Surface Engineering Alternatives for Increase Corrosion Resistance and Wear Performance of Ball Valves for the Oil and Gas Industry

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ABSTRACT
In petroleum production and separation processes frequently the components suffer wear and corrosion due to the contact with the corrosive fluid which could be contain solid particles. In certain dynamics equipment like as ball valves, the deterioration generated causes the operations equipment exit at short times about a month. The main elements of the valves deteriorated are the seats and corks, which are made of 4140 steel. The aim of the present research was evaluating extend the life time of the components using two thermal spray coatings systems: WC-12%Co alloy by HVOF and FeCrB alloy by AWS. The evaluation of wear resistance of these coatings was achieved by means of abrasion wear tests according to ASTM G65-C. The microhardness of the coating was determined by means of Vickers indentation using a load of 300g and the corrosion behavior was evaluated by potentiodynamic polarization tests. The results showed that the best performance in corrosion and abrasion conditions correspond to the HVOF WC-12%Co coating.

Keywords: abrasive-wear, corrosion, HVOF, AWS, valves, oil-and-gas.

Alternativas de Ingeniería Superficial para aumentar la Resistencia a la Corrosión y Resistenciaal Desgastede de Válvulas de Esfera de la Industria de Petróleo y Gas

RESUMEN
En los procesos de producción y separación de petróleo, frecuentemente, los componentes sufren desgaste y corrosión por estar en contacto con fluido corrosivo que generalmente contiene sólidos en suspensión. En ciertos equipos dinámicos, como las válvulas de bola, el deterioro generado ocasiona la salida del equipo de las operaciones por cortos tiempos decasi un mes. Los elementosde las válvulas que principalmente se deterioranson los asientos y obturadores (tapones y bola), en muchos casos de acero 4140. El objetivo de la presente investigación fue incrementar el tiempo de vida útil de los componentes al ser recubiertos con dos sistemas de proyección térmica: HVOF de la aleaciónWC-12%Co y AWS de la aleación FeCrB. La evaluación de la resistencia al desgaste de estos recubrimientos se logró mediante ensayos de desgaste por abrasión de acuerdo con la norma ASTM G65-C. La microdureza del recubrimiento se determinó por pruebas de indentación Vickers utilizando una carga de 300g, y el comportamiento frente a la corrosión se evaluó mediante ensayos de polarización potenciodinámica. Los resultados indicaron que el mejor rendimiento en un ambiente corrosivo y abrasivo lo tuvo el recubrimiento HVOF WC-12%Co.

Palabras clave: desgaste por abrasión, corrosión, HVOF, AWS, válvulas, petróleo.

INTRODUCTION
In the process of production, separation and collection of crude multiphase fluid, wear-corrosion synergistic fail, is generated in the components that are in direct contact with the fluid due to the presence of solid particles which are entrained from the reservoir. Some devices such as ball valves, present deterioration by sediment causes that the equipment out of service in shorts times. The main elements of the valves are worn seats and plugs (plugs and ball). For selecting a protective coating to cover these devices, hardness is not the sole criterion when there are multiple mechanisms acting to degrade a surface. Understanding these mechanisms, including erosion, sliding, abrasive and adhesive wear, and corrosion, is key to selecting the proper coating for a given application [1,2]. Carbide coatings are ceramic-metal composites or cermets

in which the metallic phase retains the carbide particles during deposition. The WC-12%Co alloy is commonly used to provide wear resistance, and it can be applied by both thermal spray process ofArc Wire Spray (AWS) or High Velocity Oxygen Fuel (HVOF).The coatings provide high hardness and these can be used at extremely high temperatures and withstand corrosive environments [2,3-5]. The aim of this research was to evaluate the performance of two coatings in order to improve the useful life times of ball valves. The research presents two proposals of Thermal Spray Technology coatings: WC-12%Co alloydeposited by HVOF and FeCrB alloy deposited by AWS.

EXPERIMENTAL

The research was divided into two stages. The first one was carried out in field to determinate the operating conditions of the valves, visiting the trains, interviewing the operators and making an inspection of a valve that went out of service (Fig.1). The second phase of the research was carried out in laboratory, where the coating was deposited on cylindrical samples of AISI 4140 steel for corrosion tests and rectangular samples of 4140 steel for the abrasion tests.

Tungsten-Carbide Cobalt Chromium alloy (WC-12%Co) and Alpha Plus® (FeCrB) alloy were deposited by High Velocity Oxygen Fuel Spraying (HVOF) and Arc Wire Thermal Spray (AWS) technologies respectably. Table I and II show the alloys nominal chemical composition.

The methodology used in this research considered both thickness and porosity measurements on coatings cross sections. Porosity was determined by performing the analysis of 20 fields at 200X magnification, using a Nikon brand Eclipse TS-100 optical microscope, coupled to a LECO IA-32 image analysis system, as established in ASTM Standard E2109-14, sweeping an area of 1.32x10^{-2} cm^{2}. The morphology and microstructure of the coatings cross sections were studied by Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy analysis (EDS)

Fig. 1. The ball valve out of service.

Table I. Nominal composition of core wire Alpha Plus (Wt%) [6]

C	Cr	B	Al	Si	Fe
0.06-0.6	25	6.1-9.5	0.02-10.02	0.02-11	Bal

Table II. Nominal composition of WC-12%Co cored wire alloys (wt %) [3,6]

W	C	Co
82.9	4.1	11.6

Vickers microhardness measurements were made on coating cross sections, according to ASTM E384-10 standard, using a load of 300 gfor a loading time of 30 s. Each value was the average of 10 measurements. The abrasion wear resistance of the coatings was determined by the “Rubber Wheel abrasion test” using ASTM G65-16 standard. All tests were performed with dry quartz sand 50-70 mesh at a feeding rate of 350 g. min^{-1}. The normal applied load was 130 N and the wheel speed was at 200 min^{-1}. Mass loss measurements during the test where determined using an analytical mass balance with a sensitivity of 0.0001g. Finally, the corrosion resistance was evaluated by potentiodynamic polarization tests according to ASTM G5-14e1 standard, using a potenciostat Gamry Interface 1000 in 3.5% NaCl solution. An Ag/AgCl electrode was used as reference electrode and graphite rods as counter electrodes.

RESULTS AND DISCUSSION

Ball valves Operating Conditions.

At present, the valve seats are being manufactured in steel 4140, this with the function of extending the valve performance. Although the steel modification increased the operation time of the equipment higher performance is required, so this work is presented as a solution to increase the lifetimes (in excess of 60 days on continuous operation) by using thermal sprayed coatings on substrate AISI4140. Figure 2 shows one ball valve that went out of service due to fluid loss. We can observe in the inner surface of the release valve the deterioration of the material as both the ball and the seats.

The ball valve failed was localized in a Flow station. The fundamental objective of Flow Stations in production operations of Petroleum industry consists of separating the fluids from the well into their three basic components: oil, gas and water, for the subsequent treatment of hydrocarbons, in order to optimize their processing and marketing (oil and gas). After the crude is extracted, it goes through a process of physical separation of gas in oil, in which both gas and water and sediments should be separated by difference in densities. These processes occur in the separation trains of the flow stations, where in addition to the separation the pressures that the fluid brings with it are lowered. In the separation trains, there are controls and blocking valves, which allow maintain the optimum level of oil phase's separation for the process to be effective, in addition to control the flow of the fluid. Valves suffer high wear internally, due to the dragging of the sand due to the pressures and speeds handled in the train.

In this study case, in line are handled mainly three pressure values: 8275 kPa (1200 psi), 3447 kPa (500 psi) and 414 kPa (60 psi). The Figure 3 shown the sand particle size determined by using a granulometric analysis of a sand sample at the exit of the multiples (M-1, M-2 y M-3) of the flow station. The highest percentage of retention on the 120 sieve was corresponding to 125 µm. The corrosive multiphase fluid with this sand content undoubtedly was out of specifications [3].

a)
b)
c)

Fig. 2. a) Indicates the location of the leak presented by the component, b) Inner part of the valve, c) Valve closing element (ball), where deterioration was observed.

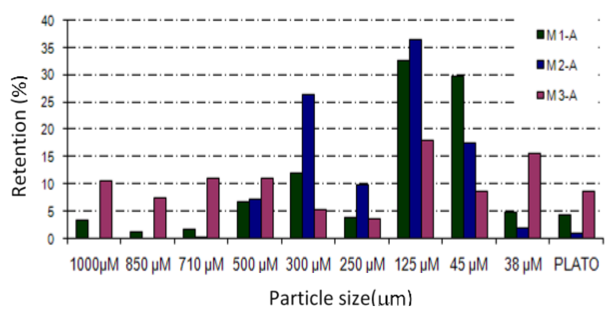


Fig. 3. Retention (%) vs. particle size.

Coating characterization

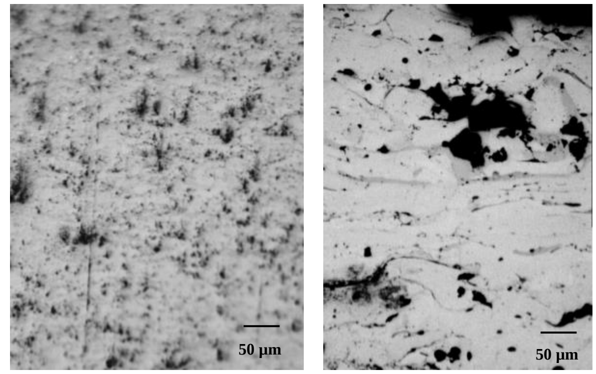
Table III, shows the thickness, porosity, and microhardness of coatings. It's evident that AWS FeCrB(10.9%) coating porosity was higher than the

HVOF WC-12%Co coating (0.5%), which its consistent with a lower temperature and velocity of the particle in flight for Wire Electric Arc thermal spray process (AWS) respect to HVOF thermal spray process [3,8,9].On the other hand, the HVOF thermal spray process, produces a very dense microstructure, with porosity typically less than 2%. Note that the HVOF WC-12%Co coatings microhardness was significantly higher than the AWS FeCrB coatings. This behavior is related with the hard phases and the microstructural integrity of HVOF WC-12%Co coatings. The main hard phase present in these coatings is Tungsten Carbide, which have a microhardness reported of around 1500 HV_{300} [3-5].

Table III. Thickness, porosity and microhardness of coatings and substrate.

Character	*AISI 4140 steel substrate*	*AWS FeCrB coating*	*HVOF WC-12 %Co coating*
Porosity (%)	-	10.9 ± 5,4	0,5 ± 0,2
Thickness (µm)	-	416.76 ± 103.45	501.44 ± 142.92
Microhardness (HV_{300})	353± 22	635 ± 259	1031 ± 105

Figure 4 presents micrographs obtained by optical microscopy of deposited coatings cross sections, where we can see the microstructure of the AWS FeCrB and HVOF WC-12%Co coatings in sprayed condition. Note that in both coatings, the typical lamellar morphology parallel to the substrate of the thermal sprayed coatings, as well as the presence of unmetlted particles which are recognized by their typical spherical morphology. The higher porosity of (AWS) thermal sprayed FeCrB coatings was visually confirmed, the darkest areas that can be seen in the Fig.4.b are the pores present. In AWS thermal spray technology, the in-flight particle velocity and temperature are significantly lower than in HVOF technology, therefore the AWS coatings porosity will be greater [3].

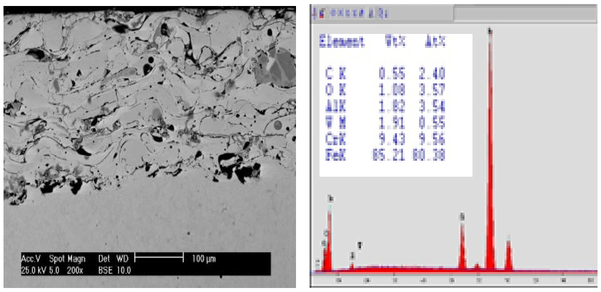


a) b)

Fig. 4. Optical image of the coatings deposited cross sections (a) WC-12%Co deposited coating (b). FeCrB deposited coating.

Figure 5 shows backscattered SEM micrograph of the AWS FeCrB coatings polished cross-section. The lamellar structure, characteristic can be observed, also the unmelted particles, indicating that the temperature of the flame was no higher enough; a great number of defects such as pores and cracks were detected. In these images obtained in backscattered electron mode (BSE), the contrast is based on the backscattering coefficient, which increases with increasing atomic number. A higher backscattering coefficient results in an increase in the number of BSE generated by the PE beam. If different phases exist on the specimen those with higher atomic number display higher brightness than those with a small atomic number. The pores and cracks are identified because they look black. The coating area EDS microanalysis revealed that the mayoritary elements presents were Fe and Cr acording with the expected for this alloy.

Figure 6a shows backscattered SEM micrograph of the HVOF WC-12%Co coating polished cross-section and Fig.6b shows the coating area microanalysis. Note that the HVOF WC-12%Co coating porosity (dark areas) is lower than the AWS FeCr coating porosity.



a) b)

Fig. 5. a) SEM micrograph in BSE mode and b) EDS spectra of AWS FeCrB coating cross section .

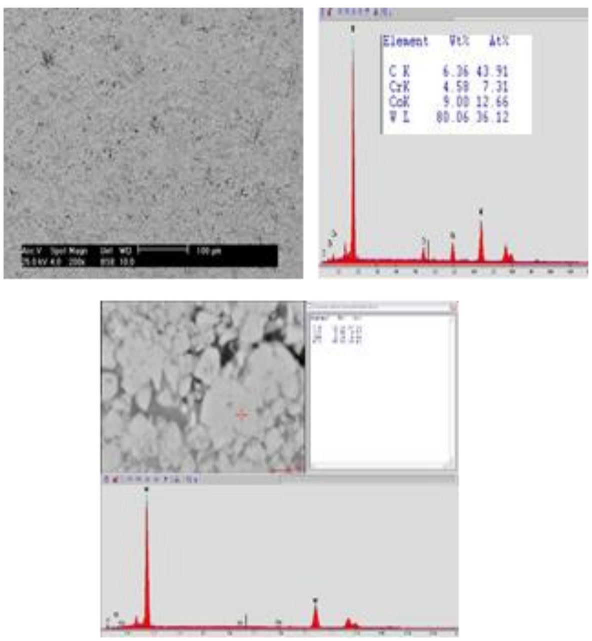


Fig. 6. SEM-BSE micrograph and EDS spectra of a) HVOF WC-12%Co coatingcross section. b) Details of Tungsten Carbide and EDS spectra.

Hard phases such as tungsten carbide (Fig.6.b) containing heavier elements such as tungsten appear lighter, and the areas with the presence of elements with lower atomic numbers such as Cr, Co are gray. On the other hand, in the HVOF WC-12%Co deposited coating the discontinuities such as pores and cracks are black, and noticeably less compared to AWS FeCr coating, which is consistent with expectationsand that was already discussed.

Abrasion Test

Table IV shows the coatings mass loss in the abrasion tests. The best abrasive wear behavior was reached by HVOF WC-12%Co coating; with a 30% lower abrasion rate respect to AWS FeCrB coating.

Since tungsten carbide is the main phase present in the WC-12%Co coating, it is expected a better behavior under abrasive wear than that of the FeCrB coating. The abrasion wear laws show that the harder a component is, the more resistant it is to wear coinciding with the results obtained in this research. Hardness generally improves abrasion resistance; however, toughness also must be taken into account[2]. Abrasive wear, a particular concern in valve bodies and seats, occurs when particles are introduced between two moving surfaces. The particles can be trapped between or attached to the surfaces. As with sliding wear, abrasive wear is affected by the type and size of particles, mechanical load, surface speed, temperature and corrosive elements [2,3,7,8].

Table IV. Volume loss during the abrasion test for the proposed systems.

System	Substrate steel 4140 (mm^3)	FeCrB coating (mm^3)	WC-12%Co coating (mm^3)
Average	105.98± 8.05	46.24±1.36	13.55± 2.68

Wear Mechanism

Figure 7 shows an SEM image of the worn surface of HVOF WC-12%Co coating. We can see as the main wear mechanism present in this condition is plastic deformation (white circles), followed by abrasion (see blue circles) and probably material detachment due to lack of cohesion of some particles (black circle).

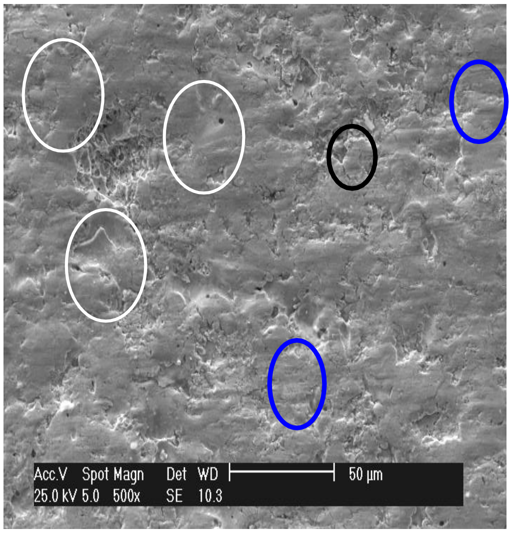


Fig. 7. SEM image of HVOF WC-12%Co coating worn surface.

Figure 8 shows an SEM image of AWS FeCrB coating worn surface. Note that the predominant wear mechanism is the detachment of particles (tungsten carbide) from the matrix (see white circles), called microcracking, which generally occurs in brittle materials. This causes the hard phases to be exposed allowing them to be removed later by the action of the abrasive, similar results were found by Rodríguez et al [9, 10].

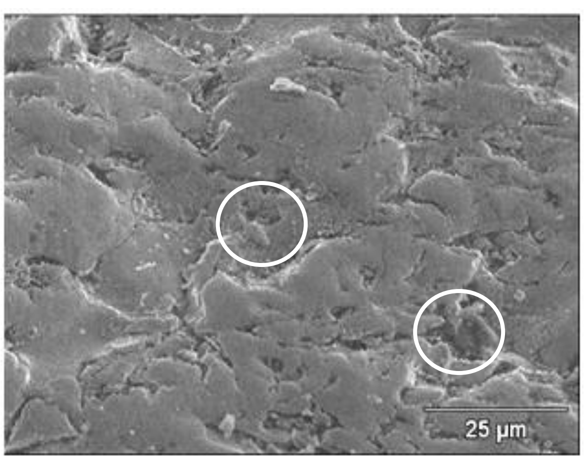


Fig. 8. SEM image of AWS FeCrB coating worn surface.

Corrosion Resistance

Figure 9 presents the potentiodynamic polarization curves representative of the behavior of HVOF WC-12%Co and AWS FeCrB coatings in a 3.0 wt% NaCl solution. Note that the HVOF WC-12%Co coating presented a more positive corrosion potential (E_{corr}) and a decreased of about one order of magnitude of the corrosion current density (i_{corr}) respect the AWS FeCrB coating, indicating a higher corrosion resistance, associated to that WC-12%Co coating offers an effective barrier layer on the substrate. The corrosion potential (E_{corr}) is related to thermodynamic tendency of a material to corrode and the corrosion current density (i_{corr}) is commonly utilized as an important parameter to evaluate the kinetics of corrosion reactions [11-12]. The corrosion rate is normally proportional to the corrosion current density. In table V, note that i_{corr} for the HVOF WC-12%Co coating (1.06 $\mu A/cm^2$) showed a important decreased compared to the uncoated substrate 4140 steel, whereas the i_{corr} for the AWS FeCrB coating (15.06 $\mu A/cm^2$) was very similar compared to the 4140 steel uncoated substrate (14.03 $\mu A/cm^2$).

Table V. Electrochemical test results for the proposed systems surfaces.

System	i_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	Beta A (mV/dec)	Beta C (mV/dec)
FeCrB	15.06	-694	308	165
WC-12%Co	1.06	-410	292	236
Subs. 4140	14.03	-717	101	211

In general, this behavior of AWS Sprayed FeCrB coating can be explained considering the defects observed by SEM in this coating, where a great number of defects such as pores and cracks were detected, which, being interconnected with the substrate, allowed to the corrosive medium to permeate and that the corrosive species reached the substrate leading to accelerated attack at the coating-substrate interface. It's evident that the coating porosity for AWS FeCrB coating was higher than the HVOF WC-12%Co coating porosity, which it's consistent with a typical lower temperature and particle velocity in flight for AWS Thermal Spray Process respect to HVOF Thermal Spray Process [2-4].

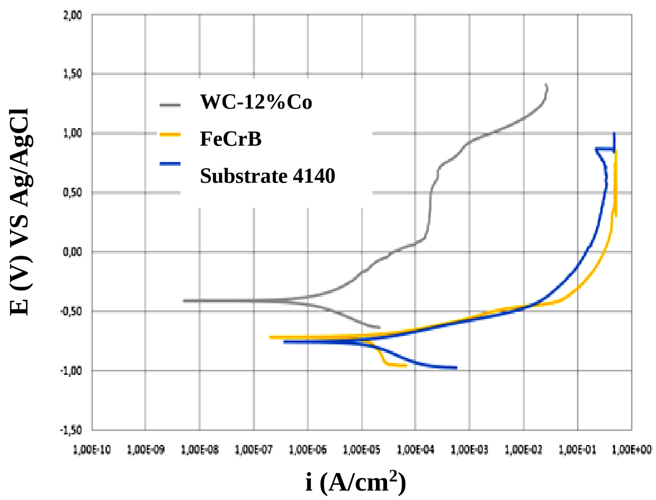


Fig. 9. Potentiodynamic polarization curve for the different systems and substrate, in 3% NaCl.

CONCLUSIONS

The analysis performed on the ball valve out of service indicated that the failure was caused by a wear and corrosion combined mechanics of the seat and plug, with a significant loss of dimensional tolerance due to the corrosive fluid with high sand content which is out of specifications.

The best microhardness corresponded to WC-12%Co HVOF coating with a value of 1031 HV_{300}.

The coating that presented the best wear resistance was the WC-12%Co, which was attributed to a better microstructural integrity and hardness.

The potentiodynamic polarization showed that HVOF WC-12%Co coating exhibit better corrosion resistance compared to AWS FeCrB coating.

The main coating corrosion mechanism was the access of corrosive medium to the substrate through the coating pores and microcracks leading to accelerated attack at the coating-substrate interface. The best corrosion resistance corresponded to WC-12%Co HVOF coating as a consequence of lower porosity and heterogeneity microstructural.

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