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# Carbon and titanium diboride ($TiB_2$) multilayer coatings

J.Rao*, R. Cruz, K.J.Lawson, J.R.Nicholls

*School of Industrial & Manufacturing Science, Department of Advanced Materials, Cranfield University, Cranfield, Bedfordshire, MK42 9GF, UK.*

## Abstract

Titanium Diboride, ($TiB_2$) is a metal-based refractory ceramic material that has been investigated in industrial applications ranging from, cutting tools to wear parts and for use in the aerospace industry. The unique properties which make this material so fascinating are, its high hardness, high melting point and its corrosion resistance. $TiB_2$ is prevented from wider mainstream use because of its inherent brittle nature. With a view to overcome this in coating form and with the aim of providing in addition inherent lubricity, in this study 50 layer $TiB_2$/C multilayer stacks have been fabricated, with varying volume fractions of ceramic, whereby the interfaces of the layers limit crack propagation in the $TiB_2$ ceramic.

$TiB_2$ has been multilayered with carbon, to make use of the unique and hybrid nature of the bonding in carbon coatings. DC magnetron sputtering with substrate bias was the preferred route for the fabrication of these coatings. AISI tool steel has been used as the substrate material. By varying the amount of $TiB_2$ ceramic from 50% to 95%, the Hardness of the coating is seen to increase from 5 GPa to 17GPa. The Hardness is observed to decrease as a function of increasing carbon content, agreeing with other studies that the carbon layers are not load-bearing. The graphitic nature of the $sp^2$ bond, however, acts as a lubricant layer.

## 1. Introduction

Titanium diboride, ($TiB_2$) is a metal-based refractory ceramic material that has been investigated in industrial applications ranging from, cutting tools to wear parts and for applications in the aerospace industry. The unique properties that make this material so fascinating are, its high hardness of 33GPa [1], its high Young's Modulus of 480GPa [2], its high melting point of 2980 °C [3] and is corrosion resistance up to 1400 °C [2], to name just a few. $TiB_2$ is limited in its mainstream use because of its inherent brittle nature. As the demand for the fabrication of high hardness, low coefficient of friction coatings increase, the needs arises for the quantification and characterisation of suitable coatings. Multilayers, formed by the deposition of alternating layers of different materials that are only tens of nanometers thick, is one method employed by several authors as a route to limit crack propagation in ceramic coatings [4,5].

In this study, carbon, either with its graphitic or $sp^2$ hybridised bonding, or with its $sp^3$ hybridised diamond-like nature, has been employed as an interfacial material to limit crack propagation in the $TiB_2$. Carbon has been used previously for similar reasons in an aluminium reinforced $TiB_2$ composite [6] and improvements in mechanical properties and tensile strength are reported. An improvement in the lubricating properties of $TiB_2$ used for cutting tool applications has been reported by Baker [7]. In this study, 50 layer stacks of $TiB_2$/C – 25 layers of $TiB_2$ and 25 layers of carbon, have been fabricated to a total thickness of 5 μm. The volume fraction of $TiB_2$ ceramic has been varied from 50 to 95%.

The deposition of $TiB_2$ – based coatings has been carried out in the literature using a variety of vapour deposition techniques, both PVD [8] and CVD [9]. In this study, DC magnetron sputtering was employed as the deposition technique for the fabrication of $TiB_2$/C multilayers. As a result of the low deposition temperatures, $TiB_2$ coatings fabricated by PVD show the best potential for tribological applications [8]. The influence of the volume fraction of $TiB_2$ ceramic on mechanical properties was characterised by its Hardness and Reduced Modulus using nanoindentation. Focused Ion Beam (FIB) milling, coupled with SEM provided metallographic confirmation of the multilayer coatings. Carbon was characterised by Raman spectroscopy.

## 2. Experimental

*2.1 Sample preparation*

In this work, $TiB_2$/C multilayer coatings were deposited onto AISI 1095 tool steel substrates. The substrates were prepared using a series of polishing wheels that had various 'grit' sizes ranging from 250 μm to 1 μm. The substrates were finished using a colloidal silicon slurry, which provided a mirror finish to the tool steel. The tool steel was then cleaned in a re-flux solvent for 30 minutes with IPA as the cleaning agent.

*2.2 PVD sputtering*

The PVD sputtering machine was a multi-target system with a rotary worktable. The machine is diffusion pumped to a base pressure better than $10^{-6}$ torr.

Multilayers of $TiB_2$/C were fabricated using conventional DC magnetron sputtering. The carbon and $TiB_2$ sputtering targets were 7cm in diameter with a purity of 99.99%. The power density on the $TiB_2$ target was approximately 8.1W/cm$^2$ and on the carbon target it was approximately 11W/cm$^2$. Ar was used as the process gas and was kept at a pressure of 10 mtorr and an Ar flow of 27 sccm. During fabrication, the substrate worktable was biased to -200V. Biasing is known to promote ion bombardment and thus improve film adhesion and it is also suggested that ion bombardment may increase the formation of $sp^3$ hybridised carbon [10].

*2.3 Nanoindentation*

Nanoindentation was carried out using a Nanotest 550, equipped with a Berkovitch indenter [11]. For the samples fabricated in this study, 5 indents were made per sample, with loads ranging from 50 to 400 mN to a maximum depth of 1800 nm. The increasing load procedure had 8 steps with a load rate of 2mN/sec with a dwell time of 15s on the highest load. Elastic contributions were determined from the unloading curves and were used for the calculation of the Reduced Modulus. The mathematical model employed to analyse the data, was the Olivier and Pharr method [11]. The method was used to determine two mechanical properties - the Hardness and the Reduced Elastic Modulus.

Hardness is defined as the resistance of a material to plastic deformation, usually by indentation. Mathematically, hardness is defined as the maximum load divided by the projected area of the indenter in contact with the sample at the maximum load as can be seen in equation [1]

$$H = \frac{P_{max}}{A_c} \qquad [1]$$

Where:

H= Hardness

$P_{max}$=maximum applied load

$A_c$ = projected contact area at the maximum applied load

The indenter tip is not rigid during indentation, therefore the elastic modulus can not be directly determined from the load-displacement curves. However, the reduced elastic modulus can be determined from the unloading portion of the curve by the following relation. Mathematically, the reduced elastic modulus is given by equation [2]:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \qquad [2]$$

Where:

$E_r$ = Elastic Reduced Modulus

$\upsilon$ = Poisson ratio of the specimen/coating

E = Elastic modulus of the specimen/coating

$\upsilon_i$ = Poisson ratio of the indenter

$E_i$ =Elastic modulus of the indenter

The $TiB_2$/C multilayers were formed by alternating the film growth between two different materials. The coating thickness was kept constant at 5 μm; however, the % of $TiB_2$ in the coating was varied from 50 to 95% by volume by varying the thickness of the layers.

*2.4 Raman spectroscopy*

Raman spectroscopy was carried out using "Dilor Labram 1B" Raman Microprobe (Instruments SA, UK). Laser excitation was provided with a 17mW HeNe laser, at an excitation wavelength of 632.8 nm. The spectra were obtained from 1000 to 2000$cm^{-1}$ in steps of 0.8$cm^{-1}$. Raman spectroscopy was conducted at several points on the substrate surface and an average Raman spectrum obtained. Lorentzian fits to the Raman data obtained for carbon peaks at 1170$cm^{-1}$, 1360$cm^{-1}$, 1490$cm^{-1}$ and 1580$cm^{-1}$ provided an excellent fit to the Raman spectra of the deposited carbon layers.

## 3. Results and discussion

### *3.1 Carbon characterisation*

Raman spectroscopy conducted in the visible range provides information on the $sp^2$ hybridised constituents of amorphous carbon films, and studies have shown that Highly oriented pyrolytic graphite (HOPG), has a peak around 1580 $cm^{-1}$ with a FWHM (full width-half maximum) of 16.3 $cm^{-1}$[12]. This peak is referred to as the G peak and originates from the $E_{2g}$ symmetry graphite chains and clusters. Amorphous carbon has an additional peak in its Raman spectra, referred to as the D peak, at around 1355 $cm^{-1}$, which originates from the $A_{1g}$ mode of the crystal [13] . Naturally occurring diamond has a peak at 1332 $cm^{-1}$ with a FWHM of 2.6 $cm^{-1}$. Raman studies conducted on diamond-like carbon films have two peaks relating to the amount of $sp^3$ disorder and $sp^2$ graphitic components in the film. Robertson and O'Reilly have proposed a structural model of the amorphous carbon [14], in which they suggest that DLC consists of mainly $sp^3$ bonds and as the graphitic component of the carbon increases, the number of $sp^2$ bonds increase. Thus, the integrated intensity ratio of the D and G peaks, ($I_D/I_G$) plays an important role in determining film properties. By calculating the intensity of the D and G peaks from Raman spectra, inferences can be made as to the type of film deposited. A high $I_D/I_G$ ratio leads to DLC behaviour [14]. For the carbon fabricated in this study, the $I_D/I_G$ ratio is 1.08, indicating the presence of $sp^3$ hybridised bonding at about the 50% level in the coating.

Ferrari [15] and Silva [16] agreed that simple two-symmetric-line fits to the characteristic Raman D and G peaks are not always suitable to fit spectra. Symmetric multipeak fits are found to provide a much better fit to the data. Figure 1 shows a Raman spectra from carbon fabricated in this study. In this study, a D peak around 1330 $cm^{-1}$, a G peak at 1590 $cm^{-1}$, plus additional peaks at 1170 and 1500$cm^{-1}$ were necessary to accurately fit the data. Additional peaks in the Raman spectra around 1100-1220 $cm^{-1}$ have been associated with hexagonal diamond [17,16]. The Raman peak at 1500 $cm^{-1}$ has been attributed to the semicircle stretching of carbon atoms in single aromatic rings [18].

### *3.2 $TiB_2$/C multilayers*

$TiB_2$/C coatings were fabricated maintaining a constant composition wavelength (sum of two layers [λ] =200nm), for an array of ceramic fractions ranging from, 50% by volume, to 95% by volume. The thickness of individual carbon layers varied between 10nm and 100nm. The thickness of the $TiB_2$ ceramic layers varied between 100nm

and 190nm. Table 1 summarises the experiments carried out and the thicknesses of the individual layers. The Hardness and Reduced Modulus as a function of indent depth for all composition of films, at variable loads ranging from 50 to 400mN, is shown in figures 2 and 3, respectively. From the Hardness results, it can be seen that the Hardness ranges from about 5 GPa for the 100nm/100nm (50% $TiB_2$), to about 17 GPa for the 190nm/10nm (95% $TiB_2$). It is also worth pointing out that the enhancement in Hardness of the $TiB_2$/C as the $TiB_2$ content is increased from 50 to 95%, is due to the layer thicknesses' involved in this study. During indentation, several of the $TiB_2$/C layers become indented and thus the Hardness values are the result of the indentation penetrating several layers. The monolayer result of the Hardness shown in figure 2 is that of pure $TiB_2$ and shows that it has a hardness exceeding 24 GPa. By comparison, the 190nm/10nm $TiB_2$/C sample has a Hardness of 17 GPa.

The values of Hardness for all $TiB_2$ ceramic compositions are seen to converge to a single value, approaching that of the substrate as the indentation depth is increased. Also shown on the graphs is the data obtained from Cruz [19] for fabricated 50 – layer of $TiB_2$/Al stacks. The Hardness and Reduced Modulus is seen to follow the same trends, converging towards the hardness value of the AISI 1095 substrate with increase in indentation depth.

Figure 4 shows the variation in the Hardness as a function of volume fraction of carbon. The Hardness is seen to decrease as a function of increasing carbon content. A similar observation has been made by Baker et al., [7], where the Hardness of a $TiB_2$/C multilayer decreased from 40 GPa for a 100 nm $TiB_2$ sub layer thickness, to 25 GPa for a 1 nm $TiB_2$ sub layer thickness. It has been demonstrated that the number of interfaces, total coating thickness and substrate type all influence the measured Hardness values [20] and thus accounts for the differences in the Hardness values obtained in this study. Baker et al., [7] concluded from their findings that carbon preferentially bonds as $Ti(B, C)_2$ and DLC only forms when the $Ti(B,C)_2$ has become saturated. This saturation decreases the hard $TiB_2$ phase content and increases the softer carbon lubricating phase. From wear measurements they measured a friction coefficient of better than 0.2. For the reduced modulus data, it was observed that at the 50% $TiB_2$ volume fraction the reduced modulus increases a function of indentation depth, from 130 GPa to 210 GPa. By comparison, the 95% $TiB_2$ volume fraction is seen to remain overall constant at around 210 GPa.

## Conclusions

- A series of 50 layer stacks of alternate layers of $TiB_2$/C have been fabricated as 5 micron thick coatings using DC magnetron sputtering with a range of $TiB_2$ volume fractions ranging from 50% to 95%.
- Multilayering has overcome the inherent brittleness of $TiB_2$ when deposited as a coating.
- The Hardness varies from 5 GPa for the 50% $TiB_2$ ceramic to 17GPa for the 95% $TiB_2$ ceramic.
- A comparison made with a similar 50 – layer $TiB_2$/Al material system, show that the Hardness behaviour is similar, dominated by the $TiB_2$ volume fraction.
- As the carbon volume fraction is increased, the hardness is seen to decrease, and this decrease has been attributed to carbon layers not being load bearing, but acting as a lubricant in a $TiB_2$/C multilayer system.

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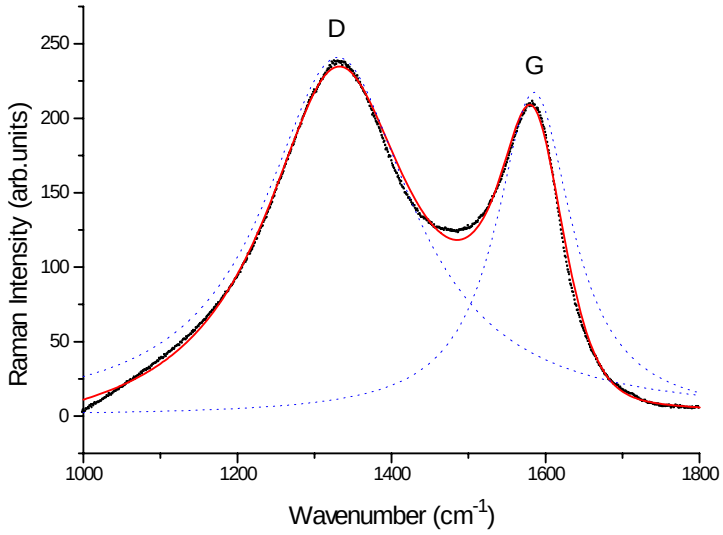


Figure 1: Raman spectra from the carbon film fabricated in this study. Lorentzian fits (only two are shown) at 1360 and 1580 $cm^{-1}$ were used to fit the positions of the D and G peaks. Additional peaks at 1170 and 1500$cm^{-1}$ were necessary to accurately fit the data. Additional peaks in the Raman spectra around 1100-1220 $cm^{-1}$ have been associated with hexagonal diamond [17,16]. The Raman peak at 1500 $cm^{-1}$ has been attributed to the semicircle stretching of carbon atoms in single aromatic rings [18].

| $T_{TiB2}$ (nm) | $T_{Carbon}$ (nm) | $TiB_2$ (%) | N° of layers | Coating total thickness |
|---|---|---|---|---|
| 100 | 100 | 50 | 50 | 5µm |
| 150 | 50 | 75 | | |
| 180 | 20 | 85 | | |
| 190 | 10 | 95 | | |

Table 1: Summarises the multilayer coatings experiments. The volume fraction of $TiB_2$ and carbon was varied by altering the thicknesses' of $TiB_2$ and carbon. The $TiB_2$ and carbon bilayer thickness was kept constant at 200 nm. $TiB_2$ volume fractions ranging from 50 to 95% were studied for a total film thickness of 5µm.

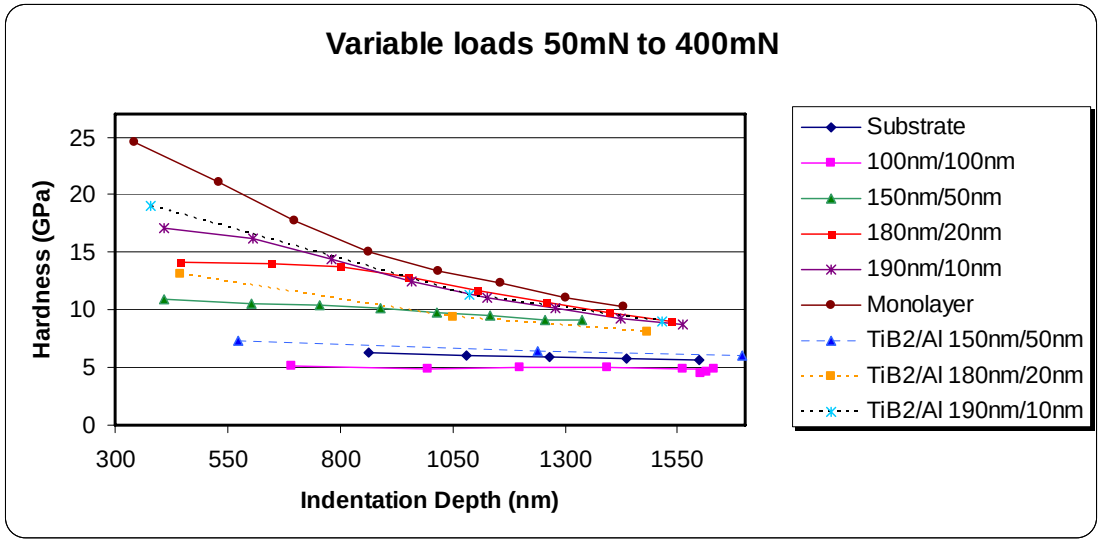


Figure 2: The variation of the hardness as a function of indentation depth for variable loads on multilayers of $TiB_2$/C. The captions in the figure show the thicknesses of the $TiB_2$/C layers. In all cases, a total film thickness of 5 μm was produced and the volume fraction of $TiB_2$ ceramic was altered by changing the $TiB_2$/C layer thicknesses'. The data for the substrate and a monolayer of $TiB_2$ is also plotted. The data from Cruz [19] for a similar $TiB_2$/Al stack is plotted for comparison.

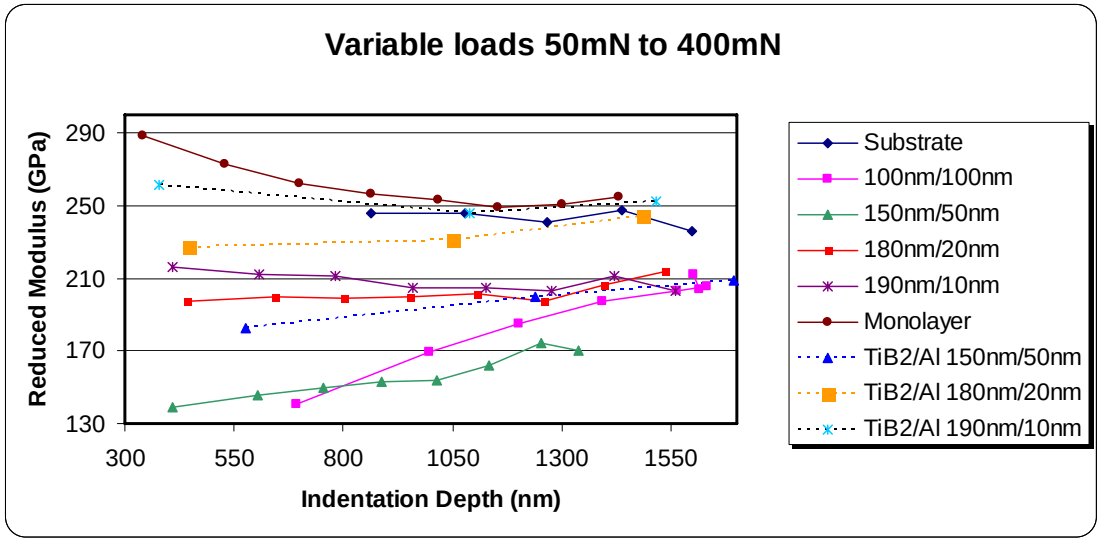


Figure 3: The variation in Reduced Modulus as a function of indent depth on multilayers of $TiB_2$/C. The captions in the figure show the thicknesses of the $TiB_2$/C layers. In all cases, a total film thickness of 5 μm was produced and the volume fraction of $TiB_2$ ceramic was altered by changing the $TiB_2$/C layer thicknesses. The data for the substrate and a monolayer of $TiB_2$ is also plotted. The data from Cruz [19] for a similar $TiB_2$/Al stack is plotted for comparison.

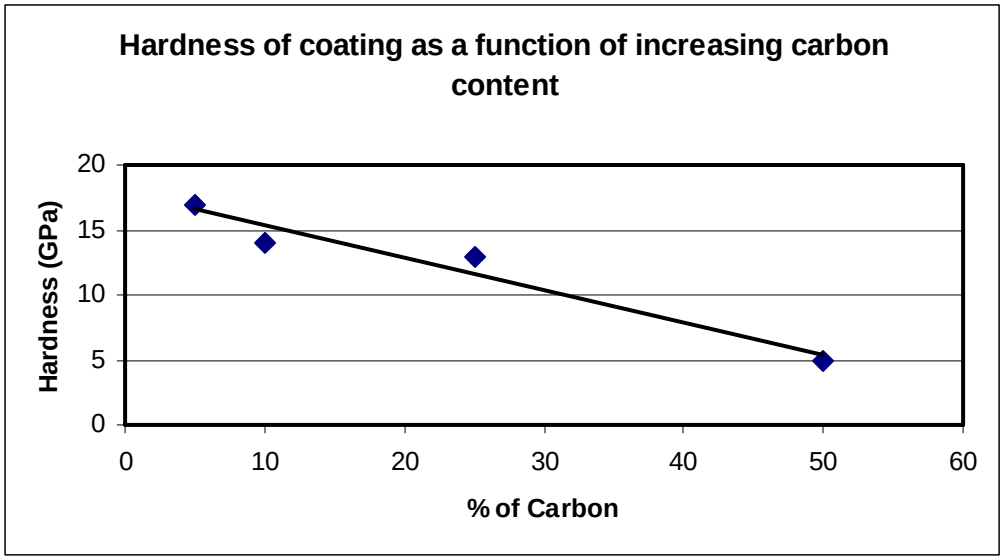


Figure 4: The variation of Hardness with % of carbon in coating. The Hardness decreases as the carbon content increases, suggesting that carbon acts as a lubricant.

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