Metal-boride phase formation on tungsten carbide (WC-Co) during microwave plasma chemical vapor deposition

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Abstract

Strengthening of cemented tungsten carbide by boriding is used to improve the wear resistance and lifetime of carbide tools; however, many conventional boriding techniques render the bulk carbide too brittle for extreme conditions, such as hard rock drilling. This research explored the variation in metal-boride phase formation during the microwave plasma enhanced chemical vapor deposition process at surface temperatures from 700 to 1100 °C. We showed several well-adhered metal-boride surface layers consisting of WCoB, CoB and/or W₂CoB₂ with average hardness from 23-27 GPa and average elastic modulus of 600-730 GPa. The metal-boride interlayer was shown to be an effective diffusion barrier against elemental cobalt; migration of elemental cobalt to the surface of the interlayer was significantly reduced. A combination of glancing angle x-ray diffraction, electron dispersive spectroscopy, nanoindentation and scratch testing was used to evaluate the surface composition and material properties. An evaluation of the material properties shows that plasma enhanced chemical vapor deposited borides formed at substrate temperatures of 800 °C, 850 °C, 900 °C and 1000 °C strengthen the material by increasing the hardness and elastic modulus of cemented tungsten carbide. Additionally, these boride surface layers may offer potential for adhesion of ultra-hard carbon coatings.

Keywords Boriding, Ternary Boride, Thin-film, Cemented Carbide, Tungsten Carbide

1. Introduction

Cemented tungsten carbide (WC-Co) is a high strength, high hardness sintered ceramic composed of tungsten, carbon, and cobalt. The exact percentages of these elements vary depending on desired properties. Due to the sintering process small amounts of oxygen and nitrogen are also present in the porous ceramic structure[1]. Tungsten carbide is one of the most durable materials available for mining, drilling and cutting operations. Despite the incredible hardness, a carbide bit can wear down in seconds[2]. In the ongoing search for better industrial materials, boriding and diamond coatings are viable solutions to reduce wear and increase tool life[3, 4]. Unfortunately, unlike many existing diamond coating processes, well adhered diamond cannot be grown directly onto cemented tungsten carbide alloys due to graphitic nucleation caused by the presence of cobalt[5, 6]. To this end, boride treatments have been explored as a means to strengthen materials, both as an individual metal-boride surface layer and as an interlayer for nanostructured diamond[5-9].

Boriding is widely used to improve material properties, and can be successfully implemented as a surface treatment for diamond deposition in an array of materials, including tungsten carbide[9, 10]. Boriding is shown to result in higher hardness and improved durability when compared to other surface modifications, such as, carburizing or nitriding[11-13]. Transition metal borides (TiB_2 , ZrB_2 , Fe_2B and Co_2B) are good candidates for diamond deposition; they are stable, compatible with carbon, densely packed, and inhibit carbon diffusion[3, 13]. Significant research has been conducted on the boriding process, but there are still gaps in existing knowledge. Most boriding research for tungsten carbide has been performed using conventional chemical vapor deposition (CVD), molten salt, or powder packed methods for longer time periods from 4 to 12 hours with typical temperatures at or over 1000 °C[14-17]. Research using plasma enhanced chemical vapor deposition (PECVD) boriding, shorter time durations, and lower temperatures is relatively unexplored. Furthermore, an analysis of boride phase transitions with smaller (50 °C) increments from 700 °C – 1100 °C for PECVD has not been previously performed.

Recently, we have shown that microwave PECVD is an effective method for thermo-chemical surface modification using diborane (B_2H_6) in the feedgas to form metal-boride surface layers on cobalt-chromium alloys[18]. These borides often include orthorhombic CoB and body-centered tetragonal Co_2B structures, among others. PECVD boriding of tungsten carbide can also form the less explored ternary borides (WCoB , W_2CoB_2 and W_3CoB_3) with reported hardness ranging from 23.4 GPa[11] to 45 GPa[19]. In the current work, we explore the formation of borides on tungsten carbide during PECVD using diborane and a range of substrate temperatures. Material properties of metal-boride layers, including ternary borides, without diamond deposition are investigated.

2. Experimental methods

2.1 Sample Preparation

The WC-Co investigated here was a TM6 grade sintered carbide composed of 94% WC, 6% Co binder; carbides had a known hardness of 89.6-90.4 (Ra) and 1500-2000 (Hv), density of

14.95 (g/cm³), and a medium grain size[20]. The carbide bits measured 10mm diameter by 3mm height. Prior to boriding bits were polished at 350 rpm for 10 minutes with each of 125, 70, 30, 15 and 9 micron metal-bonded diamond pads, and then polished with diamond solution at 9, 6, 3, and 1 microns for 30 minutes at each size. Polished samples were then cleaned via sonication with acetone and then methanol for 20 minutes each, followed by a deionized water rinse.

Post-boriding, sample cross sectioning was performed with an Allied High Tech Techcut 4 low speed metal sectioning tool. Samples were mounted in epoxy to increase edge retention, then sectioned using a 6 inch diameter resin bonded diamond wafering blade at 300 rpm. After sectioning, the cross-sectional surface was polished at 350 rpm for 10 minutes with each of 70, 30, 15 and 9 micron metal-bonded diamond pads, and then polished with diamond solution on Allied Tech-Cloth pads at 9, 6, 3, and 1 microns for 30 minutes at each size. Polished samples were then cleaned with an acetone rinse followed by deionized water.

2.2 Boriding

A 2.45 GHz microwave-plasma CVD (Wavemat, Ann Arbor, MI, USA) chamber was utilized. Boriding was performed with a diborane (B₂H₆) and hydrogen (H₂) feedgas mixture consisting of 500 sccm of high purity 99.9% (H₂) and 3.0 sccm of B₂H₆ (provided as a 10% dilution in H₂). Pressure and power were incrementally increased until the desired trial specific parameters were met, typically between 30-60 Torr and .6-1.5 kW. Substrate temperature was measured using a two-color optical pyrometer centered at 1.6 μ m. The WC-Co substrate reached a steady state temperature in H₂, at which point the combined H₂ and B₂H₆ feedgas mixture was introduced. Borided WC-Co samples were produced for a range of target substrate temperatures (700-1100 °C at 50-degree intervals) using a 1 hour duration.

2.3 Characterization

X-Ray Diffraction (XRD) patterns were measured using a thin-film diffractometer (X'pert MPD, Philips, Eindhoven, The Netherlands) with Cu anode ($\lambda = 0.154154$ nm), generator voltage of 45 kV, tube current of 50 kA, and glancing angle of 3°. Scans were compared against the Joint Committee on Powder Diffraction Standards database[21], Crystallography Open Database[22], and diffraction simulations using MAUD software[23]. Rietveld refinement was used to evaluate the relative individual phase composition[24].

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) was done using an FEI QuantaTM 650 field emission gun with 1.2 nm spatial resolution at 20kV. SEM images were captured in secondary electron mode and EDS line scans were performed on the cross-section of the boride layer to observe change in chemical composition across the interface. It is important to note that boron is within the detection limit for this particular equipment configuration; although boron was near the limit of detection a significant signal was observed. The topography of the coatings was imaged using optical and atomic force microscopy (AFM). AFM images were obtained using contact mode and the roughness values were recorded.

Nanoindentation was performed using a Nanoindenter XP system to evaluate hardness up to a maximum depth of 400 nm. Nanoindentation was performed on the bare alloy and on the

surface layer after boriding to evaluate changes in hardness and elastic vs. plastic depth. Indents were carried out at a distance of greater than 100 microns from the sample edge, and with an indent separation of at least 25 microns.

Progressive load scratch tests were performed to observe the extent of cracking or delamination of the coatings, determined in accordance with ASTM C1624[25]. Scratch tests were performed with a commercial diamond stylometer (Romulus IV, Quad Group Inc., Spokane, WA, USA) with a 125 μm radius spherical diamond tip. The maximum force used was 50 N with a load rate of 2 N/s over a distance of 3 mm. Resulting indents and scratches were examined by optical microscopy to observe cracking and delamination.

3. Results and Discussion

3.1 XRD of WC-Co Boride Layer

The effects PECVD boriding on WC-Co were investigated across a range of times and temperatures. The crystal phase composition of the WC-Co surface was analyzed using XRD. Figure 1 shows WC-Co borided at 700-1100 $^{\circ}\text{C}$ at 100-degree intervals, as well as a control sample which experienced no boriding. The phase analysis was representative for samples prepared at the same temperature. These results show a considerable transition in metal-boride structure with increasing temperature.

This chemical transition is consistent with previous CVD boriding observations[26, 27], but here we provide a more detailed temperature analysis. From Figure 1 it is observed that at 700 $^{\circ}\text{C}$ there is not sufficient energy to form tungsten boride compounds, so the more readily formed cobalt boride is observed. As temperature increases to 800 $^{\circ}\text{C}$ tungsten begins to react forming WCoB. It is assumed that at this temperature the reaction of tungsten is still limited preventing the formation of W_2CoB_2 . At 900 $^{\circ}\text{C}$ tungsten ions become significantly reactive and in much greater concentration than cobalt, leading to both W-B phases and W_2CoB_2 . The transition from W_2CoB_2 to WCoB is the result of increased cobalt diffusion at even higher temperatures above 900 $^{\circ}\text{C}$, balancing the excess of tungsten. This relative cobalt concentration seems to increase further at 1100 $^{\circ}\text{C}$ forming Co-B compounds. Previous CVD boriding results agree well with these observations. A transition from W_2CoB_2 to WCoB has been observed at over 900 $^{\circ}\text{C}$ [26, 27].

A Rietveld refinement[24] was used to evaluate phase composition by percent weight for each sample deposited in the range of 700-1100 $^{\circ}\text{C}$ at 50-degree intervals. A plot of surface phase percentage vs temperature, Figure 2, shows a more complete dataset where each point was represented by $n=5$ samples. This reveals the transition from bulk hexagonal WC-Co, followed by masking of surface elemental Co via the formation of various borides, and then the eventual surface etching and re-emergence of Co at high temperatures. With increasing temperature, formation of boride compounds increased, reducing the presence of tungsten carbide from 94% to 18% on the surface. Cobalt boride was observed at temperatures from 700 $^{\circ}\text{C}$ to 850 $^{\circ}\text{C}$, but was reduced from 18% to 0% as WCoB and W_2CoB_2 phases emerge. At 900 $^{\circ}\text{C}$ there was a stable maximum for W_2CoB_2 at 39%, which was replaced by WCoB with increasing temperature. At very high temperatures, above 1000 $^{\circ}\text{C}$, the presence of borides was reduced;

leading to increased tungsten carbide and hexagonal cobalt phases. This is likely due to increased substrate atom mobility and reduced condensation on the surface for higher temperatures. Of note, the presence of hexagonal cobalt found in the control sample was not present between 700 °C and 850 °C, and existed only in trace amounts until above 1000 °C. For longer time durations above 900 °C, a phase transition from hexagonal Co to cubic Co is expected. Hexagonal and tetragonal B₂W phases were observed at 3% and 4% composition, respectively, but only for 900 °C (data not shown).

These results indicate that boriding creates a complex set of metal-boride surface layers with a delicate temperature dependence for boride phase formation. For temperatures above 1000 °C, etching of surface borides was observed and therefore further investigation of potentially interesting boride phases was not pursued. Temperatures below 800 °C led to poorly adhered boride soot formation. Temperature conditions with unique boride phase mixtures of interest were found to occur at 800 °C, 850 °C, 900 °C, and 1000 °C to form CoB with WCoB, W₂CoB₂, and WCoB respectively. In the 800-1000 °C temperature range, surface elemental cobalt was masked and a sufficient metal-boride surface layer was formed. It is possible that these boride coatings could also be applied for improved growth and adhesion of nano-structured diamond and diamond-like carbon thin films as a result of the masked cobalt.

3.2 SEM and EDS of WC-Co Boride Layer

The surface of the boride layer and its cross section were further explored using scanning electron microscopy and energy dispersive spectroscopy. The planar boride surface, Figure 3a, contains micro-fractures and darker pitted regions throughout the explored temperature ranges. Micro-fracturing of the surface is likely caused by residual thermal stress from the deposition process[28, 29]. No adhesive failure or long range fracturing of the film was observed. Pitting could have been a consequence of existing pits in the bulk carbide, a result of fabrication, or the often porous nature of borides[30, 31]. Figure 3b and 3c show the same cross-sectioned surface of a typical PECVD borided WC-Co sample at different magnifications. The upper most surface of the boride layer, is only a few micrometers thick; however, the boriding process also created a deep, graded boron diffusion layer. The diffusion of boron was investigated using an EDS line scan (Figure 3d), indicated by the dashed line (Figure 3b). The line scan confirms boron diffusion into the bulk. Boron concentration decreases with increasing depth into the bulk carbide and peaks at the surface.

The EDS line scan (Figure 3d) shows that the lighter, jagged grains were primarily tungsten, carbon and boron. Interstitial space consists of cobalt binder with boron and reduced tungsten. The surface layer contains a high carbon mixture along with tungsten, cobalt, and boron. In general, tungsten concentration decreases from the bulk to the surface; cobalt, carbon and boron increase from the bulk to the surface. The boron diffusion into the carbide as well as the thermal diffusion of cobalt and tungsten within the carbide give rise to the CoB, WCoB, W₂CoB₂ borides, as seen from XRD (Figures 1 and 2).

The thick graded boron diffusion layer combined with the ternary metal-boride surface coating are promising for applications in material strengthening. Furthermore, a vacancy-assisted

mechanism is expected to be the primary mode of cobalt diffusion toward the surface[32]. The strong covalent bond energy and the relatively high atomic density of the metal-boride layer should limit the presence of surface cobalt during NSD deposition. The graded boron diffusion layer may be useful for improving adhesion of a subsequently deposited CVD diamond coating by preventing the catalytic graphite-forming interaction of cobalt with carbon on the surface.

3.3 Surface structure of WC-Co boride

Optical microscopy was used to characterize the surface structure before and after boriding, and to compare structural changes based on surface temperature. Figure 4 shows the borided surface for samples prepared at 600 °C (a), 800 °C (b), 1000 °C (c), and 1200 °C (d). For lower temperatures, below 800 °C, the surface coating appeared as a thick brown soot that was easily removed. At and above 800 °C the surface formed randomly oriented borides creating a roughened morphology. At 1000 °C, the typical boride morphology transitioned into a smooth metallic-looking structure. At higher temperatures, above 1100 °C, the surface revealed coalesced regions of varying contrast attributed to metallic cobalt and crystalline tungsten carbide and borides (as measured by EDS).

Analysis by AFM provided a quantitative measurement of the surface roughness for these samples (not shown). Untreated WC-Co polished down to 1 micron grit contained pitted features resulting in an average surface roughness (R_a) of 150 nm. These features were reduced during the boriding process. Borided surfaces prepared at 800, 900 and 1000 °C showed significant variation in surface roughness. At 800 °C the surface roughness measured 75 nm, with height profile (R_t) of 1000 nm. This roughness is diminished at 900 °C to 50nm R_a and 600 nm R_t . Further increase in temperature to 1000 °C resulted in decreased roughness (R_a) to 40 nm and R_t of 500nm. Higher temperatures seem to result in more coalesced films, with reduced surface roughness.

3.4 Nanoindentation Hardness

Nanoindentation was used to evaluate the hardness, modulus and elastic vs. plastic depth for polished WC-Co and WC-Co borided at 700-1100 °C in 100 °C increments. The data with error bars represent average and standard deviation for $n=100$ indents (20 indents on 5 samples at each temperature). Tests on the un-borided alloy to 400 nm depth show an average hardness of 23 ± 1 GPa, and elastic modulus of 660 ± 20 GPa. For all temperatures, the surface of the borided alloy shows increased hardness ranging from 25 ± 2 GPa to 28 ± 2 GPa and elastic modulus ranging from 600 ± 20 GPa to 780 ± 20 GPa at 400 nm depth (Figure 5a and 5b). From the glancing-angle XRD data, the surface hardness is expected to result from a mixture of the constituent metal-borides.

Some level of variation exists due to the rough nature of ceramic tungsten carbide. Even when polished to a mirror finish, the ceramic material has an inhomogeneous grain structure that results in inconsistent nano-scale hardness measurements. Furthermore, the carbides have a porous and pitted surface that was only partly filled in by boriding. Nevertheless, a clear increase in hardness and elastic modulus is observed at many boriding temperatures, as expected. Substrate effects are reduced by using an indent depth of less than 10% of the surface coating

thickness. The effect of adjacent indents is reduced by using an indent spacing of 25 microns, a distance many times greater than the indent depth. The distance from the sample edge is greater than 100 microns, reducing edge effects. Due to the consistency in the elastic modulus between the coating and the substrate, plastic flow of coating compared to substrate or vice-versa should not be significant.

The as provided carbide is expected that have a hardness of 14.7 GPa[20] for medium grained carbide. Our tests on the carbide show a control hardness of 23 ± 1 GPa. This discrepancy is likely the result of polishing the surface down to a 1 micron roughness, creating a surface that is more in line with a finer grain structure which have known hardness as high as 23 GPa[20]. As-received carbides have an expected elastic modulus (young's modulus) of 640 GPa[20], this agrees with our measured value of 660 ± 20 GPa. Previously reported values for WCoB hardness vary, but include values from 23.4 GPa[11] to 45 GPa[19]. Our data falls within this range with data points as high as 45 GPa. Studies involving WCoB and W_2CoB_2 often evaluate its hardness as a component of bulk ceramic material rather than a surface coating, and report a hardness of 89-90 (HRA)[33] and 84.4-92.2 (HRA)[34].

3.5 Surface Adhesion

Progressive load scratch tests were used to study the adhesion of boride coatings on the WC-Co substrate. A typical result is presented in Figure 6. Scratch testing was performed for 5 samples of each 800 °C, 900 °C, and 1000 °C, with 5 scratches per sample for a total of n=25 tests per temperature. The CoB and WCoB (800 °C) layer shows cohesive failure at $28N \pm 3N$ (arc tensile cracking) and adhesive failure at $34N \pm 3N$ (edge spallation) and $50N \pm 3N$ (buckling spallation). The W_2CoB_2 (900 °C) layer shows cohesive failure at $37N \pm 3N$ (arc tensile cracking) and adhesive failure at $42N \pm 5N$ (edge spallation) and $65N \pm 7N$ (buckling spallation). The WCoB (1000 °C) layer shows cohesive failure at $42N \pm 2N$ (arc tensile cracking) and adhesive failure at $48N \pm 8N$ (edge spallation) and $72N \pm 4N$ (buckling spallation).

Cohesive failure was below the threshold for the acoustic signal, and was determined by secondary optical examination. Figure 6c shows the region of cohesive failure with arc tensile cracking along the edges of the scratch. Arc tensile cracking is attributed to tensile stress pulling apart the boride coating as the scratch propagates. Adhesive failure is indicated by a sharp rise in drag coefficient then acoustic signal in Figure 6a. This is attributed to significant edge recovery spallation (Figure 6e), followed by interface buckling spallation (Figure 6b and 6d). Edge spallation is the result of significant plastic and elastic deformation which has a maximum deformation along the edge of the scratch. Buckling spallation occurs when the combined transverse and normal load are sufficient to simultaneously overcome the adhesive bonding and cohesive strength of the film[25]. The drag coefficient seen in Figure 6a, is a function of the measured transverse load on the indenter and the applied normal load. It is not a measure of the sliding coefficient of friction. The transverse load, and thus the drag coefficient is expected to increase as scratch depth increases as a result of increased "plowing" into the material. The sudden increase in drag coefficient seen at 5mm is likely due to edge spallation and build-up of debris along the scratch path. The spike in acoustic signal at 7.5mm is due to buckling spallation. These patterns are consistent with a hard film on a hard substrate[25].

Residual scratch depth is estimated by SEM observation to be 70 μm . Cracks and surface delamination did not propagate beyond the scratch indicating a well adhered surface film. The increase in load for adhesive failure with deposition temperature may be the result of increased metal-boride formation within the carbide surface as temperature increased. As shown by EDS, boron diffuses into bulk material and higher temperatures are expected to increase ion diffusion and interaction within the substrate. Also, there is a distinct boride phase difference at each of these temperatures; adhesion to the surface may be the result of each specific phase. An estimation of residual surface stress for each phase is made difficult by a complex phase mixture of borides with uncertain coefficients of thermal expansion. A best estimate of residual surface stress ranges from 1 to 4 GPa. The WCoB (1000 $^{\circ}\text{C}$) layer can be more accurately estimated at $3.2 \pm .3$ GPa[35, 36]. In all cases this stress is expected to be partially relieved by the surface microfractures seen in Figure 3a.

4. Conclusion

These results show distinct temperature-sensitive phase transformations for PECVD metal-borides on WC-Co. This expands on previous data via a more detailed evaluation of phase evolution with temperature showing a detailed transition between phases. The PECVD process results in ternary borides that are consistent with other boriding techniques. Plasma boriding of tungsten carbide at surface temperatures from 600-1200 resulted in an array of metal-boride surface layers, including ternary borides, which exhibited increased hardness and elastic modulus with excellent surface adhesion. The borides that formed include: orthorhombic CoB, WCoB, W_2CoB_2 and BCo_3 , Hexagonal B_2W and Tetragonal B_2W . Boriding temperatures below 800 $^{\circ}\text{C}$ resulted in loosely adhered soot composed of mixed orthorhombic CoB and orthorhombic WCoB. At 800 $^{\circ}\text{C}$ a coalesced, adhered film of equal parts WCoB and CoB was formed. Hardness and modulus at 800 $^{\circ}\text{C}$ was 26 ± 2 GPa and 604 ± 20 GPa respectively. At 850 $^{\circ}\text{C}$ the surface coating was W_2CoB_2 and equal parts WCoB with a hardness and modulus of 29 ± 2 GPa and 760 ± 20 GPa. Samples prepared at 900 $^{\circ}\text{C}$ had a W_2CoB_2 surface structure with less than 4% each of hexagonal and tetragonal WB_2 . Thin surface hardness and modulus values were 27 ± 2 GPa and 710 ± 20 GPa, respectively. This composition transitioned into primarily WCoB at 1000 $^{\circ}\text{C}$ with a hardness and modulus of 26 ± 2 GPa and 651 GPa. Above 1100 $^{\circ}\text{C}$ surface borides gave way to substrate tungsten carbide and cobalt phases. Cross-sectional electron dispersive spectroscopy confirmed the elemental constituents at the surface and showed a boron surface layer of 3-5 microns depth and boron diffusion into the carbide grain structure. Scanning electron microscopy revealed a smooth boride surface that filled in the natural porous structure of sintered WC-Co. Micro fracturing on the boride surface may have helped to relieve residual thermal stress thereby preventing delamination of the boride layers. Scratch testing resulted in cohesive failure at $28\text{N} \pm 3\text{N}$ and adhesive failure at $34\text{N} \pm 3\text{N}$ and $50\text{N} \pm 3\text{N}$ for CoB and WCoB, cohesive failure at $37\text{N} \pm 3\text{N}$ and adhesive failure at $42\text{N} \pm 5\text{N}$ and $65\text{N} \pm 7\text{N}$ for W_2CoB_2 , and cohesive failure at $42\text{N} \pm 2\text{N}$ and adhesive failure at $48\text{N} \pm 8\text{N}$ and $72\text{N} \pm 4\text{N}$ for WCoB. These results indicate that the temperature range from 800 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ results in boride treatments that could be used for the strengthening of WC-Co. At least four specific deposition parameters (800 $^{\circ}\text{C}$, 850 $^{\circ}\text{C}$, 900 $^{\circ}\text{C}$, and 1000 $^{\circ}\text{C}$) present with unique metal-boride phase mixtures for material enhancement. Furthermore, the dense, coalesced boride structure

combined with a boron diffusion layer suggests that these films may be promising candidates for future nanostructured diamond deposition experiments.

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Figure Captions

Figure 1: XRD scans of the metal-boride surface layer for a range of substrate temperatures. Three-degree glancing angle XRD shows the formation of orthorhombic CoB, WCoB, W_2CoB_2 and BCo_3 , Hexagonal B_2W and Tetragonal B_2W on the WC-Co substrate for 700-1100 °C using 100-degree intervals. No boride compounds were present in the control sample.

Figure 2: Evolution of surface phase with temperature. Rietveld analysis of phase composition vs temperature shows the transition from bulk WC-Co to various cobalt boride phases as temperature increases. Phases shown included hexagonal WC, hexagonal Co, orthorhombic CoB, orthorhombic W_2CoB_2 , and orthorhombic WCoB. Each point represents an average with standard of deviation for n=5 samples prepared under identical conditions.

Figure 3: Scanning electron microscopy and energy dispersive spectroscopy of boride on WC-Co. Figures 3 a-c are a false color SEM scan of backscattered electrons (blue) and secondary emission (yellow). (a) SEM scan of the boride surface shows micro-cracks across the entire coating. (b) Cross-section image shows a smooth, thin (~ 3-5 μm) WCoB coating on the rough porous substrate. SEM and EDS performed on the cross-sectional face reveal the grain structure of the ceramic material. The solid red line is an indicator for Figure 3d (c) Figure 3c shows a higher contrast cross sectional image with a more clear distinction between the boride layer and the substrate. (d) An EDS line scan of the cross-sectioned, borided WC-Co, corresponding to the line scan on Figure 3b. This shows boron diffusion into the bulk carbide and significantly increased concentration in the surface layer. Relative tungsten concentration decreases toward the surface. Cobalt is present throughout, but also is present in high concentration areas between defined carbide grains. The interface between the boron surface layer and the bulk material, indicated by the red vertical line, shows an increase in boron near the surface.

Figure 4: 1000X magnification of borided WC 600-1200 °C: Optical images of surface boride show variation in surface roughness and contrast for (a) 600 °C (b) 800 °C (c) 1000 °C (d) 1200 °C

Figure 5: Nanoindentation hardness and modulus. Nanoindentation hardness testing on the polished WC show an average bulk hardness of 23 ± 1 GPa and modulus of 660 ± 20 GPa, indicated as an open diamond symbol in figures a. and b. (a.) The average hardness measured at 400 nm for boron treated WC-Co vs temperature ranges from 25 ± 2 GPa at 1100 °C to 28 ± 2 GPa at 850 °C (b.) The average modulus measured at 400 nm ranges from 600 ± 20 GPa at 800 °C to 780 ± 20 GPa at 850 °C. In all cases vertical error bars have been calculated using the standard of deviation (n=100).

Figure 6: Progressive load scratch testing of borided WC-Co. (a.) An optical image of progressive load scratch testing for adhesion is shown above the corresponding scratch tester normal load (dotted line), drag coefficient (dashed line), and acoustic signal (solid line). Y-axis units of force apply to normal load and transverse load; the acoustic signal has been scaled to fit. Cohesive failure is observed around 40N (no acoustic signal). At 52N edge recovery spallation results in increased drag coefficient. Near 78N, adhesive failure occurs, indicated by acoustic signal. (b.) Optical microscopy shows buckling spallation indicative of adhesive failure of a hard film on a hard substrate. (c.) Cohesive failure, shown by optical microscopy, resulted in cracking of the boride layer along the scratch edges. (d.) A 5kv secondary electron SEM scan shows another example of buckling spallation in the central scratch area. (e.) A 5kv secondary electron SEM scan of the scratch sides reveals adhesive failure cracking and recovery spallation. The residual scratch depth is determined to be 70 μm . No long range surface delamination is observed.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6