Armorlube LLC

Plasma Nitriding of Steel alloys

Abstract

This application notes reports the latest developments of ARMORLUBE LLC in the field of plasma process nitriding of steel substrates.

The document will highlight how the proprietary Hollow Cathode technology is able to perform nitriding processes at a much-reduced time compared to conventional nitriding processes, including plasma nitriding.

The Armorlube HC nitriding processes are tunable to provide the desired case thickness and hardness, and can result in nitriding with no formation of white layers.

Interestingly, the Armorlube HC nitriding process was able to comply with specific requests from customers to supply a single process able to nitride the material surface while hardening the core at the same time, thus resulting in making unnecessary any hardening thermal pre-treatment.

The second section of the paper will present ARMORLUBE LLC Duplex Coating.

Our production platforms are, in fact, capable of running both nitriding processes and DLC deposition steps within the same process, saving all the time related to a multiple stage production process.

The benefit of the duplex coating will become evident when submitting the coated parts to specific tests, (such as VDI 3198), required for coating approval under high load / harsh environment applications.

A production example, with real customer part, will be also presented.

Plasma nitriding process

Steel is the main material utilized in industry for several applications from building construction to armaments. Its nature is defined by its composition that, being mainly dominated by iron, is modulated by alloy elements which provide specific characteristics to the material. High alloy steels, especially when at high concentration of chromium, are usually utilized for their anticorrosion properties (stainless steel). According to composition, production and heat treatments, steels have different values of hardness. However, their hardness is not such as to protect them from premature wear issues in tribological applications.

To improve the tribological and corrosive properties of steel components a case hardening process is needed. A useful and common process is nitriding of the surface which is reported to increase also the anticorrosion properties of non-stainless steel [1].

Nitriding is typically achieved by high temperature long duration processes. Gas nitriding uses large high temperature furnaces with run which can last from 10 hours to 5 days typically with temperature around 510°C. Salt bath nitriding has a few different types, but all are submersion processes in molten salt baths with temperatures around 570°C for about 12 hours. Plasma nitriding is a vacuum based process which utilizes a high energy mixture of ions, radicals, neutrals to create the free nitrogen needed to diffuse into the steel. Plasma nitriding can also take advantage of bias voltage to assist driving positive nitrogen atoms into the surface by accelerating the positive ions across a sheath toward a negatively biased component. As such plasma nitriding runs can have shorter durations and lower operating temperatures [1]. Published data from Li et al. [2], for instance, report nitriding processes on 17-4 stainless steel producing nitride layers thickness in the range of 5 to 12 um nitriding, with process duration of 4 hours at temperatures in the range 350-480 °C. Specifically, plasma nitriding is of rather large interest for treating stainless steels as it can be performed to not exceed the precipitation temperature for nitride alloy elements (typically reported to occur at 400 °C). Above that temperature, the process induces segregation of the alloying elements of the stainless steel reducing the anticorrosion properties of the treated substrate. [3, 4]

Plasma nitriding has been reported by several authors to increase the surface hardness of steel by various extents, depending upon the nitriding conditions and substrate starting materials. A short and non-exhaustive overview of some literature data reports hardness data in the range 1160 to 1900 HV [5,6,7,8], although the general consensus for nitride steel hardness is in the range of 1000-1200 HV for Stainless Steel and somewhat below for carbon steel, due to the absence of alloying elements [9].

ARMORLUBE LLC is a solution provider in the surface modification industry tackling customers hardest applications. ARMORLUBE LLC designs and manufactures high tech automated vacuum equipment and processes based on the company's patented hollow cathode (HC) technology. This proprietary method generates plasma densities orders of magnitude higher than traditional plasma processing and enables conformal plasmas inside and outside of components generating simultaneous surface modification of both interior and exterior surfaces. Armorlube's processes can be used for both plasma nitriding and hard coating deposition with uniform properties on complex 3D geometries.

By making use of the HC technology, it is possible to ignite N2-rich plasma with the intent of plasma nitriding similarly complicated structures, with the added advantage of increasing nitrogen diffusion rate of several times compared to conventional nitriding [10].

Armorlube's Emperion platform requires no external heaters as the chamber and parts work together to generate the dense nitrogen rich plasma. The parts and internal chamber wall are heated through ion bombardment which serves the dual purpose of cleaning and activating the surface while removing unwanted oxides dependent upon the programmed recipe. By controlling the power input and other process parameters, it is possible to target specific treatment temperatures. For testing we proceeded with several steel typologies. Test coupons 20x50x4mm, the material surfaces were ground and polished to a mirror finish with 1200 grit paper. The thickness of the nitrided steel samples were characterized using optical microscopy and nital etch to visualize nitride depth, micro-indentation to measure hardness and calculated modulus, and a Mercedes Indenter (VDI-3198) to measure Rockwell Hardness (HRC) and characterize the indents. Formed nitride phases were investigated using X-ray diffraction (XRD) with Bragg-Brentano configuration.

Figure 1 shows the effect of a generic high-power nitriding test performed on AISI 316 stainless steel coupon. The hardness profile shows the case hardening effect through the diffusion layer depth as shown in the etched cross section.

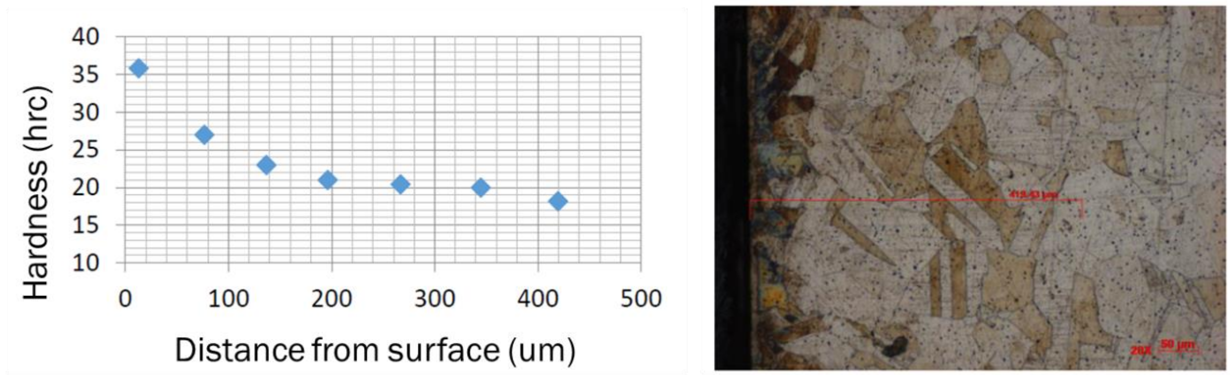

Figure 1: AISI 316L - hardness profile and sectioned sample for a HC nitriding process performed at Duralar

Figure 2 shows the influence of nitriding temperature (using power delivered as a relative metric) during the process on the material properties of the stainless steel. Figure 2a shows the influence of nitriding temperature on the corrosion properties of SS316. Figure 2b reports the XRD spectra achieved at the different nitriding temperatures.

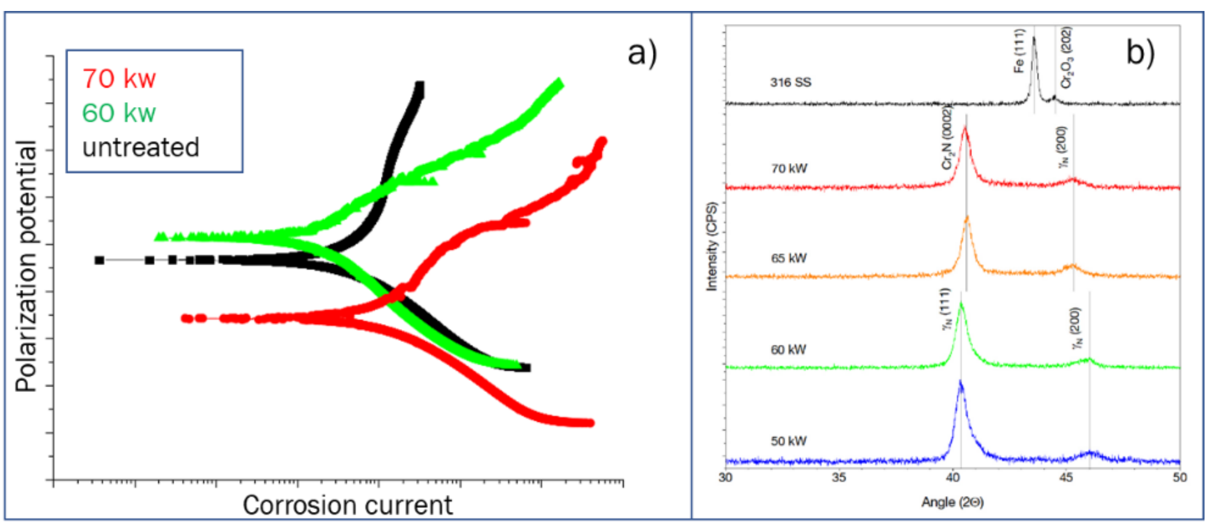

Figure 2 – panel a) Tafel plot for AISI 316 in HC plasma for 60 minutes at 60kw and 70 kw; panel b) XRD spectra of untreated and samples nitride at 50, 60, 65 and 70 kw

If the temperature is too high (70kW), the anticorrosion properties are reduced, while a lower temperature test shows improved corrosion performance. This corresponds to the XRD spectra for the 70kW sample where a phase shift is observed showing the formation of Cr2N indicating that some protective chromium oxide has been converted. The process performed at 60 kw instead, shows an improvement of the anticorrosion properties with respect to the bare substrate. This is related to nitrogen stabilizing the chromium oxide layer and to the formation of an expanded austenite structure restricting the diffusion of corrosive species through the iron matrix of the substrate material [11, 12]. The hardness measured for the 60kW process was 12.1 GPa with a nitride thickness of about 10 μm

The thickness of the nitride layer can be tailored tuning the process in terms of power and time, as the two parameters drive the temperature of the process, the availability of the nitrogen ionic and atomic species diffuse into the substrate, and the diffusion time.

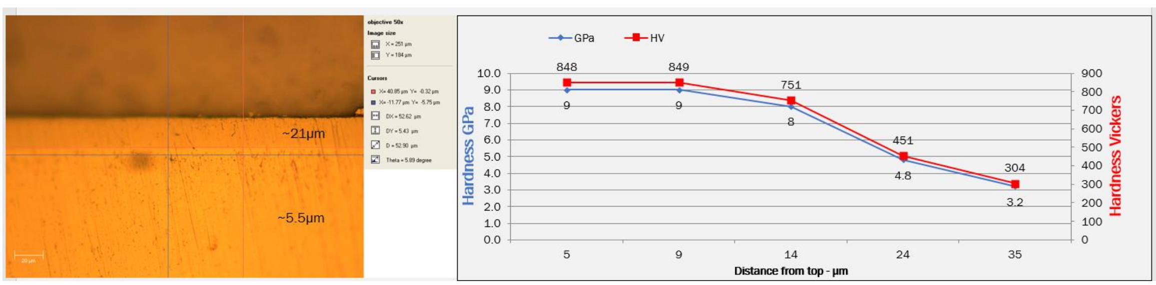

Figure 3 – metallographic section and hardness profile for a 20um nitride layer

Figure 3 shows the metallographic section of a process targeting 20 μm nitride thickness. A nitride layer about 21 μm thick followed by a 5.5 μm modified layer is visible. The surface hardness is >9 GPa and retains its value until a distance of 9 μm from the surface.

A similar case hardening was observed on A2 tool steel (disks 25mm diameter 4mm thick).

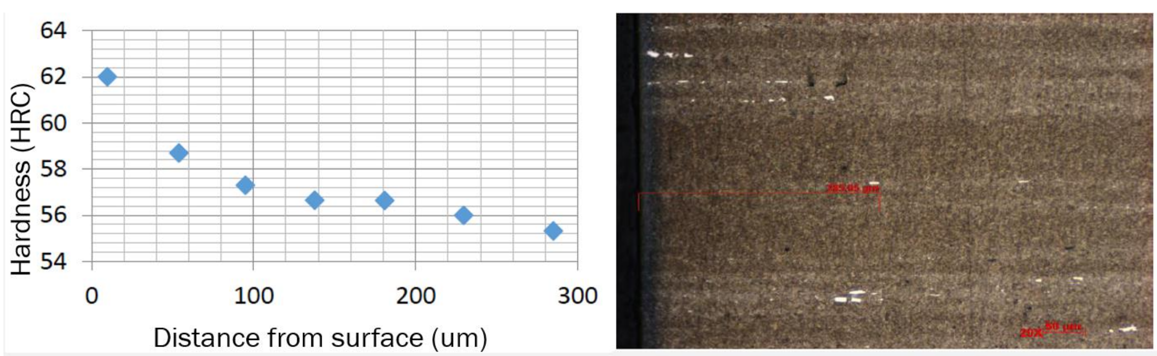

Figure 4 : D2 Tool steel- hardness profile and sectioned sample for a HC nitriding process performed at Duralar

And on 4140 steel (disks 25mm diameter 3mm thick).

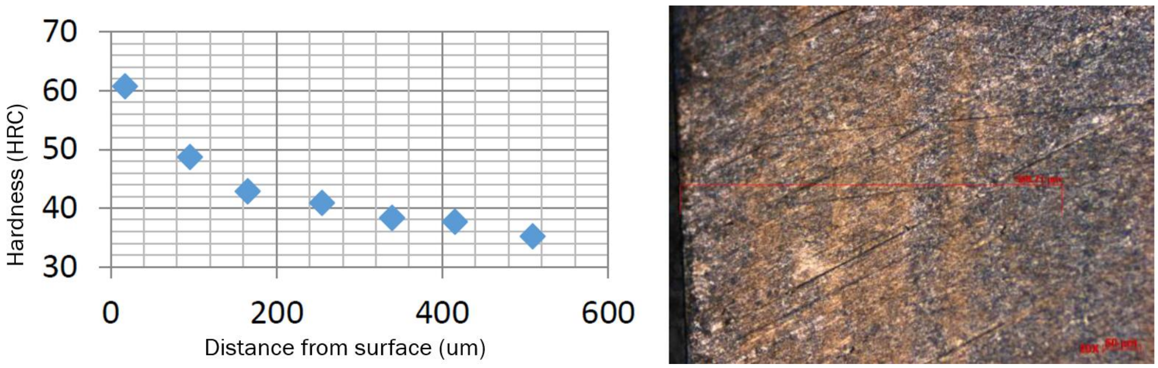

Figure 5 4140 steel - hardness profile and sectioned sample for a HC nitriding process performed at Duralar

A 1h 500 °C process, induced on a 1215 steel the formation of a white layer about 5 µm thick with a superficial hardness higher than 6 GPa

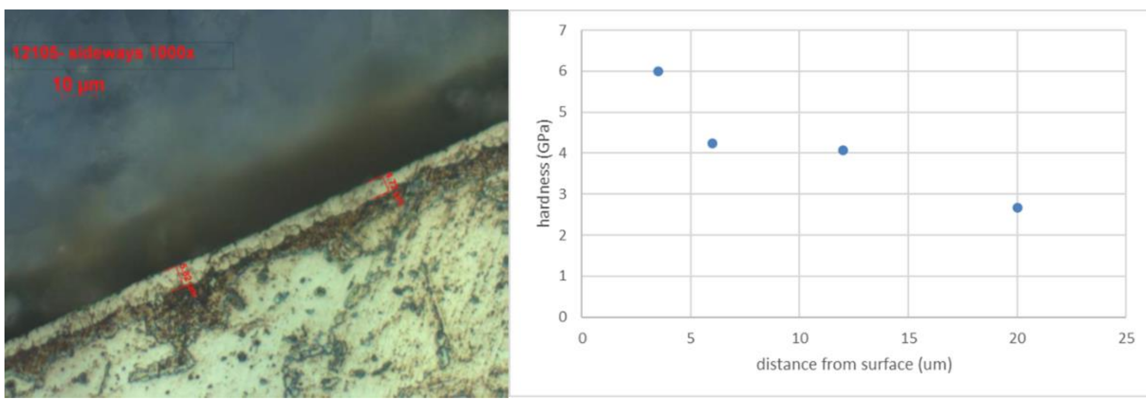

Figure 6 metallographic section and hardness profile for steel 1215 grade nitride at Duralar with a 1h process at 500 °C

By varying nitriding conditions, it was possible to range the thickness of the nitride layer up to 15 µm within one hour process.

As the comparison between 316L and carbon steel (A2 and 4140) suggests, nitriding case hardness and thickness strongly depend upon the steel chemical composition. It is expectable to have similar differences when comparing nitriding effects on stainless steels with different composition. Figure 7 depicts the nitriding outcomes as a function of the nitriding temperature for 1 hour process performed on 17-4 and 316L stainless. 17-4 stainless steel has a higher nitriding rate compared to 316L. This might suggest a lower content of alloying elements, allowing for a faster thermal diffusion of nitrogen into the substrate. This conclusion seems to be corroborated by the hardness trend, with nitride on 316L being harder than in 17-4. Moreover, by comparison with the previously mentioned published data [2], Armorlube LLC nitriding shows a 4 times higher nitriding rate compared to conventional plasma nitriding processes.

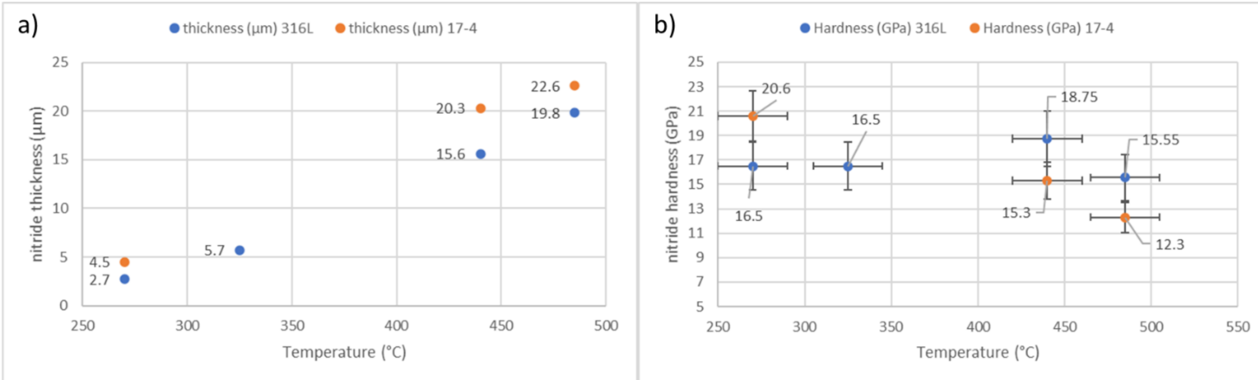

Figure 7: nitriding effects on 17-4 and 316L. 1hour process at different temperatures. Panel a) case thickness; Panel b) case hardness.

Interestingly, the nitriding process on 17-4 stainless steel resulted in the production of nitride layers without the formation of white layers. This would allow, for specific applications, to skip the time-consuming procedures related to the white layer removal. Figure 8 shows the metallographic section of 316L and 17-4 samples upon same nitriding treatment (1h at 440 °C).

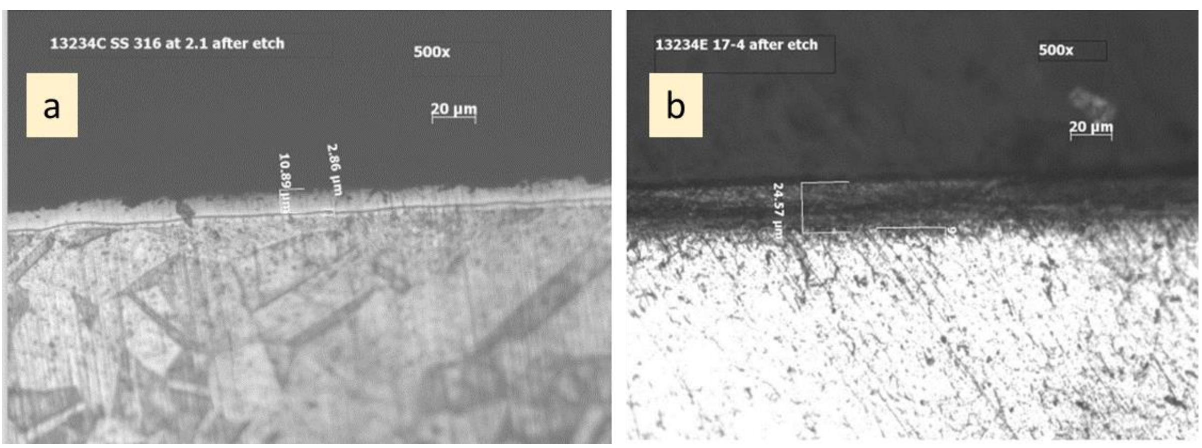

Figure 8 1h nitride process at 440 °C on 316L (panel a) and 17-4 (panel b)

316L shows a distinct white layer formation which is not detectable in the 17-4 sample.

Due to the peculiarity of the Armorlube LLC HC process, nitriding has been proven to be effective both the outer and inner surfaces of a cylindrical cup-shaped part with and internal diameter of approximately 15mm and a depth of 30mm.

In recent developments ARMORLUBE LLC was able to accomplish the request of a specific customer willing to replace the tempering process on its material. In this specific case 17-4 substrates were nitrided for 1 hour at a temperature in the range of 450 °C, leading to a nitride layer 22 um thick with a superficial hardness of 10 GPa. The hardness of the core of the material, measured by means of Rockwel C test, resulted to be increased from 35 to 38 hrc.

Duplex coating process

Armorlube HC patented technology has been originally developed for depositing DLC coatings. The processes performed shows good adhesion and toughness on the deposited substrate. Compared to hybrid technologies (PVD/PECVD), the full PECVD HC process, though, lacks a gripping layer having the hardness and ductility of the metal/metal carbides stacks, which are usually utilized in industry to provide an adequate support for the adhesion of the overstanding DLC in high-load friction environments. This is particularly relevant when dealing with destructive adhesion tests, such as the VDI 3198 norm used for assessing coating performances on high load applications [14].

To obviate to these limitations, in recent year interest has been placed towards the development of duplex coatings, where the DLC is deposited on the top of a pre-nitrided surface.

Dalibón et al. report the increase in scratch resistance (from 16.3 to 27N) of their DLC layers when deposited as a duplex coating on a plasma nitride austenitic stainless steel [13], and assume that to be related to reduction of the interface stresses, as well as improvement on the load bearing capacity of the film. When comparing VDI indentation marks, they still observed unacceptable failures (VDI HF 6), but with a reduced delaminated area around the indentation mark.

Likewise, Armorlube LLC has performed development work in this direction. Figure 8 depicts the typical VDI indentation mark achieved on tool steel and stainless steel samples for a 10 um thick DLC coating deposited on as-is substrates.

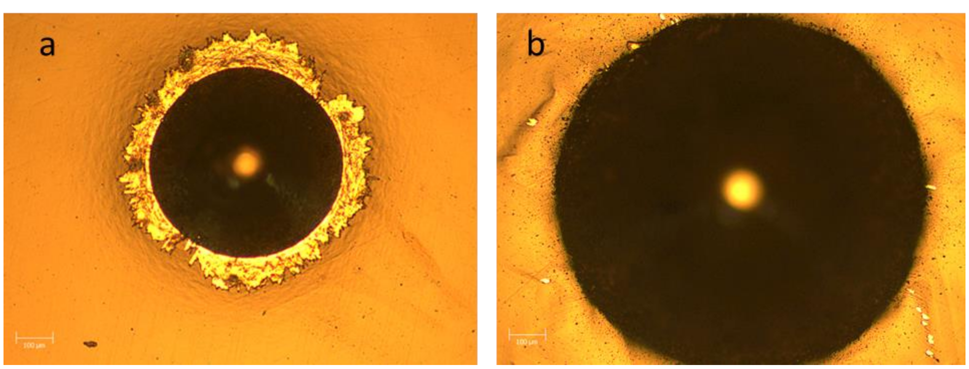

Figure 9: VDI indentation of 10 um coating deposited on A2 tool steel coupon (panel a) and 316 L stainless steel (panel b)

The image clearly shows a large level of delamination on the tool steel coupon (VDI HF6); the much softer 316, allows a much larger indentation depth, which accommodates for reduced strain conditions of the coating at the indentation edges. Nevertheless, on this substate also, spot-like delaminations are visible.

Figure 9 reports the outcome of a similar test on a duplex coating, achieved by depositing a 10 um DLC coating on a pre-nitrided substrate within the same process.

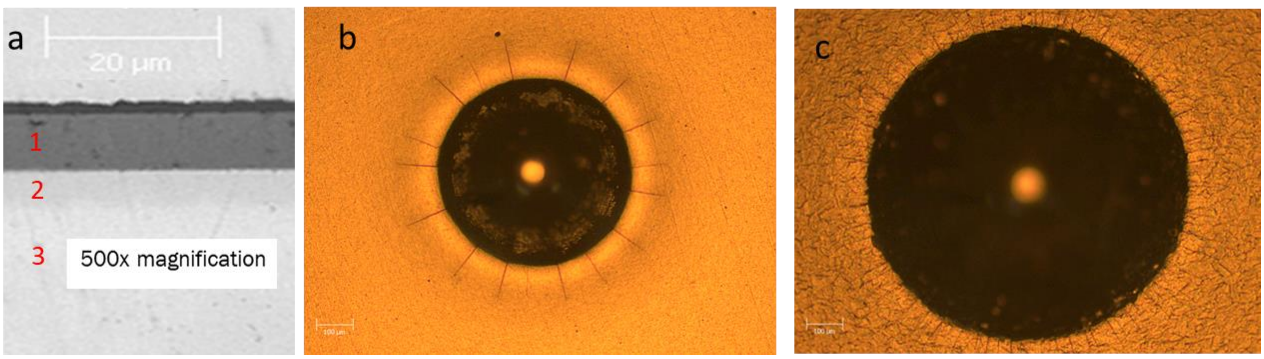

Figure 10 metallographic section and VDI indent of a duplex coating (10m DLC on the top of a 8um thick nitride layer). Panel a) metallographic section of the sample. 1 is the coating, 2 is the nitride compound layer, 3 is the diffusion area. Panel b) VDI indent on the coating on a A2 tool steel sample; panel c) VDI intend of the coating on a 316L stainless steel sample

By comparison with image 8, is immediately visible the benefit of the pre-deposition nitriding process. The A2 tool steel coupon (fig 8.b) does not show any visible delamination, and the indentation would pass the criteria of the VDI 3198 norm (HF1). The stainless-steel sample (fig 8.c) shows a reduced VDI indentation area, presumably related to a slight increased core hardness. Despite the smaller indentation radius, no visible delaminations appear, leading to an assessment of an improved adhesive behavior of the coating.

What discussed above has been already validated for production on real parts. The following figure depict the typical outcome on firearm parts (bolt carrier). The figure is organized in 4 panels. The panel “a” depicts a as-is bolt carrier and a processed with duplex process. The panel “b” shows the cross-section of the two bolt carriers. Panel “c” shows the micrograph of such a cross-section for the untreated bolt carrier. The panel “d” shows the micrograph of the cross-section of the duplex processed bolt carrier. The presence of the nitrided area is clearly detectable in the processed part.

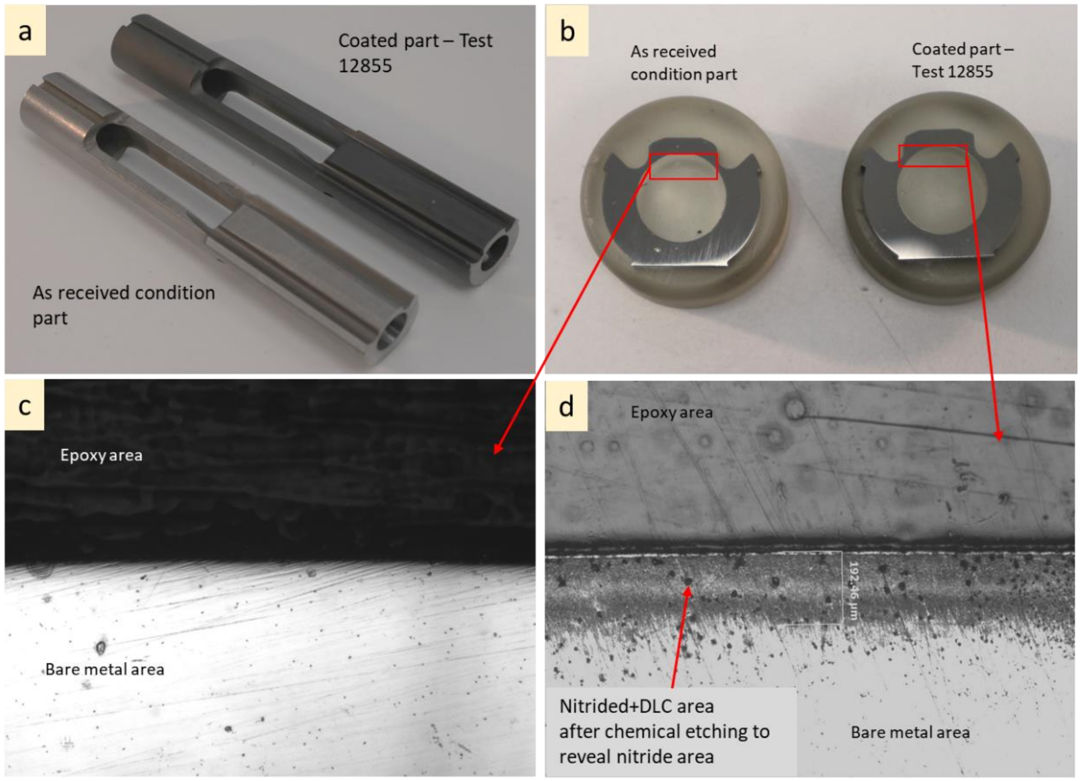

Figure 11: bolt carrier as-is and after duplex (nitriding+dlc) coating. The figure reports the status in 4 panels, depicting the bolt carriers as-is and coated (panel a), the cross section (panel b), and the micrographs (panels c and d)

Figure 12 reports the micro-hardness profile measured as a function of the depth inside the bolt carrier substrate. The comparison of the processed carrier with the untreated ones shows the superficial hardening effect induced by the nitriding process.

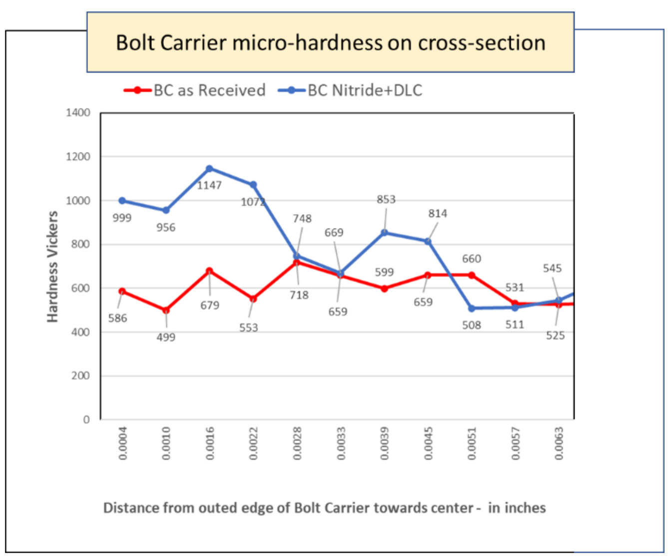

Figure 12: microhardness of the bolt carrier cross-section as a function of the distance from the substrate surface

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