Comparison of the Properties of PVD and IBED Hardcoats (TiN and Cr_2N)

Arnold H. Deutchman, Ph.D. and Robert J. Partyka, M.S.

8270 Estates Parkway Plain City, OH 43064
www.beamalloytechnologies.com

Abstract

Metallic nitride hardcoatings (titanium nitride and chromium nitride) are routinely deposited on a wide variety of cutting tools, forming tools, and other components using high temperature 538 °C (1000 ºF) physical vapor deposition (PVD) processes. This family of hardcoatings can also be deposited at temperatures below 93 °C (200 ºF) using an advanced ion beam enhanced deposition (IBED) process. The metallurgical compositions of IBED-deposited titanium nitride and chromium nitride coatings are verified by Rutherford Backscattering Spectroscopy, and mechanical properties including scratch adhesion and abrasive wear-resistance are measured. These mechanical properties were also measured for titanium nitride and chromium nitride hardcoatings deposited by physical vapor deposition (PVD) as well as hard chrome plated coatings. The IBED deposited hardcoatings are shown to be viable, low temperature alternatives to PVD deposited hardcoatings and industrial hard chrome plating.

Keywords: IBED, PVD hardcoating mechanical property comparison

Introduction

Both titanium and chromium each can combine with nitrogen to form a number of stable stoichiometric metallic nitride compounds[1,2]. All of the metallic nitride compounds have different crystal structures and exhibit slightly different mechanical properties[3], and are usable as tribological coatings for mechanical components[4]. Physical vapor deposition (PVD) processes are used to deposit these nitride compounds as coatings[5] on many tools and engineered components. The PVD process operates at temperatures in excess of 538 °C (1000 ºF), and is not universally usable for many applications because of the possibility of thermal distortion of dimensions and bulk properties. These nitride coatings can also be deposited by the ion beam enhanced deposition (IBED) process, and since IBED operates at temperatures below 93 °C (200 ºF) a wider variety of materials and components can be coated. However, before the IBED process can be considered for use as an alternative to the PVD process, the metallurgical and mechanical properties of the IBED-deposited nitrides must be measured and analyzed. To this end, IBED process deposition parameters were developed and used to deposit titanium nitride coatings with a TiN stoichiometry and chromium nitride coatings with a Cr_2N stoichiometry, on test coupons for a detailed analysis of their metallurgical compositions and mechanical properties.

Metallurgical Composition of IBED Coatings

The metallurgical compositions of IBED TiN and Cr_2N coatings were measured and confirmed by Rutherford Backscattering Analysis (RBS), and the uniformity of composition and physical morphology were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS).

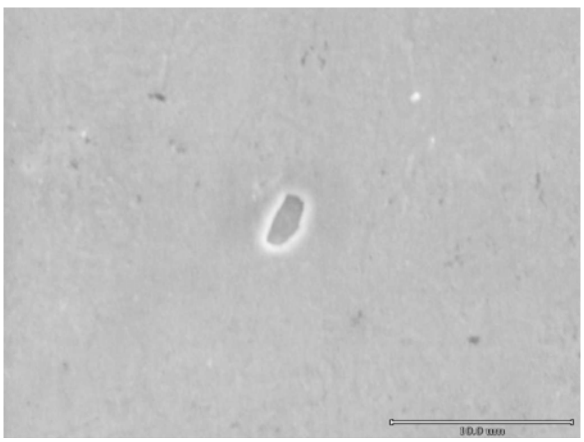
Rutherford Backscattering Analysis

Rutherford Backscattering Analysis (RBS) is a nuclear analysis technique that is used to measure the absolute stoichiometric composition of materials[6]. Thin films of the materials to be analyzed are deposited on carbon substrates and bombarded with energetic (2 Mev) alpha particles ($_2He^4$ nuclei). The bombarding alpha particles undergo elastic scattering events with the nuclei in the material to be analyzed and the energy distribution of the backscattered alpha particles is measured at a fixed angle. The backscattered alpha energy distribution can be analyzed and provides an absolute measurement of the stoichiometric composition of the material.

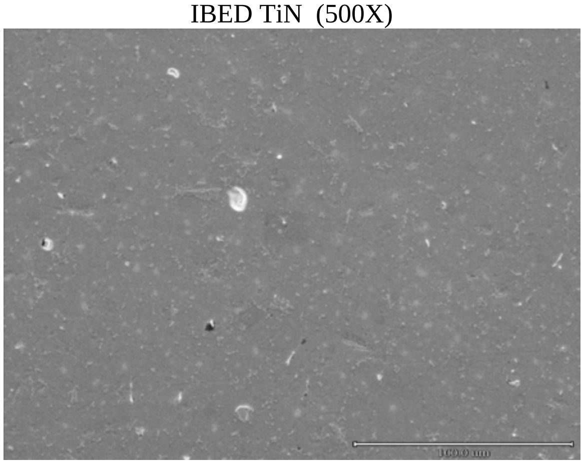
Thin films of TiN and Cr_2N were deposited on carbon sample substrates and submitted to the Ion Beam Analysis Laboratory at Case Western Reserve University[7] for RBS analysis using a National Electrostatics Corporation[8] "Pelletron." The compositions of both films (see Table 1) confirmed the 1:1 stoichiometry for the IBED-deposited titanium nitride (TiN) and the 2:1 stoichiometry for the IBED-deposited chromium nitride (Cr_2N) coatings. The stoichiometric composition of the PVD-deposited coatings were not measured but were reported to be TiN and CrN by the coating vendor (Balzers, Inc.).

Composition and Physical Morphology

IBED and PVD titanium nitride and chromium nitride coatings were deposited on the surfaces of hardened, polished (0.025 μmeter Ra or 1 μinch AA) high speed steel samples to a thickness of between 4 and 5 microns. The coatings were imaged with a CAMSCAN scanning electron microscope (SEM) in the secondary electron mode[9]. Image magnification used was 500X and 2,500X. Since the original surfaces of the samples were highly polished the morphology of the coating surface seen at these magnifications will be determined by the structure of the coating itself. The SEM images of the IBED and PVD deposited titanium nitride coatings are seen in Figs. 1 and 2.



IBED TiN (500X)

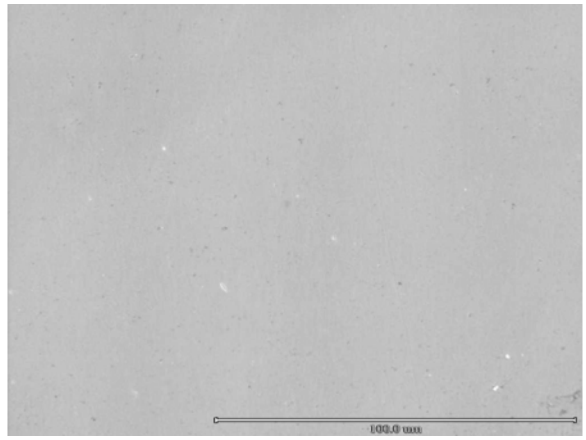


PVD TiN (500X)

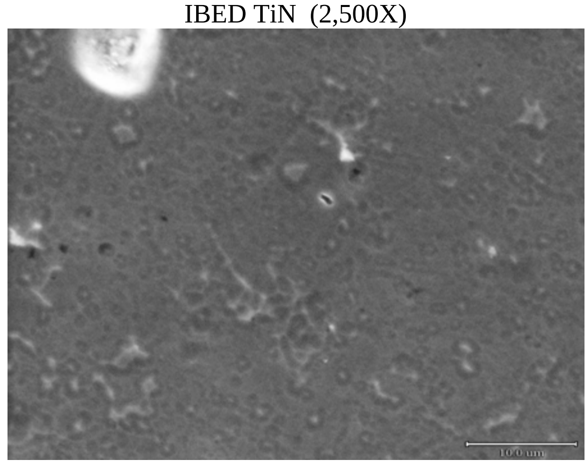
Figure 1: Surface morphology IBED and PVD deposited TiN coatings (SEM, 500X).

Table 1 IBED Coating Stoichiometry as Determined By RBS

Coating	% Composition			Ratio
Cr_2N	Cr	N	O	Cr/N
	64	34	2	1.88
TiN	Ti	N	O	Ti/N
	51	49	0	1.04



IBED TiN (2,500X)



PVD TiN (2,500X)

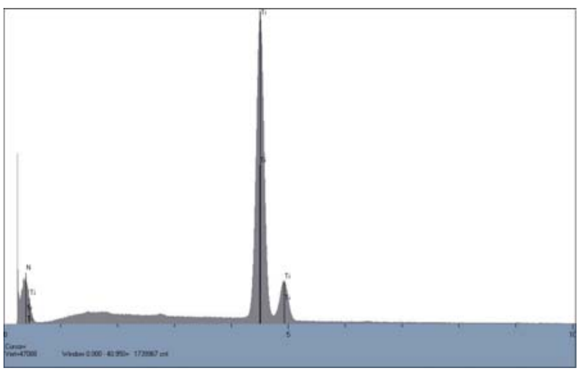
Figure 2: Surface morphology IBED and PVD deposited TiN Coatings (SEM, 2,500X).

At 500X magnification an area approximately 200 microns X 250 microns (0.2 mm X 0.25 mm) is imaged and the general smoothness and uniformity of the coatings can be compared. At 2,500X magnification an area approximately 40 microns X 50 microns (0.04 mm X 0.05 mm) is imaged and the fine-structure present in the coatings at the sub-micron level can be resolved.

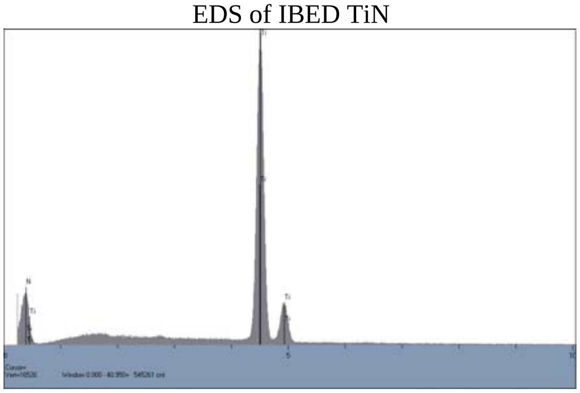
In Fig. 1 (500X magnification), the IBED TiN appears much smoother and uniform than the PVD TiN coating. Pits in the original surfaces of both samples show as small zones with bright margins. Energy dispersive spectroscopy (EDS) of the pits in both coatings showed no iron (Fe) signals from the underlying substrate indicating good coverage of the pit in both cases.

In Fig. 2 (2,500 magnification), the IBED TiN coating still appears significantly smoother and more uniform than the PVD TiN coating. There is no texture at all seen at the sub-micron level in the IBED TiN coating indicating that the coating is close to amorphous with no large crystal grains. The PVD TiN coating shows ordered structure over 5 –10 micron distances indicating the presence of crystalline grains.

The EDS spectra of the IBED and PVD TiN coatings are seen is Figure 3. Both spectra showed the presence of titanium and nitrogen with no peaks for other contaminating elements with atomic numbers greater than 6 (Carbon). Both the IBED and PVD TiN coatings are identical in compositional purity however the exact chemical composition (bonding) and stoichiometry of the two coatings cannot be correlated with the EDS measurements.



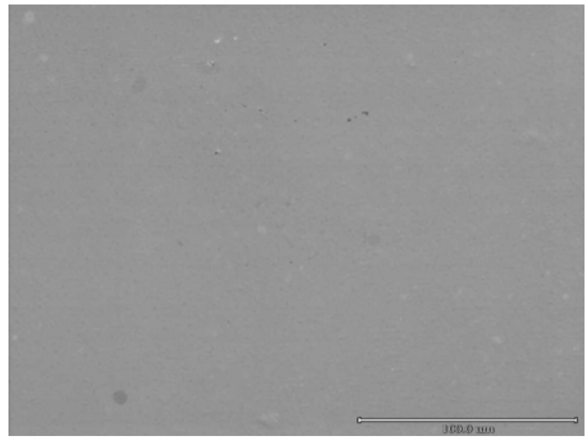
EDS of IBED TiN



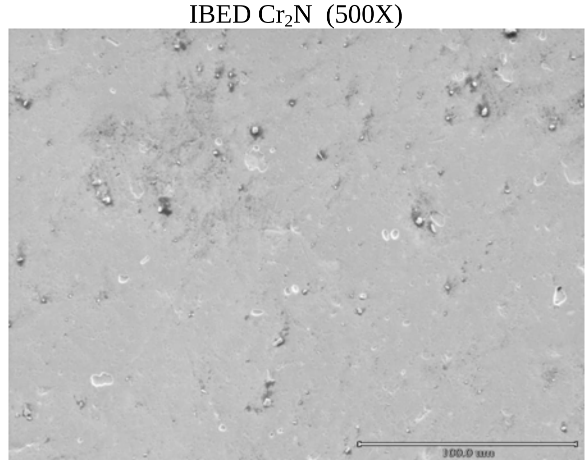
EDS of PVD TiN

Figure 3: EDS of IBED and PVD TiN coating (15 keV).

The SEM images of the IBED and PVD deposited chromium nitride coatings are seen in Figs. 4 and 5. In Fig. 4 (500X magnification), the IBED Cr_2N appears significantly smoother and more uniform than the PVD chromium nitride coating. The PVD coating shows a relatively high density of small micron-sized nodules appearing in the surface as well as small pits in the coating. The nodules appear as small diameter bright zones surrounded by a darker ring. These nodules are likely due to particulate contamination present in the PVD processing chamber during coating. A possible source is flakes of coating coming off the walls of the PVD coating chamber. The pits in the coating appear as small areas surrounded by a bright margin. These pits are most likely due to pits in the surface of the substrate that are deeper than the thickness of the coating at that site.



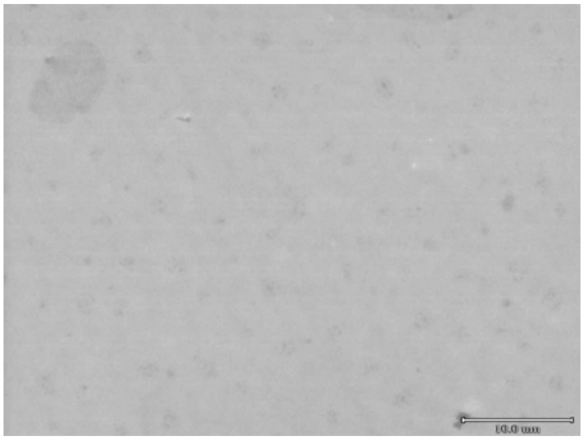
IBED Cr_2N (500X)



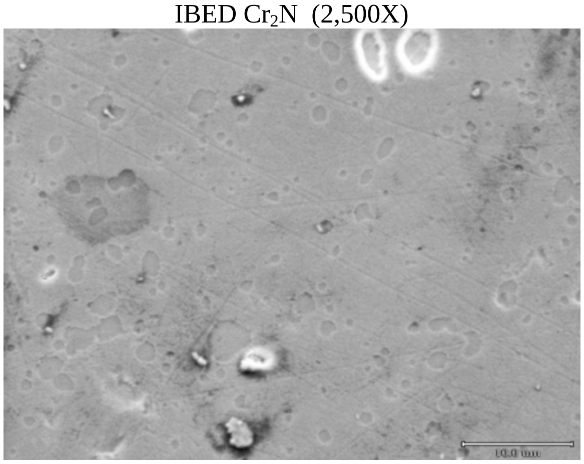
PVD CrN (500X)

Figure 4: Surface morphology IBED and PVD deposited chromium nitride coatings (SEM, 500X).

In Fig. 5 (2,500 magnification), the IBED Cr_2N coating still appears significantly smoother and more uniform than the PVD chromium nitride coating. There are no nodules or other structures in the IBED coating. Five or six small diameter and one large 3 micron diameter nodule are seen on the surface of the PVD coating. An EDS spectra was taken of the large diameter nodule and it showed the presence of chromium and nitrogen, confirming that the surface nodules are caused by flakes of coating material coming off the PVD chamber and falling on the surface being coated during the coating run. The PVD coating also shows an orange-peel appearance due to localized areas where the coating seems not to grow as rapidly as surrounding areas. This leaves shallow craters in the surface.



IBED Cr_2N (2,500X)

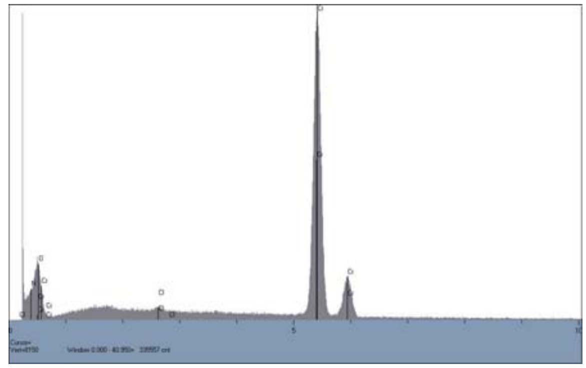


PVD CrN (2,500X)

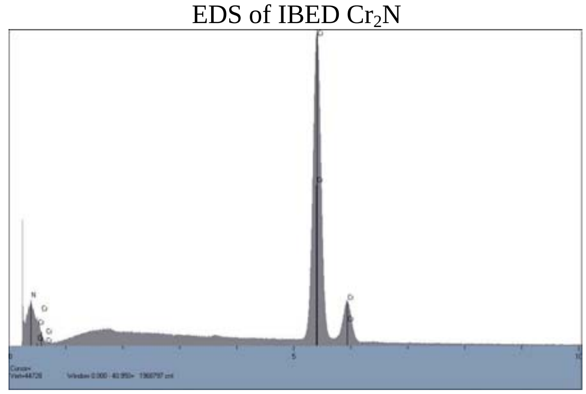
Figure 5: Surface morphology IBED and PVD deposited chromium nitride coatings (SEM, 2,500X).

The EDS spectra of the IBED and PVD chromium nitride coatings are seen in Fig. 6. Both spectra showed the presence of chromium and nitrogen with no peaks for other contaminating elements with atomic numbers greater than 6 (Carbon). Both the IBED and PVD chromium nitride coatings are identical in compositional purity however the exact chemical composition (bonding) and stoichiometry of the two coatings cannot be correlated with the EDS measurements.

The mechanical properties of the IBED and PVD nitride hardcoatings, as well as industrial hard chrome, are next measured using a series of standard tests, and comparisons made.



EDS of IBED Cr_2N



EDS of PVD CrN

Figure 6: EDS of IBED and PVD Chromium Nitride Coatings (15 keV).

Comparison of Mechanical Properties

The mechanical properties of IBED deposited TiN and Cr_2N coatings were measured using a series of standard procedures and compared to the properties of these nitride coatings deposited by PVD and also electroplated industrial hard chrome. All of the coatings were deposited on metallurgically equivalent substrate coupons in order to eliminate the effects of substrate properties such as composition, hardness, and surface finish. All coupons were round, 2.54 cm (1 inch) diameter, 4.8 mm (3/16 inch) thick; cut from hardened high speed steel (M Series) bar stock. The Rockwell "C" scale hardness (R_C) of the test coupons ranged from 62 to 64. The top surface of each coupon was lapped to a highly polished finish of 0.025 µmeter Ra (1 µinch AA).

All coatings were deposited with approximately the same thickness, 4 microns. The coating thicknesses were confirmed by Ball/Crater[10] measurements done by Teer Coatings, LTD[11] and are listed in Table 2.

Table 2 Ball/Crater Thickness Measurement

Coating	Coupon (R_C)	Thick (μ) (Ball/Crater)
IBED TiN	64	4.5
PVD TiN	62	3.8
IBED Cr_2N	65	4.1
PVD CrN	65	5.2
Hard Cr	64	3.3

The mechanical tests performed included: ASTM C33-79 (adhesion), VDI-3198 (adhesion/durability), Scratch Test (scratch adhesion), Vickers Hardness, and Taber Abraser (abrasive wear).

ASTM C633-79 (adhesion)

A preliminary investigation of coating adhesion was done by tensile testing, even though the adhesion was expected to exceed the limits of a tensile test. The tensile testing was done according to ASTM[12] standard C633-79 using an adhesive (FM-1000) with a published tensile strength of 12,436 PSI. Testing of the various coated samples was done by Protech Laboratories[13]. Each of the IBED, PVD, and hard chrome coatings were deposited on four test coupons. All coatings deposited by all processes showed equivalent performance. None of the coatings delaminated from the coupon surface. The tensile pull failure occurred in the FM-1000 adhesive in every case. Table 3 lists the average tensile measurements at failure for each of the coatings deposited by each of the processes in units of pounds per square inch. Adhesion of all of the coatings to the test coupon surfaces was at least as good as the tensile limit of the adhesive. And since the test coupon surfaces were highly polished, the coating adhesion measured is due solely to chemical adhesion as opposed to mechanical interlocking of the coating with the coupon surface.

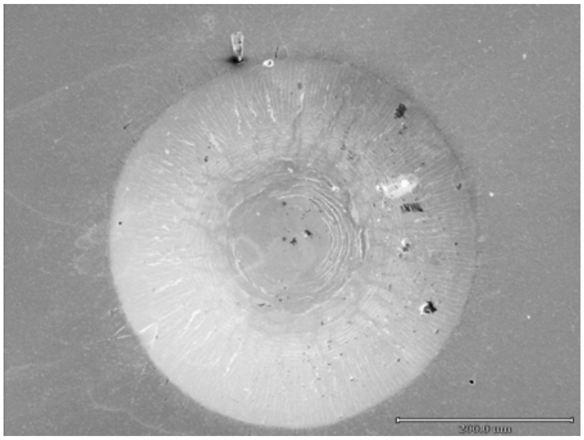
Table 3 ASTM C633-79 Adhesion Test Results

Coating	Process	Failure	PSI
CrN	PVD	Adhesive	12,450
Cr_2N	IBED	Adhesive	12,896
TiN	PVD	Adhesive	12,126
TiN	IBED	Adhesive	12,440
Hard Cr	Plating	Adhesive	12,293

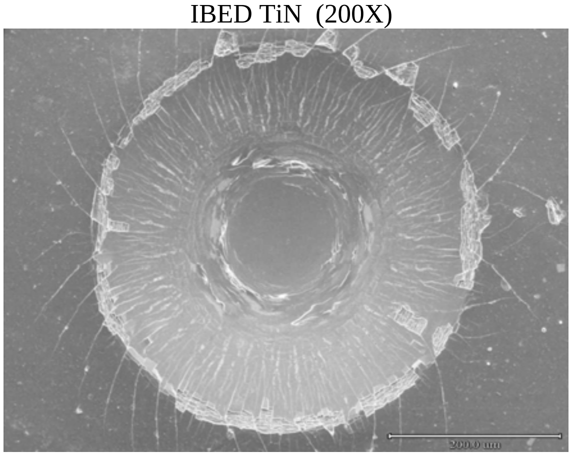
Since the adhesion of all coatings tested exceeded the limits of the C633-79 tensile adhesion test, additional more strenuous tests were employed.

VDI-3198 (adhesion/durability)

The VDI Guideline 3198 procedure was developed as an easy-to-apply, more strenuous test to measure the adhesion of hardcoatings deposited on hardened metal substrate materials[14]. It is based on the use of a Rockwell "C" scale indent, and yields a visual measurement of hardcoating adhesion and durability. Hardcoatings are deposited on a polished, hardened steel coupon (R_C >60) to a thickness of between 1 and 3 microns. A standard Rockwell diamond indenter is used to indent the surface for a "C" scale measurement (150 Kg). The indented area is examined at a magnification of 100X and the cracking pattern is observed. Hardcoatings with good cohesion show little or no fracture lines extending radially from the center of the indent outward towards and beyond the perimeter of the circular indent. Also, no cracked islands appear in the indent crater or along the crater perimeter. Hardcoatings with good adhesion show no delamination of the coating either in the crater or adjacent to the coating perimeter. The VDI-3198 test results are seen in Figs. 7 and 8.

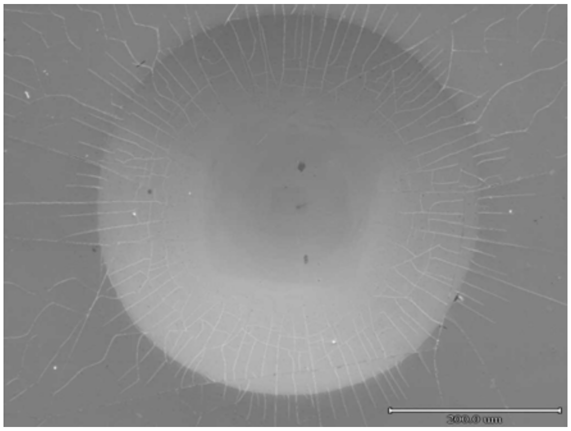


IBED TiN (200X)

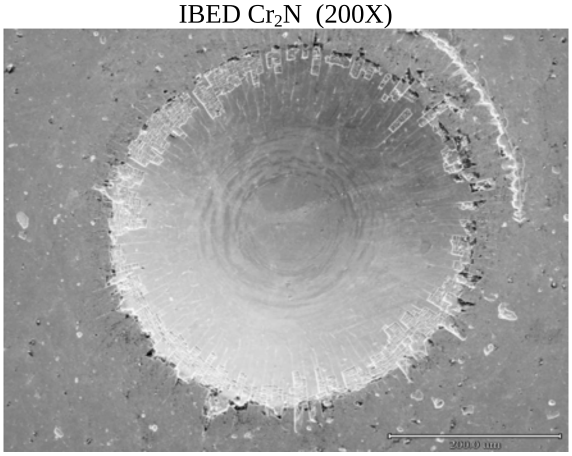


PVD TiN (200X)

Figure 7: Appearance of R_C indent patterns on IBED and PVD deposited TiN coatings.



IBED Cr_2N (200X)



PVD CrN (200X)

Figure 8: Appearance of R_C indent patterns on IBED and PVD deposited chromium nitride coatings.

Both of the IBED deposited coatings showed better performance than the equivalent PVD deposited coatings. The crack pattern radiating from the indent on the IBED TiN coating was much smaller and the cracks were much shorter than those seen in the PVD TiN coating. This is an indication that the IBED-deposited TiN coating shows improved cohesion. There is significant delamination of flakes of the PVD deposited TiN and no delmaination of cracked islands of the IBED deposited coating. This is an indication that the IBED deposited TiN coating shows improved adhesion to the substrate.

The radial crack pattern in the IBED-deposited Cr_2N coating was significantly longer that the PVD-deposited chromium nitride but the PVD-deposited coating showed significantly more delamination. Thus even though the PVD-deposited coating showed better cohesion the IBED-deposited coating showed better adhesion.

Scratch Test (scratch adhesion)

Scratch testing is a recognized technique for obtaining a quantitative measurement of the adhesion of thin hardcoatings[15]. A diamond stylus is pulled across the coating surface at a fixed rate with an increasing normal load. The lateral frictional force is measured along with recording of the acoustic emission from the moving stylus. When the normal load increases to the point where the coating fractures and delaminates from the surface, there is a rapid increase in the lateral friction force and acoustic emission. At this point the coating adhesion limit is considered to have been exceeded, and the normal force applied at that point is considered to be a numerical index of coating-substrate adhesion.

IBED and PVD titanium nitride and chromium nitride, and hard chrome, coatings were deposited on polished, hardened steel coupons and submitted for scratch adhesion testing on a Teer Coatings ST3001 Scratch and Wear Tester[16]. The lateral force measurements at failure for all five coatings are listed in Table 4. The IBED and PVD TiN coatings and the hard chrome all failed at an equivalent normal force and therefore are considered to exhibit equal levels of surface adhesion. The normal force at failure measured for the IBED Cr_2N coatings was 23 N (5.2 pounds) lower than that measured for the PVD–deposited CrN coating, indicating poorer adhesion.

Table 4 Scratch Adhesion Test Results

Coating	Coupon (R_C)	Normal Force at Failure (N)
IBED TiN	64	118
PVD TiN	62	120
IBED Cr_2N	65	62
PVD CrN	65	85
Hard Cr	64	120

Vickers Hardness (hardness)

The hardness of the coatings was measured on the Vickers scale at an indent force range of 0.4 – 50 mN on a Teer Coatings ST3001 Scratch and Wear Tester[16]. The hardness measurements for all of the coatings are listed in Table 5.

Table 5 Vickers Hardness Measurements

Coating	HV (kg/mm^2)
IBED TiN	3,842
PVD TiN	3,079
IBED Cr_2N	1,885
PVD CrN	5,038
Hard Cr	1,164

Taber Abraser (abrasive wear)

The abrasive wear performance of metallic and refractory nitride hardcoatings can be tested using a Taber Abraser[17]. Performed according to a standard procedure, SAE/AMS-2438A (SAE International[18]), coatings are deposited on 9.5 cm (3.75 inch) diameter disks that are run against resilient rollers impregnated with 50-micron diameter alpha-phase aluminum oxide grits. The coated disks are weighed, run for a fixed number of cycles, and then re-weighed. The thickness of coating material worn away can then be calculated. Since standard test parameters are used (grit sizes, wheel RPM, and surface loading), the wear rates obtained are directly comparable as measures of abrasive wear resistance.

All coatings were deposited on hardened (R_C 64-66) high speed steel disks, 9.5 cm (3.75 inch) diameter and 1.3 mm (0.05 inch) thick. Both front and back faces of the disks were lapped to a highly polished finish of 0.025 μmeter Ra (1 μinch AA). All coatings were deposited with thicknesses in the range of 3.8 to 5.2 microns (see Table 2).

The abrasive wear rates are listed in Table 6 for TiN deposited by PVD and TiN deposited by IBED were exactly the same, 0.02 microns per 10,000 cycles. The abrasive wear rate for CrN deposited by PVD was 0.03 microns per 10,000 cycles and the wear rate for Cr_2N deposited by IBED was 0.12 microns per 10,000 cycles. The abrasive wear rate for hard chrome was 0.4 microns per 10,000 cycles. The wear rates for all of the nitride hardcoatings were lower than the wear rate measured for hard chrome.

Table 6 Taber Abraser Wear Test Results

Coating	# of Cycles	Thickness Worn (microns)
IBED TiN	10,000	0.02
PVD TiN	10,000	0.02
IBED Cr_2N	10,000	0.12
PVD CrN	10,000	0.03
Hard Cr	10,000	0.40

Summary and Conclusions

The variety of quantitative and qualitative tests showed that the IBED TiN hardcoatings performed at a level equivalent to or better than the PVD TiN hardcoatings. Qualitative testing showed IBED Cr_2N demonstrated better adhesion than PVD CrN coatings, but all the quantitative tests showed the opposite. Both IBED Cr_2N and PVD CrN performed better than industrial hard chrome in all cases.

SEM studies of the surface morphology of the IBED and PVD coatings showed significant differences. All coatings deposited by IBED were significantly smoother than the same coatings deposited by PVD. The PVD coatings showed a high density of cratered areas probably caused by slight differences in coating growth rate on areas of the substrate with different grain orientation. This crater effect was not observed with the IBED coatings. The IBED coatings also showed no voids or pinholes in the surface that were seen often in the PVD coatings.

The qualitative VDI-3198 test, which stresses the coating beyond the yield point, showed the most graphic differences between the PVD and IBED coatings. For both titanium and chromium nitride, the cohesion and adhesion of the coatings deposited by IBED were superior to that seen with the coatings deposited by PVD.

The scratch adhesion test showed that the IBED and PVD TiN coatings were equivalent, 118 N and 120 N respectively at failure. The hard chrome scratch adhesion was equivalent to both the IBED and PVD TiN, also failing at 120 N. The scratch adhesion test of the IBED and PVD chromium nitride coatings showed that the PVD CrN coating adhesion exceeded the IBED Cr_2N coating adhesion (85 and 62 respectively at failure).

The Vickers hardness measurement showed that the IBED TiN was harder than the PVD TiN (3,842 and 3,079 respectively). The Vickers hardness of the PVD CrN was significantly harder than the IBED Cr_2N (5,038 and 1,885 respectively). The hard chrome was the softest of all of the coatings with a Vickers hardness of 1,164.

The Taber abrasive wear rate results for the IBED- and PVD-deposited TiN coatings did correlate with the Vickers hardness measurements. Harder coatings are expected to show lower wear rates. The IBED and PVD TiN were close in hardness and exhibited almost equivalent wear rates. The IBED Cr_2N was significantly softer than the PVD CrN and did exhibit a higher wear rate. However the PVD CrN was significantly harder than both the PVD and IBED TiN but did not show a significantly lower wear rate. The adhesion of the PVD CrN coating, which was not as good as either PVD or IBED TiN, could be a reason the wear rate for PVD CrN was not that much better than either of the TiN coatings. The hard chrome was the softest of all of the coatings and exhibited the highest wear rate, significantly greater than both the PVD and IBED chromium nitrides.

Both qualitative and quantitative performance test results show TiN hardcoatings as deposited by the low temperature IBED process are viable alternatives to TiN hardcoatings deposited by the high temperature PVD process. The quantitative performance test results do not confirm the same for PVD- and IBED-deposited chromium nitride coatings. Discrepancies in the scratch adhesion, Vickers hardness, and wear resistance of the chromium nitride coatings can be attributed to differences in the chemical bonding and stoichiometry of the coatings. The properties of CrN and Cr_2N are different and could lead to differences in mechanical behavior. The hardness and wear-resistant performance of both PVD- and IBED-deposited chromium nitrides did however exceed the performance of hard chrome.

The results of the experiments completed indicate that the low temperature IBED process enables the use of nitride hardcoatings as alternatives to high temperature PVD-deposited hardcoatings and industrial hard chrome plating.

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The industrial hard chrome plating services were provided by Teikuro, Inc., 4500 Gateway Blvd., Springfield, OH 45502.

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