XXXI International Conference on
Surface Modification Technologies (SMT31)

JULY 5-7, 2017, MONS, BELGIUM

WEAR AND ADHESION PROPERTIES OF A PVD DUPLEX COATED MEDIUM ALLOY STEEL FOR PLUNGERS IN THE OIL AND GAS INDUSTRY

Sonia P. Brühl[a,*], Eugenia L. Dalibon[a], Amado Cabo[b], Pablo Cirimello[c], Alberto Aguirre[c], Guillermo Carfi[c]

a National University of Technology (UTN), Faculty of Concepción del Uruguay, Argentina.
b IONAR S.A., San Martín – Buenos Aires, Argentina.
c YPF Tecnología S.A, Y-TEC, Berisso, Argentina.

Abstract

A duplex coating consisting in plasma nitriding of V820 steel (Boehler®) and a CrAlN coating (Balinit©, Oerlikon Balzers) was designed to enhance wear properties of hydraulic fracture pumps plungers used in the O&G Industry. On subsequent reciprocating motions, pumped slurry (containing solid particles) would eventually penetrate the interstice between the plunger´s operating surface and the seal, thus causing permanent damage.

The duplex system was analyzed comparing to a standard treatment for these pistons (thermal sprayed coating over carbon steel): optical and electronic microscope, depth hardness profiles, EDS and DRX. Two groups of coated samples were selected with different surface finishing, and the nitrided sample was used for comparison, so as the untreated steel. Scratch Test at different constant loads and Rockwell C indentation were used to test adhesion. Abrasion wear tests were carried out following ASTM G65. Finally, laboratory results were compared to field tests.

The PVD coating were 2500 HV hard, 3-4 microns thick, and the nitrided layer provided a soft hardness depth profile of about 320 microns width. The standard thermal spray coating was 800 microns thick, with an average hardness of 750 HV but with an abrupt change in hardness with the substrate. The adhesion was extremely good, critical load was 125 N. In the abrasive tests, the mass loss in the PVD coated samples was reduced 30 times respect to the standard coated samples. In the field technological test the PVD coated pistons improved the quantity of pumping cycles in almost 300%.

Keywords: abrasive wear, O&G plungers, hard coatings

1. Introduction

The production of crude oil and natural gas can be maintained on a continuous and expanding basis only if the exploration, drilling and production operations of the industry are carried forward on an uninterrupted basis. In order to drill the necessary number of new wells and maintain existing wells and equipment, the petroleum industry is highly dependent on certain essential materials, primarily, carbon and alloy steel.

In oil well hydrocarbon extraction, hydraulic fracturing, also referred to as “fracking”, is a good stimulation technique in which pressurized fracture liquid is pumped into an oil well in order to increase the extraction rate of oil and/or gas by fracturing rock formations. Since hydraulic fracturing increases reservoir pressure and permeability, it allows for the extraction of oil and gas from much deeper reservoirs than conventional extraction

---

* Corresponding author. Tel.: +54 3442 425541 ext. 130, fax: +54 3442 425541.
E-mail address: sonia@frcu.utn.edu.ar, sbruhl@gmail.com

means. Hydraulic fracturing is also used in the extraction of unconventional oil and gas reservoirs through the fracture of shale rocks.

Hydraulic fracturing uses a fracturing fluid which is typically a water-based slurry comprising a proppant and chemical additives. The proppant is a solid additive that keeps the cracks -that are formed on the rocks by hydraulic pressure- from closing. The proppant is present usually as 1% to 10% of the volume of the hydraulic fluid. Typical proppants include sand, gel, ceramics, sintered bauxite and foams.

This hydraulic fracturing fluid is pumped into the wellbore by a high-pressure reciprocating pump comprising a plunger powered by a crank mechanism. During operation, the pressure inside the pump chamber, can reach up to or over 15,000 psi, depending on the injection rates and well characteristics. The surfaces of the chamber in sliding contact with the plunger are sealed. However, considering that the fluid being pumped into the well is a high pressure slurry composed of both liquid and fluid components, and that the plunger is operating with a reciprocating motion, it is possible that a proppant particle would eventually penetrate the interstice between the plunger surface and the seal, thus causing permanent damage to the surface of said plunger on subsequent reciprocating motions. As such, solid particles lodged in the interstice of the seal are the main cause of surface damage to the plunger in hydraulic fracturing fluid pumps. Damage to the plunger is further exacerbated by localized removal of the protective surface coatings in heavily damaged areas, thereby resulting in corrosion of the substrate.

In an effort to prevent or reduce the damage caused to the surface of the plunger during operation, the same can be subjected to one or more surface protection treatments such as a protective surface coating, Robinson (2005), Civan (200).

Protective coatings are used to improve wear degradation in many metal components, Davies (2001), ASM International (1994). One of the most used are the Thermal Spray thick coatings, which cost effective and they are versatile for a large number of surfaces and materials. Usually is s soft metallic matrix with hard precipitates, and thickness can be in a range from 0.1 to 1-2 mm. They are usually wear and corrosion resistant in many environments can be applied even over soft materials, just because the coating is not very hard nor fragile. As in abrasion wear situations the relation between asperities hardness and surface hardness determines the wear rate, in continuous and severe wear processes involving hard particles as sand, these coatings can suffer degradation.

PVD coatings are produced commonly in vacuum arc plasma processes and as every ceramic coating, they are known to be very hard, depending on composition (metal carbides, borides or nitrides), even as deposited as a thin film of about2-3 micrometers. Because of its high hardness which can reach 2500 HV, deposition over plain steel is not recommended, and also a diffusion treatment like nitriding can be used a pre treatment to improve adhesion and mechanical properties of the system. This process is called duplex system, nitriding+coating, and it is well known for improving mechanical properties and adhesion of the system substrate-film. Podgornik et al. (2001), Wierzchon (2004), Azzi et al. (2010), Rousseau et al. (2015).

In this work, a new design of plungers (pistons?) fabricated with a medium alloy steel and a duplex treatment was analyzed and tested against the traditional one. V820 nitriding steel, treated by plasma nitriding, without compound layer, and then coated with a commercial film, CrAlN, Balinit® from Oerlikon was compared to other one, made of AISI 1020 low alloy steel, covered with a thermal spray film, called Colmonoy®.

2. Experimental

2.1. Samples and coatings characteristics

The base material from which the pistons were fabricated were AISI 1020 steel, 0.2% carbon steel, hardness 200 HV, in the case of the traditional pistons. The thermal spray coating was Colmonoy ®, composed by a nickel-base alloy, containing hard borides and carbides, mainly form Cr, Fe and Si. The new design involved a different steel as base material to fabricate the plungers: V820® form Buehler was chosen. It is a Cr-Ni-Al nitriding steel for components with large cross sections, with the following atomic composition, 0.34% C; 0.3 Si; 0.5 Mn; 1.70 Cr; 0.2 Mo; 1.0 Ni; 0.95 Al and Fe as balance, according to the supplier (Böhler® DIN34CRAlNi7). It was nitrided in a commercial facility, a DC plasma Reactor, in a mixed atmosphere of nitrogen 20% and hydrogen. The excess of hydrogen assures a minimum growing of a compound layer or white layer, which would affect the adhesion of the PVD film. The nitrided surface is composed of nitrogen in slid solution of a martensite matrix. The PVD film was also deposited in a commercial facility in Argentina, with Oerlikon Balzers technology. The coating is called Balinit® ALCRONA and it is basically (Cr,Al)N, a very hard, abrasion and oxidation resistant coating, designed as coating for cutting, punching and die casting tools.

Samples were cut from a non-used cylinder. This piece of material was made of V820 and had the same surface treatments of the plungers. The cylinder has the same external diameter of the plungers.

The samples destined to abrasion were parts from the cylindrical surface (4 inches in diameter), as it is shown in Figure 1. Samples for Scratch Test were cut also form the cylindrical surface but smaller, and the curvature was reduced to minimum (Fig. 1(b)).

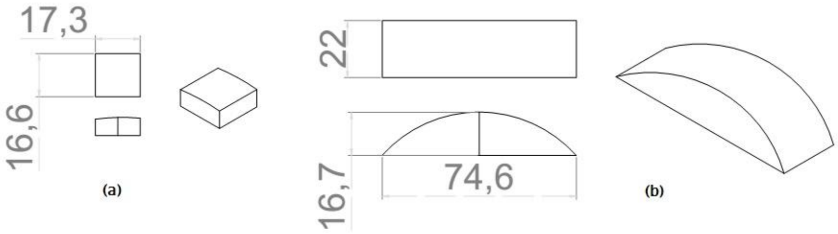

Fig. 1: Schematics of the samples size and geometry. (a) for the Scratch test, (b) for the abrasive wear tests.

2.2. Mechanical tests

Hardness depth profiles were carried out on the cross sections of the two groups of samples, and also in only nitrided samples. A Microhardness Tester (Shimadzu HV2) with a Vickers indenter with 25 g load was used.

These three groups were tested in abrasion wear tests, following ASTM G65 “Dry Sand/rubber Wheel” standard, ASTM International (1995), using AFS 35/50 sand, 130 N load and 25 minutes of test duration. Wear loss was measured by means of an analytical weighing balance with a precision of 0.1 mg. Worn surface was photographed and also was observed by SEM.

The two kinds of coatings were also tested in adhesion using a Scratch Test, with constant loads, between 20 N and 130 N, with 5 mm stroke length, and using a Rockwell C indenter, following ASTM 1624 standard, ASTM International (2010). Wear tracks were observed by optical microscope and the track profile was registered using a mechanical profilometer.

Four samples of each group were tested. Results are presented as the mean value of the individual experiments.

2.3. Field Tests

Ten plungers with duplex treatment were machined and tested in a Field Technological Test. Also plungers with traditional surface treatment were tested. Durability of the components was measured, expressed as number of fracture stages (cycles). When the plungers suffered an extended surface degradation, they had to be discarded.

Tests were carried on in Loma Campana – Neuquén in YPF oil wells. Schlumberger Company provided the fracture pumps. Plungers were tested in normal fracture operations. Maximum pressure reached was 10500 psi. Four types of sand /proppant were pumped.

3. Results and discussion

3.1. Characterization of the coatings

In the case of the traditional treatment, the thermal spray coating , the coating thickness was measured in a cross section and it resulted approximately 0,8 mm, with a noticeable interphase with the base material, with a ferrite-perlite structure, as it can be observed in Fig. 2(a). The PVD coating was also measured in the cross section and it resulted to be between 2.5 and 2.8 thick, Fig. (2b).

Both coatings were observed using optical microscope and SEM on the surface, and the PVD coating is rough and opaque, meanwhile the thermal spray Colmonoy, roughness is smaller and is bright. Using SEM and EDS, it could be proved that the Colmonoy® coating contains mainly Ni and the metal forming carbides: W, Si, Cr, Fe. On the other hand, the PVD coating EDS signals are mainly Al, Cr, Mn, Si and N.

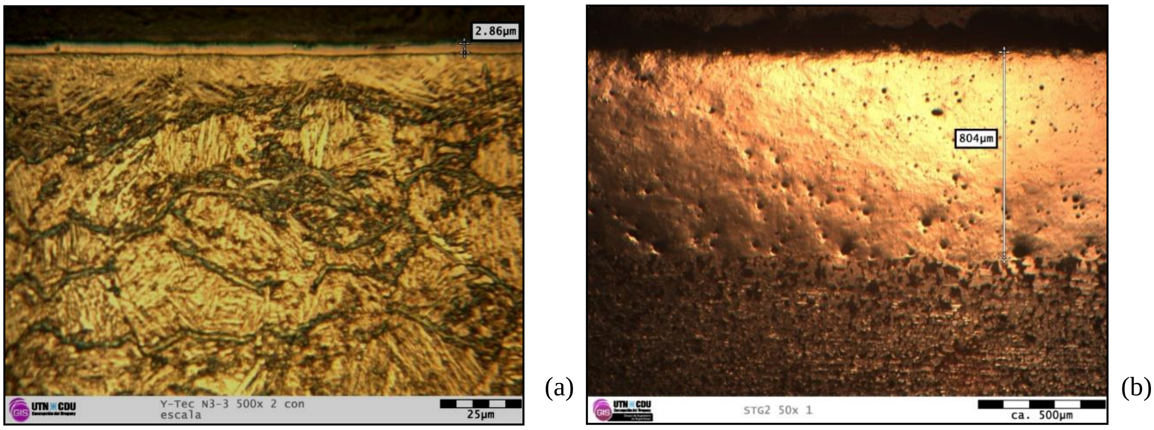

Fig. 2: Optical micrographs of the cross sections to observe the films: (a) PVD coating, Balinit®, 500x magnification. (b) Thermal Spray Colmonoy®, 50x magnification.

3.2. Hardness profiles

The profiles were constructed from microhardness indentations with 25 g load taken in the cross section, form the surface to the inside. One typical profile of the new design, V820 nitrided + PVD is shown in Fig. 3(a). It can be observed that the nitrided layer provides a soft hardness profile leading to the base material hardness, Chicot et al. (2011). Using the DIN standard criteria for nitriding penetration (50 HV over the core hardness), in this case was established in 435 HV. On the contrary, the hardness profile of the traditional treatment, AISI 1020 plus thermal spray, shows a step, between the film hardness, that is considerable lower than the PVD film, very irregular and there is a clear interphase with the substrate hardness, that is indeed very low. The film thickness measured with this technique is similar to the one observed in the micrographs shown before in Figure 3.

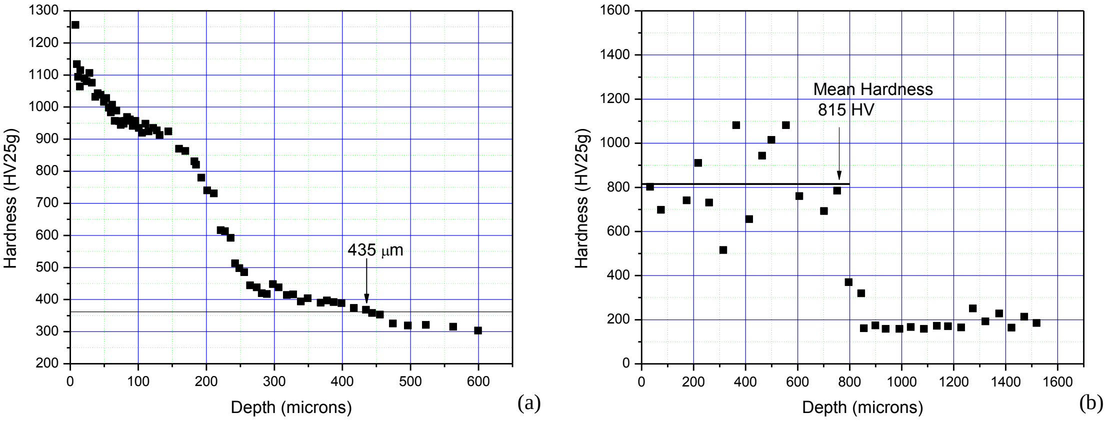

Fig. 3. Microhardness depth profiles of both systems: (a) new design Nitr+PVD, (b) traditional design, Thermal spray

3.3. Abrasion tests

Four samples of each group, traditional and new design, were tested in abrasion, and results are depicted in Fig. 4. It can be observed that the mass loss in the new design is almost 30 times lower. A group of only nitrided samples was also tested for comparison, and wear loss was even higher, reaching 200 mg as mean value. The good wear behaviour of the PVD film is not only dependent of its on properties but also in the mechanical properties of the system, including the nitrided interlayer the toughness of the interfaces, such as other authors described before, De Las Heras (2008).

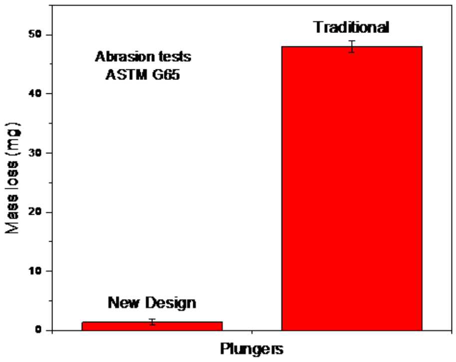

Fig. 4. Mass loss comparison between the two plungers surface design in the ASTM G65 Wear Test

Wear tracks were photographed and in one PVD sample the coating was broken, as it is shown in Figure 5(a). Mass loss in this case was approximately equal to other samples of the same group, so it can be assumed that the film resulted broken at the end stages of the test. In the case of the traditional thermal spray coating, it was not broken but damaged, and the mas loss was very high in comparison with the PVD but very good in comparison with a hardened steel so as the nitrided sample. This can be explained by the fact that the coating is soft but very thick, having a good capability of absorbing energy in severe wear processes. Nevertheless, as it is less hard than the abrasive, it is eroded during the test, and what is worse, sand get caught in this degradation process within the film.

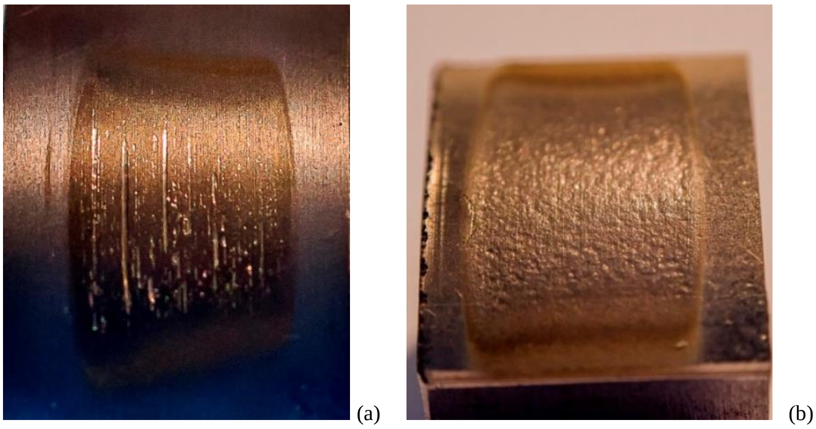
(a) (b)

Fig. 5: Pictures of the worn surfaces after ASTM G63 abrasion test: (a) A sample of the new design (nitr+PVD). (b) A typical sample of the traditional treatment (thermal spray).

3.4. Adhesion tests

Scratch tests were carried out at loads of 20, 30 40 50, and the scratches were undetectable in the PVD coatings. This is remarkable, in traditional TiN coatings the critical load is usually under 50N. On the contrary, the scratch could be observed on the thermal spray coating, but the coating was only deformed, not broken or detached. Working loads were increased and at 85 N a little failure was detected in some parts of the wear track in the case of the PVD coating, but no spalling, buckling or any of the classical modes of film failures in scratch tests. In Fig. 6, SEM pictures of the tracks can be observed, and it is remarkable, the plastic deformation on the sides of the thermal spray coating. The good mechanical behaviour of the PVD coating is

Wear tracks profiles were recorded with a profilometer and two typical results are observed in Fig. 7. It can be seen that the amount of plastic deformation is higher in the traditional coating and the tracks are deeper. Following concepts described by Vilar and Colaco (2009), an analysis of the wear tracks profiles can be carried out. If the groove is formed by a purely ploughing mechanism, no material removal occurs and the material is just displaced from the groove by plastic deformation, forming lateral ridges. Conversely, if cutting is the only abrasion mechanism, the material from the groove is totally removed and no lateral ridges form. Once the geometry of the sliding indenter is kept constant (as in the present study), the size of the lateral ridges is related to materials properties, in particular on its ductility and toughness: as ductility and toughness increase, lateral ridges grow. In this case, the PVD case is clearly tougher than the thermal spray film.

In addition, it is worth noticing that in the case of the PVD, the track is still within the film, which was 3 microns thick at least.

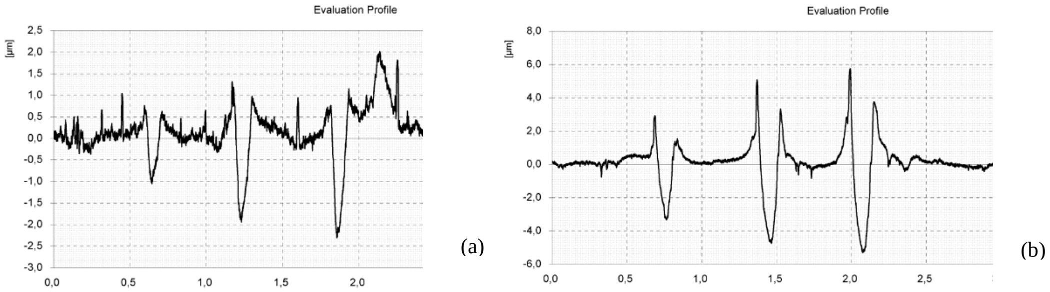

Fig. 7: wear tracks profiles after the scratch tests, with 60, 75 and 85 N. (a) PVD coating – new design, (b) thermal spray coating – traditional design. Note: as the profilometer defines scales automatically, they are different.

Load was increased even more until 130 N and 150 N where spallation could be detected in the PVD film, and a severe deformation was observed in the traditional thermal spray coating. SEM micrographs of the scratch tracks are showed in Fig. 8.

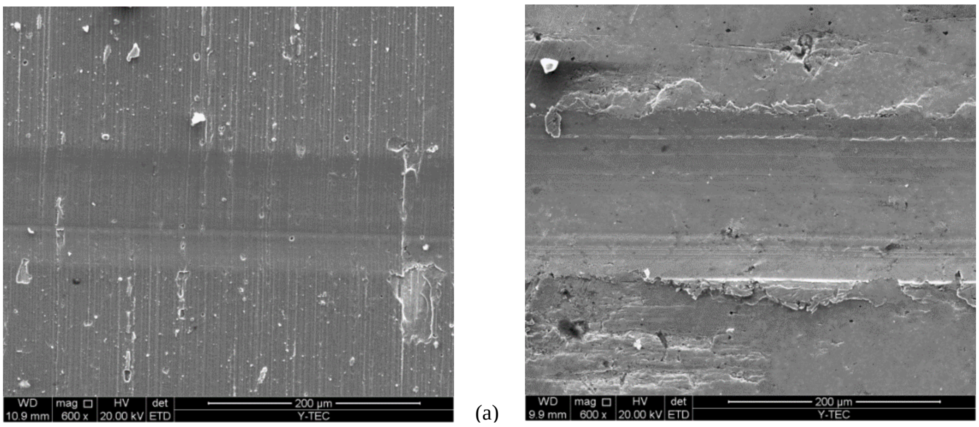

Fig.8. SEM observation of Scratch Test tracks, 130 N load: (a) PVD film, (b) Thermal Spray film

With the highest load, 150 N, the critical load was clearly reached, and film spallation could be observed in the PVD coated sample, at both sides of the tracks, as it can be observed in Fig. 9(a), taken with the optical microscope. In Fig. 9(b) the traditional coating can be also observed. In this case, the damage level increased, the film is deformed and broken all along the track. The failure has been induced at a very unusual high load, and these pictures and profiles of the scratch tests tracks show that the PVD film, besides a very superior performance in the abrasion test, remained almost without damage or any deformation during the tests at loads until 130 N. In this case, plasma nitriding as pre treatment could also have influenced in the good adhesion, as other authors pointed out previously, Pujante et al. (2014).

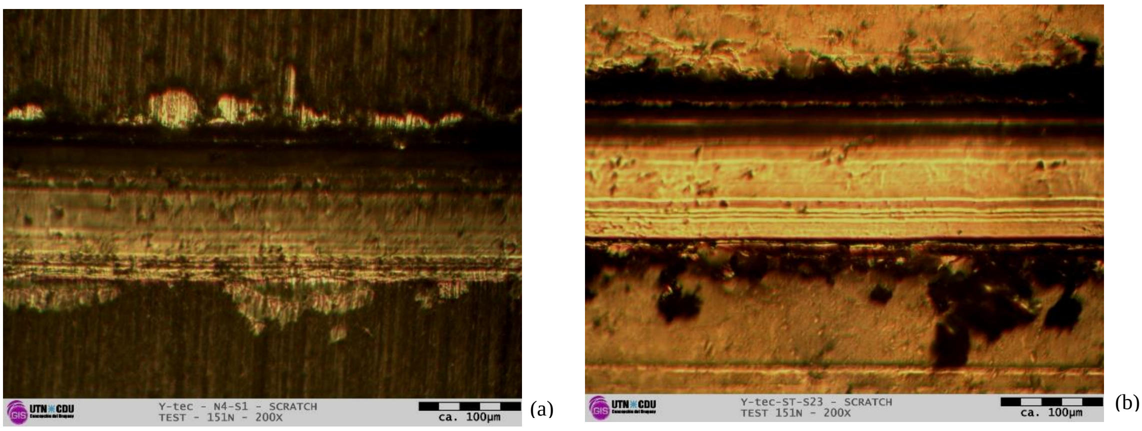

Fig.9. Optical micrographs showing the tracks left by the indenter at maximum load, 150N: (a) PVD film, (b) Thermal Spray film

3.5. *SEM observation of worn surface*

In the case of the PVD which was broken and in thermal sprayed coatings, SEM observation of the abrasion wear tracks was carried out. It can be observed in Fig. 10 that the film is detached in some zones, but scratches are fairly visible. It can be inferred that the film is far harder than the asperities, but a certain load, can be broken. It is worth to say that in four abrasion tests; only one was broken as this example.

The white part is the substrate material since the Fe signal is observed (a) and the dark part is the remaining film, since CR, Al and N signals are observed.

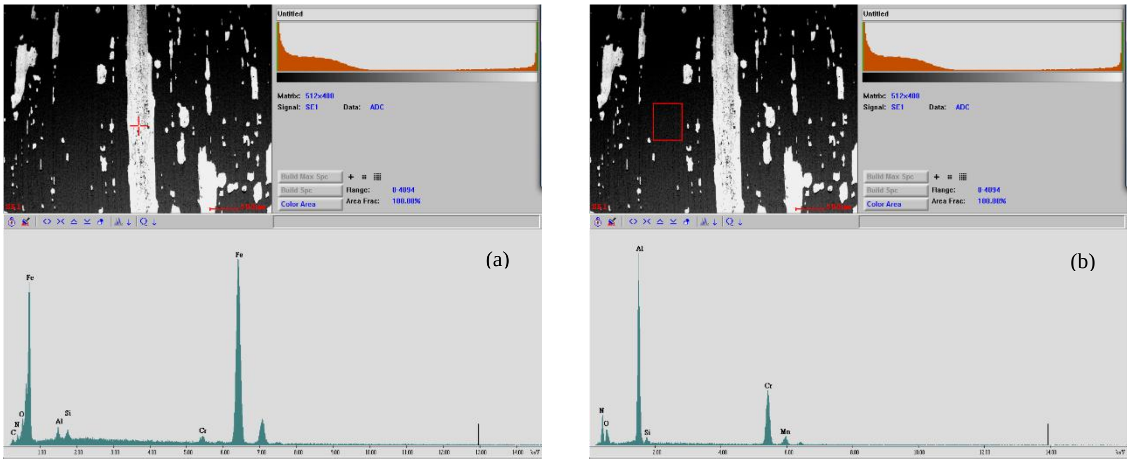

Fig. 10. SEM and EDS analysis of two zones of the abrasion wear track

3.6. *Field tests*

The durability of the new designed plungers was superior to the traditional ones, expressed in fracture stages. The increment in work life could be calculated as 113%.

This difference in performance is smaller than the one observed in the abrasion tests where the increment in work life (measured as the inverse of mass loss) would be more than 30 times. This can be explained by the fact that the ASTMG65 test is not meant to calculate absolute wear performance nor relative, it was meant to rank wear resistance of materials in abrasive situations. The experiment has controlled variables, uniformity in the abrasive size, angularity and flux, fixed load. In the field tests many variables involving the abrasives are not controlled, and also some corrosive liquids are added, this could explain the difference in the two performance comparisons.

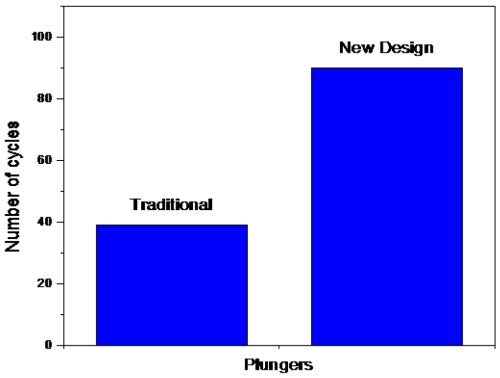

Fig. 11. Comparative work life of the plungers measured in stages

4. Conclusion

The new material and surface design for plungers, comprised by a medium alloy steel, the nitriding treatment and the subsequent PVD coating resulted a clear advantage in the work life, compared to the traditional design, low alloy steel plus thermal spray coating. The adhesion is superior, the critical load is about 130 N, higher than many ceramic coatings, the abrasion resistance was very good, and almost no mass loss was detected after 25 min of a severe wear test. It can be concluded that the good performance in wear and adhesion test rest on the nitrided layer, which provides a gradual hardness profile, making hardness of the film and the substrate closer, thus increasing the load baring capacity of the system. Plungers with new surface treatments were made in Argentina, with the possibility of technical support in the O&G area.

Acknowledgements

Sonia Brühl appreciates all the dedication and work of the students of the Surface Engineering Group: Massimo Uccellini, Gonzalo Schierloh, Valentín Ronconi. Tomás Lonardi. Also the financial support of UTN-SECYT and the Faculty of Concepción del Uruguay.

References

ASM International, 1994. ASM Handbook, Vol.5. Surface Engineering, ASM International, Materials Park, OH, USA.

ASTM C-1624, 2005 (2010). Standard Test Method for Adhesion Strength and Mechanical Failure Modes of Ceramic Coatings by Quantitative Single Point Scratch Testing, ASTM International, West Conshohocken, PA, USA.

ASTM G65 1995. Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus. ASTM International, West Conshohocken, PA, USA.

Azzi, M., Amirault P., Paquette M., Klemberg-Sapieha, J.E., Martinu L., 2010. Corrosion performance and mechanical stability of 316L/DLC coating system: role of interlayers. Surf. Coat. Technol. 204, 3986–3994.

Chicot, D., Puchi-Cabrera, E. S., Decoopman X., Roudet F., ,Lesage, J:, Staia M.H., 2011. Diamond-like carbon film deposited on nitrided 316L stainless steel substrate: a hardness depth-profile modeling. Diam. Relat. Mater. 20, 1344–1352.

Davis J.R, 2001. “Surface Engineering for Corrosion and Wear Resistance”, ASM International, Materials Park, OH, USA.

De Las Heras, E., Egidi, D.A., Corengia, P., González-Santamaría, D., García-Luis, A., Brizuela, M., López G.A., Flores Martínez M., 2008. Duplex surface treatment of an AISI 316L stainless steel; microstructure and tribological behaviour. Surface and Coatings Technology. 202, 2945-2954.

Papavanisam S., 2014. Corrosion Control in the Oil and Gas Industry, Elsevier, Netherlands.

Podgornik B., Vižintin, J., Wänstrand, O., Larsson, M., Hogmark, S., Ronkainen, H., Holmberg, K., 2001. Tribological properties of plasma nitrided and hard coated AISI 4140 steel. Wear 249, 254–259.

Pujante J, Vilaseca M, Casellas D, Riera M.D, 2014. High temperature scratch testing of hard PVD coatings deposited on surface treated tool steel. Surface and Coatings Technology 254, 352-357.

Rousseau, A. F, Partridge J.G., Mayes E.L.H., Toton J.T, Kracica M., McCulloch D.G,. Doyle E.D, 2015. Microstructural and tribological characterisation of a nitriding/TiAlN PVD coating duplex treatment applied to M2 High Speed Steel tools. Surface and Coatings Technology 272, 403-408

Vilar, R, Colaco, R., 2009. Laser-assisted combinatorial method for rapid design of wear resistant iron alloys. Surface and Coatings Technology 203, 2878-2885.

Wierzchon, T., 2004. Structure and properties of multicomponent and composite layers produced by combined surface engineering methods. Surface and Coatings Technology 180–181, 1 458-464.