the Ti-6Al-4V-4B₄C coatings were carried out with different coating times and loads. According to the investigational work, the succeeding findings were made:

- Ti-6Al-4V-4B₄C coatings are effectively coated on AISI 1040 steel by way of the magnetron sputtering technique. Ti-6Al-4V-4B₄C coatings are characterized by XRD, SEM, FT-IR, EDS, and AFM.
- The maximum coating thickness of 115 nm and its normal surface roughness of 30 nm was attained by AFM. The addition of B₄C in the coating could perform as ‘grain refiners’; after effect is the conversion of columnar structure to dense as well as amorphous-like texture while the coating with B₄C exposes a nanocomposite microstructure where nanocolumns were fashioned by a B₄C rich phase.
With the addition of B4C, the nanohardness of coatings was boosted considerably, had nanohardness (~22 GPa) and elastic modulus of (~218 GPa) in addition to high resistance to cracking. The adhesion behavior of the substrate is nearly interconnected to the nanohardness and elastic modulus of the substrate.

The TG/DTA authorizes that the inclusion of B4C enhances the ignition period of the coating. The diffusion of Ti, Al, V, and B4C ions were reacted with atomic oxygen and form a (TiO2 and Al2O3), layer on the thin film coating surface. The oxidation rate of the thin film was very negligible in the initial stage. The oxidation rate is controlled by way of mass oxygen transference to the inside of the coating.

The wear rate of the coating against the E-52100 ball counter body with a speed range of 0.2 to 2 m s\(^{-1}\) was lower at room temperatures and slightly affected by oxidation in addition to the transfer of material amongst the counter body and the coating. Adhesive wear, delamination, and cracking occurred on the AISI 1040 steel lower at room temperatures and slightly affected by oxidation in addition to the transfer of material amongst the counter body and the coating. Adhesive wear, delamination, and cracking occurred on the AISI 1040 steel substrate caused at higher load and sliding velocities of the tested coating. The counter body experience also abrasive wear because of the higher nanohardness of the coating.

The CoF was enhanced progressively for the Ti-6Al-4V-4B4C coated AISI 1040 steel due to the increase in nanohardness and the enriched structural properties. The existence of an oxide layer also controls the wear depth as well as CoF in dry wear situations. Ti-6Al-4V-4B4C coated AISI 1040 steel had the best friction characteristics at different coated thickness, sliding speed and load against a smooth counterface under dry conditions.

**References**

[1] Yang Y-S, Cho T-P and Lin Y-C 2014 Effect of coating architectures on the wear and hydrophobic properties of Al–N/Cr–N multilayer coatings Surf. Coat. Technol. 259 172–7
[2] Lorenzo-Martin C, Ajayi O, Erdemir A, Fenske G R and Wei R 2013 Effect of microstructure and thickness on the friction and wear behavior of Cr3N coatings Wear 302 963–71
[3] Zhu H, Niu Y, Lin C, Huang L, Ji H and Zheng X 2013 Microstructures and tribological properties of vacuum plasma sprayed BaC–Ni composite coatings Ceram. Int. 39 101–10
[4] Mo J L and Zhu M H 2008 Sliding tribological behavior of AlCrN coating Tribol. Int. 41 1161–8
[5] Robinson G M and Jackson M J 2005 A review of micro and nanomachining from a materials perspective Journal of Material Processing Technology 167 316–37
[6] Chiccoa B, Borbidgeb W E and Summervillea F 1999 Experimental study of vanadium carbide and carbonitride coatings Materials Science Engineering A 266 62–72
[7] Xia Y, Bigerelle M, Bouvier S, Iost A and Mazeran P E 2015 Quantitative approach to determine the mechanical properties by nanoindentation test: application on sandblasted materials Tribol. Int. 82 297–304
[8] Ozmetin A E, Sahin O, Ongun E and Kuru M 2015 Mechanical characterization of MgB2 thin films using nanoindentation technique J. Alloys Compd. 619 262–6
[9] Sheng-RuiJian G J, Chen and Hsu W-M 2013 Mechanical properties of Cu2O thin films by nanoindentation Materials 6 4305–13
[10] Polyakova I G and Hubert T 2001 Thermal stability of TiN thin films investigated by DTF, DTA Surfaces and Coatings Technology 141 53–61
[11] Selvakumar N, Sivaraj M and Muthuraman S 2016 Microstructure characterization and thermal properties of Al-TiC sintered nano composites Appl. Therm. Eng. 107 625–32
[12] Azhagurajan A, Selvakumar N and Yasin M M 2012 Minimum ignition energy for micro and nano flash powders Process Saf. Prog. 31 19–23
[13] Kailasanathan C and Selvakumar N 2012 Comparative study of hydroxyapatite/gelatin composites reinforced with bio-inert ceramic particles Ceram. Int. 38 3569–82
[14] Yang Y-S, Cho T-P and Ye H-W 2014 The effect of deposition parameters on the mechanical properties of Cr–C–N coatings Surf. Coat. Technol. 259 141–5
[15] Pengfei H and Bailing J 2011 Study on tribological property of CrCN coating based on magnetron sputtering platting technique Vacuum 85 994–8
[16] Silva V M, Trava-Airoldi V J and Chung Y W 2011 Surface modification of steel substrates for the deposition of thick and adherent diamond-like carbon coatings Surface and Coating Technology 205 1703–7
[17] Nedfors N, Tengstrand O, Lund P, Persson P O A, Hultman L and Jansson U 2014 Superhard NbB2-x thin films deposited by dc magnetron sputtering Surf. Coat. Technol. 257 295–300
[18] Sahin S 2009 Effects of boronizing process on the surface roughness and dimensions of AISI 1020, AISI 1040 and AISI 2714 J. Mater. Process. Technol. 209 1736–41
[19] Selvakumar N, Mohamed M J S, Narayanasamy R and Venkateswarlu K 2013 Forming limit diagram and void coalescence analysis of AA5052 coated with molybdenum-based ceramic nanocomposites Mater. Des. 52 393–403
[20] Selvakumar N and Malkiya Rasalin Prince R 2017 Microstructure, surface topography and sliding wear behaviour of titanium based coatings on AISI 1040 steel by magnetron sputtering Archives of Civil and Mechanical Engineering 17 281–92

**ORCID iDs**

R Malkiya Rasalin Prince https://orcid.org/0000-0003-3145-9511
T Ramkumar https://orcid.org/0000-0003-1654-8022
[21] Polychronopoulou K, Rebholz C, Baker M A, Theodorou L, Demas N G, Hinder S J, Polycarpou A A, Doumanidis C C and Bobel K 2008 Nanostructure, mechanical and tribological properties of reactive magnetron sputtered TiCX coatings Diamond & Related Materials 17 2054–61

[22] Najafi A, Golestani-Fard F, Rezaie H R and Ehsani N 2012 A novel route to obtain B4C powder via sol–gel method Ceram. Int. 38 3583–9

[23] Hang W, Zhou L, Shimizu J and Yuan J 2013 A robust procedure of data analysis for micro/nano indentation Precis. Eng. 37 408–14

[24] Jongwannasiri C, Li X and Watanabe S 2013 Improvement of thermal stability and tribological performance of diamond-like carbon composite thin films Materials Sciences and Applications 4 630–6

[25] Selvakumar N and Vettivel S C 2013 Thermal, electrical and wear behavior of sintered Cu–W nanocomposite Mater. Des. 46 16–25

[26] Musil J 2012 Hard nanocomposite coatings: thermal stability, oxidation resistance and toughness Surface and Coatings Technology 207 50–65