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Fracture and yield behaviour of wear and erosion resistant boron phosphide coatings for aerospace and automotive applications

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ABSTRACT

Purpose: The investigation of mechanical properties of boron phosphide thin film coatings prepared by PECVD.

Design/methodology/approach: The hardness of the films was determined by nano-indentation. The fracture toughness was measured by Vickers indentation and the yield strength of the films on ZnS and <100> silicon substrate was measured by a simplified form of the spherical cavity model.

Findings: The measured mechanical properties indicate that boron phosphide coatings have potential engineering applications beyond protecting infrared substrates from sand erosion in aerospace environments.

Research limitations/implications: Their mechanical properties are comparable to those of DLC and Si-DLC films, in addition to their superior corrosion and sand abrasion resistance.

Practical implications:

Originality/value: Experimental data on the mechanical properties of boron phosphide coatings that indicate their surface protection promise in engineering applications.

Keywords: Boron phosphide; Thin films; Mechanical properties

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PROPERTIES

1. Introduction

Boron phosphide (BP) coatings hold promise for wear and erosion protection of engineering components that could include automotive, tribological and aerospace applications .The present authors and others in the literature [1-4] have evaluated the corrosion, wear and physical properties of Boron Phosphide films prepared by plasma enhanced chemical vapour deposition (PECVD) and other methods. Boron phosphide (BP) films are currently used to enhance the abrasion resistance of infra-red transmitting substrates for aerospace applications [5-7]. Diamond like carbon films have also been evaluated for the same application. The results of Sand/wiper abrasion test have indicated that BP is more resistant to sand abrasion than DLC films [8]. This implies that BP films have a potential as protective coatings. BP is harder than the typical impinging sand particles [3,9,10], giving it the ability to provide protection against particle erosion. Another major limitation with DLC films is the intrinsic residual stress. This residual stress puts a thickness limit of about 1μm thickness on DLC coatings, after which adhesion failure starts to occur. DLC films also have a limit on their thermal stability of about 250°C. However, before BP films can be deployed in service in any of the above areas, there is a need for a thorough investigation of the following properties of the films as a function of preparation conditions; hardness, fracture toughness and yield strength.

2. Experimental investigation

The BP films were prepared by a Nordiko PECVD facility located at Thales Optronics, Glasgow, Scotland, U.K. The precursors gases used for the deposition on ZnS and <100> silicon substrates were diborane (B_2H_6) and phosphine (PH_3), diluted in hydrogen gas, which served as the carrier gas. Argon gas was used to initiate and maintain the plasma during the deposition process at an rf frequency of 13.56 MHz. The chamber pressure was maintained at 30 mTorr and the substrate temperature during deposition was 350°C. The diborane flow rate was held at 15 sccm, whilst the phosphine flow rate was varied from 60 sccm to 90 sccm in 5 sccm increments. The deposition conditions are as shown in Table 1.

Table 1.
The gas flow rates used during the deposition of the boron phosphide coatings

Diborane flow rate (sccm)	Phosphine flow rate (sccm)	Ratio PH_3/B_2H_6
15	55	3.7
15	60	4.0
15	65	4.3
15	70	4.7
15	75	5.0
15	80	5.3
15	85	5.7
15	90	6.0

A Hitachi S- 4100 SEM was used for the examination of the BP films at magnifications that ranged between 20x and 5,000x. A combined AFM and Nano-indenter, Nanoscope III scanning probe microscope manufactured by Digital instruments was used for further surface characterisation and hardness measurements. The nano-indentation was performed with a Berkovich diamond tip at a load of 5000 μN. The Berkovich diamond is a three-sided tip, with a face angle of 63.5 degrees and a projected area $A = 2.5\ h_c$, where h_c is the contact depth. The Young's modulus of the investigated films was determined by nano-indentation. XPS investigation was carried out with a VG Escalab 200D spectrometer with a HSA analyser. Mg K_α X-ray was used for the excitation at energy of 15 keV and an emission current of 20 mA. The elemental sensitivity was about 0.1 atomic % and the pressure during the examination was better than 8×10^{-10} mbar. A range of boron phosphide films with different phosphine (PH_3) flow rates was used for the fracture toughness measurement. The films were deposited on ZnS and <100> silicon substrates. We used a Vickers indenter which is a four-sided diamond pyramid with a face angle of 136°. This tip was attached to a Shimadzu Micro Hardness Tester of type M. An indentation time of 5 seconds with loads ranging from 5 N to 6.8 N was applied to the film surface, sufficient to initiate cracks from corners of the indentation area. Omnimet 3 software from Hitachi was used at magnifications of 200x to 1000x to measure the crack length.

Table 2.
Surface roughness of the BP films for different PH_3 flow rates

B_2H_6 flow rate [sccm]	PH_3 flow rate [sccm]	Roughness R_a [nm]
15	60	7.9
15	65	9.1
15	70	17.5
15	75	14.9
15	80	4.4
15	85	10.5
15	90	15.6

3. Results and discussion

AFM images of the deposited BP thin films coatings are shown in Fig. 1. The growth mode seems to be dominated by surface globules, with the regions between the globules containing nano-porosities. The surface roughness is calculated using the AFM images with a 10x10μm lateral scale. All data are shown in Table 2.

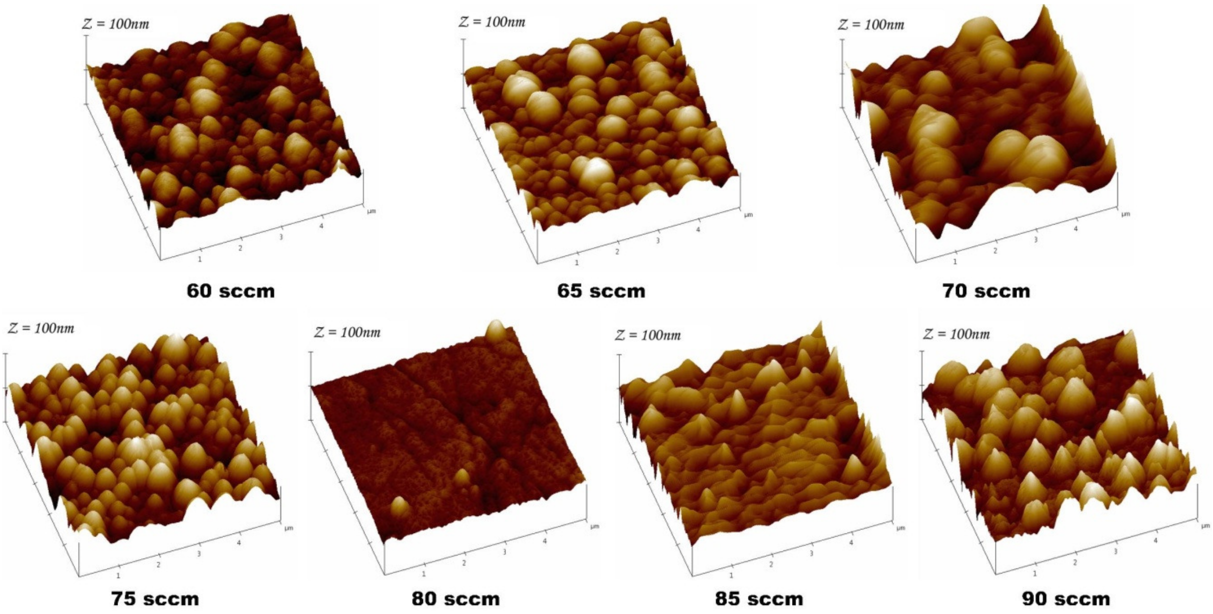

Fig. 1. AFM images of the BP surfaces at different PH3 flow rates

Table 3.
Relative % atomic concentration and binding energies-BP

PH_3 [sccm]	B1s B.E.	B		P2p B.E.	P		P:B	
		at.%	wt.%		at. %	wt. %	at.%	wt.%
60	187.8	36	16	130.0	64	94	1.78	3.9
75	187.9	47	24	130.1	53	94	1.13	4.0
90	187.9	48	24	129.9	52	93	1.08	5.6

The results of the XPS investigation on the prepared films are summarised in Table 3. All of the BP films investigated were found to be non-stoichiometric, with a B/P ratio greater than one.

The results of the nano-indentation tests on the BP films are shown in Fig. 2. The average hardness of the BP films in the composition range examined was 14.7 GPa with a standard deviation of 3.6 GPa. The films showed a decreasing hardness of ~ 0.3 GPa per sccm as the phosphine flow rate during deposition was increased from 60 to 90 sccm. This could be associated with a relative increase in P-P bonds, compared to B-P and B-H bonds. Boron is known to form hard and wear-resistant compounds.

The reduced elastic modulus of the films had an average value of 170 GPa for phosphine flow rates between 60 and 65 sccm, and an average value of 140 GPa for phosphine flow rates between 70 sccm and 90 sccm. These values are comparable to the reported values of hardness of 25-30 GPa and reduced elastic modulus values of around 164 GPa for Diamond-like carbon (DLC) films [11].

We used the relationship below from Anstis et al. and others [12,13] to evaluate the K_{IC} values.

$$K_{IC} = \alpha \left(\frac{E}{H} \right)^{1/2} \left(\frac{P}{c^{3/2}} \right) \quad (1)$$

where: α = 0.016 is a constant for a Vickers tip and depends on the geometry of the indenter, E is the elastic modulus and H the hardness of the film. The applied load is given by P and the measured crack length is c. The hardness measurement from the nano-indenter was used in the calculation to minimise substrate interference from the macro-indentation with the Vickers indenter. We used an average of data from 10 indentations for each sample.

The results of the K_{IC} measurements on the BP films are given in Table 4, below. As shown in Table 4, the average fracture toughness of the boron phosphide films is 2 GPa/m $^{0.5}$, which is comparable to values previously reported for other wear resistant protective coatings by other researchers in the literature as shown in Table 4, except TiN. A. Roman et al [16] obtained K_{IC} values of 1.5 GPa/m$^{0.5}$ on nickel phosphorus films and Field [17] previously reported K_{IC} values of 1.3 GPa/m$^{0.5}$ for BP films. There was little variation between the fracture toughness obtained on ZnS and silicon substrates for the BP films.

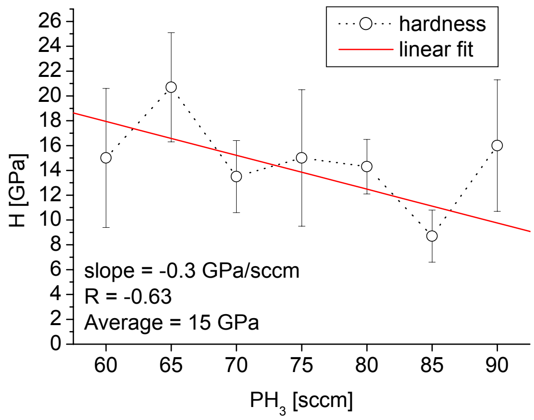

Fig. 2. Hardness of BP films prepared for phosphine flow rates between 60 and 90 sccm obtained by Nano-indentation

Table 4.
K_{IC} values for each PH_3 flow rate

Phosphine flow rate	Fracture toughness,
60	2.7
70	2.0
80	2.0
90	1.9
DLC (14)	1.4
TiN (15)	4.51
NiP (16)	1.5
BP (17)	1.3

The yield strength was measured using the same indenter used for fracture toughness tests. A range of loads was used to introduce the plastic zone circumferential cracking around the indentation zone, as shown in Figure 3. The width of the outer shear bands shown in Figure 3 was measured. The yield strength was calculated using a simplified form of the Johnson spherical cavity model [18-20], given by

$$C = \left[3P / 2\pi\sigma_{ys}\right]^{1/2} \tag{2}$$

where:
P - applied load,
σ_{ys} - yield stress,
C - plastic zone radius.

The measured width and hence plastic zone radius is plotted against the square root of the applied load as shown in Fig. 4 for BP films deposited on ZnS substrates obtained by the spherical cavity model. The yield strength σ_{ys} is extracted from the gradient of this plot multiplied by the relevant constants. The average value of the yield strength obtained by the spherical cavity model is 3 GPa. The value of the yield strength obtained is less than those reported for Si-DLC [21] of 7.5 GPa and TiN of 12.5 GPa [22]. This might be due to nano-porosities on the surface of the deposited BP films.

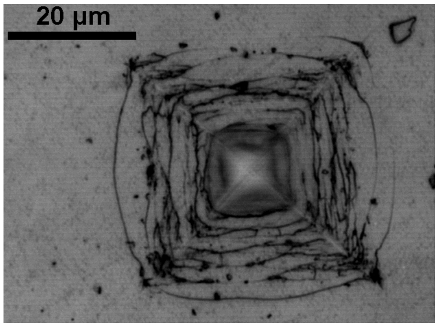

Fig. 3. A typical circumferential cracking zone around indents observed on the BP films deposited on ZnS substrates

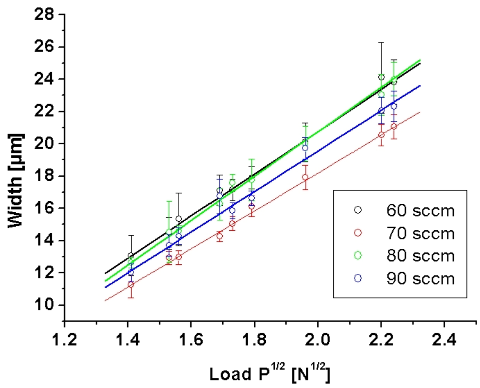

Fig. 4. The measured width or plastic zone radius is plotted against the square root of the applied load

4. Conclusions

In summary we provide experimental data on the mechanical properties of Boron Phosphide coatings that indicate their surface protection promise in engineering applications. Their mechanical properties are comparable to those of DLC and Si-DLC films, in addition to their superior corrosion and sand abrasion resistance.

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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