ARMOURED AGAINST CORROSION

D. Lusk, Sub-One Europe, UK and T. Casserly, M.Gupta, K. Boinapally and Y. Cao, Sub-One Technology, USA, examine thick DLC based films with excellent corrosion resistance for applications in the oil and gas industry.

Corrosion issues have forever been a problem and challenge to the oil and gas industry. Having such problems can have a massive impact on sustained periods of production and be extremely costly where unexpected downtime and essential maintenance can have a large impact on production. Crude oil and natural gas can carry various high impurity products, which are inherently corrosive.[1] In the case of oil and gas wells and pipelines, such highly corrosive media are carbon dioxide (CO_2), hydrogen sulfide (H_2S) and free water. As well as the downtime and high maintenance cost, corrosion problems create pollution and safety hazard issues. With the need to continually dig deeper to maintain extraction rates, deeper waters are thus being explored which in turn leads to more hostile environments being opened up. Increased government legislation concerning oil and gas is becoming more stringent. Minimising risks and potential breakdowns is becoming more important to producers.

Continual extraction of CO_2, H_2S and free water through oil and gas components can, over time, cause the internal surfaces of these components to suffer from corrosion effects. A point will be reached where the component may completely breakdown and the assembly will need to be replaced while production is stopped. Internal corrosion in wells and pipelines is influenced by temperature, CO_2 and H_2S content, water chemistry, flow velocity and surface condition of the steel.[2] Having a greatly reduced corrosion rate (mm/yr), can dramatically increase component life, which leads to much greater benefits such as reduced maintenance costs. Currently

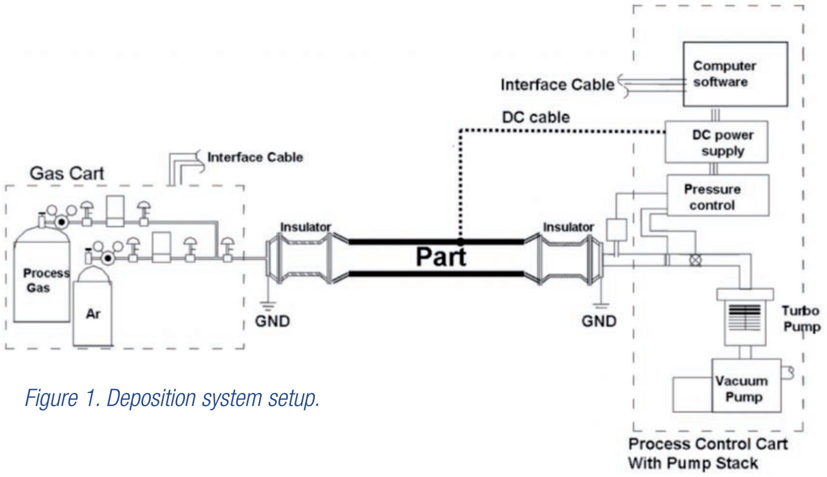
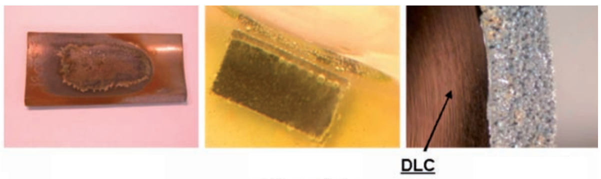


Figure 1. Deposition system setup.



Figures 2a, 2b and 2c (left to right). Room temperature HCL test.

many components used for oil and gas extraction are made from carbon steel based alloys. Now, organisations are looking to move away from these types of alloys to a more corrosion resistant alloy at a much higher cost.

Within this article, a coating described as InnerArmor, that has been developed by Sub-One for application on the internal surfaces of oil and gas components, will be discussed. The coating is a diamond-like carbon (DLC) based coating which has excellent corrosion and wear resistant properties as well as being hard, pinhole free, dense and chemically inert. This coating can significantly reduce corrosion effects on oil and gas components and be of great financial benefit to the oil and gas operators. The coating can be applied on low grade alloys thus eliminating the need to use expensive exotic alloys.

The InnerArmor coating is a multilayer film where various environmentally safe gas precursors, such as acetylene, are used for depositing the layers. A silicon based adhesion layer is initially deposited on the metallic substrate to provide a superior bond and thereafter subsequent layers of Si: DLC are deposited on top of each other to make up the full coating. Doping intermediate layers with silicon helps to act as a stress reliever.[3] A pure DLC cap is the final (surface) layer which provides an inert surface which is good for corrosion resistance and exhibits very low friction. Recent studies have suggested that using a multilayer stack in this way can provide improved corrosion resistance.[4, 5]

Deposition technologies for corrosion resistant coatings

Several attempts and techniques have already been explored to coat oil and gas components, such as chemical vapour deposition (CVD), physical vapour deposition (PVD), electroplating, polymer linings and sol-gel. In particular, with sol-gel and polymer linings attempts have been made to coat the internal surface of components. However, coatings applied in this way do not provide a dense, hard, low friction coating which is good enough to act as an inhibitor. These coatings can also be very thick which restricts flow. In the case of CVD and PVD, the component to be coated must be contained within a vacuum coating chamber which typically cannot accommodate high aspect ratio (length/diameter) parts. Sub-One has developed a plasma enhanced chemical vapour deposition (PECVD) technique whereby the component part itself is the vacuum chamber. Figure 1 details the system setup.

The plasma deposition technique involves using a hollow cathode discharge to generate a very high density plasma inside the part. Gas is continually fed from one side of the system and fills up the volume inside the component. As the component itself is the vacuum chamber, the part itself is biased, which creates an energy inside the part, igniting the gas and resulting in plasma generation. By maintaining a hollow cathode discharge within the part, InnerArmor dramatically increases the deposition rate of the coating to approximately 0.5 µm/min. The internal diameter and operating pressure are the critical parameters when it comes to understanding the behaviour of hollow cathode discharges. Biasing the part negatively allows deposition to take place on the inside of the component and the cathode bias helps to improve the stress, adhesion and density of the films through ion bombardment energy.

Asymmetric bipolar pulsing is used to control the temperature of the part as the coating is growing through variation in the duty cycle. When the pulse is in a positive polarity state this allows any positive charge build up on the coating surface to be dissipated and this quick removal of charge helps to maintain a high deposition rate and continual coating. It also helps to eliminate any arcing effects from the coating due to its insulative nature.

Extensive details of the coating technology described can be found elsewhere.[6]

Corrosion testing

Corrosion tests have taken place to understand how the coating would perform under some very aggressive environments. In particular tests have been carried out using hydrochloric acid (HCL) at both room and raised temperatures and also under sour autoclave testing. Figure 2 shows images from a room temperature HCL test.

The initial test involves an 18% HCL concentrated solution where a drop of acid was placed on a bare metal substrate. Figure 2a shows how the acid impacts the metal surface. After 30 minutes, there is clear evidence of how acid can attack a bare metal substrate. It is easy to understand how this kind of instant corrosion attack would create problems for the oil and gas components. Figure 2b shows a metallic substrate coated with InnerArmor, which was then submerged in an 18% HCL concentrated solution for 65 hours. It is evident that some kind of corrosive attack has taken place. Most likely that the bare metal was attacked from the solution and not the coating. Figure 2c shows the InnerArmor coated sample after test. As can be seen, there is no damage to the coating. This test confirms that the coating is pinhole free and very dense. The adhesion of the film to the substrate is also impressive as there appears to be no undercutting of the corrosive solution

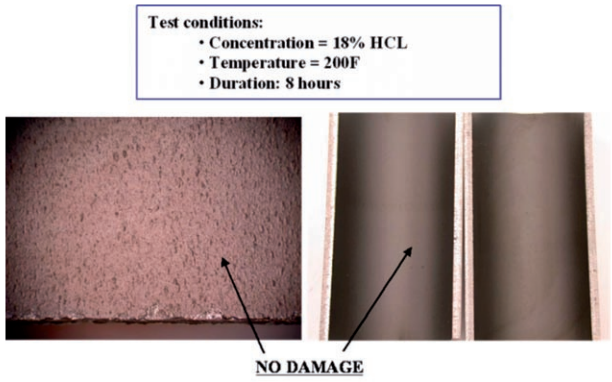


Figure 3. Hot raised temperature HCL test.

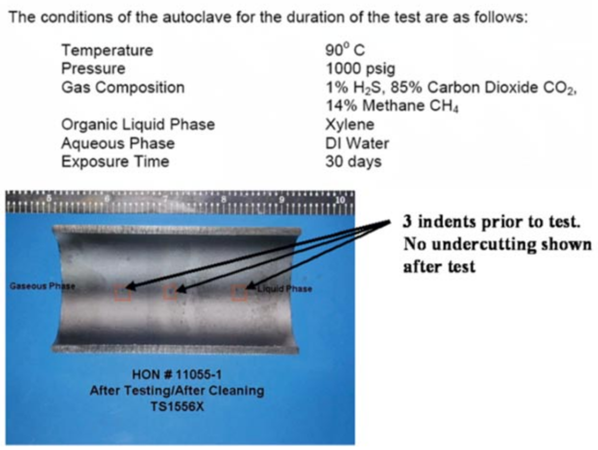


Figure 4. 30 day sour autoclave test.

between the boundary of substrate to film and hence no delamination of the film.

A further test with HCL was then conducted at a raised temperature. A pipe cell was created using a DLC coated carbon steel pipe and an 18% HCL concentrated solution was filled inside the pipe. A heat jacket was used to maintain the solution at 200 ˚F for 8 hours. This coating was 65 µm thick, hardness of 1 0GPa and had excellent scratch adhesion resistance of more than 30 N. Figure 3 shows the coated pipe before and after test. No damage to the coating was observed.

A more aggressive test involving a sour autoclave was also carried out. This test follows the procedure outlined in the NACE TMO 185 standard which is a well known test condition in the oil and gas industry. The three phase autoclave test (liquid, hydrocarbon, gas) under high temperature and high pressure, has been used extensively to test corrosion performance of coatings. Figure 4 shows the test sample and conditions used for the 30 day test. As can be seen in the gas composition, H_2S and CO_2 are used which are chemicals associated with oil wells and pipelines. The hydrocarbon phase is 100% xylene and the main liquid phase uses DI water. Prior to the test, three indents were made to the coating surface to allow Sub-One to evaluate the coating below the surface and discover if there are any pinholes below the surface which would potentially cause long term corrosion problems.

Figure 4 shows the sample after test and it is clear that no undercutting, hence no delamination of the film has taken place. This result gives confidence that the film is indeed pinhole free all the way through.

Table 1. Wear rate and COF test data

Substrate	Media	COF	Wear rate (mm^3/Nm)
1020 carbon steel	Drill mud	0.04	6.55E-07
	Crude oil	0.03	2.65E-07
	Latex paint	0.03	1/40E-07
	Tap water	0.16	8.10E-07
316 stainless steel	Drill mud	0.02	1.20E-06
	Crude oil	0.05	1.45E-07
	Latex paint	0.1	8.40E-07
	Tap water	0.09	4.05E-07
Uncoated steel	Dry	0.4 - 0.6	> E-04

In summary, the corrosion test data shows InnerArmor coatings acting as an excellent corrosion resistor under various conditions.

Wear resistance

In addition to good corrosion resistance, coating wear properties are also of importance. In particular, the wear rate and coefficient of friction (COF) values have to be as low as possible to reduce any friction losses as media passes inside the pipe. Table 1 shows data for InnerArmor on two different substrates for various media as well as for a bare steel substrate.

The test used here to establish the wear rate and COF data is based upon a linear reciprocating tribometer, where a tungsten carbide ball with a certain force is traversed across the coating surface for a certain distance (standard ASTM G133-02 followed). An optical profiler is then used to determine how much material has been worn during the test. This worn area also known as a wear track is used to calculate the wear rate. Table 1 shows a big improvement to the COF and wear rate for an InnerArmor coated steel substrate compared to the bare steel result. Various liquid based media have also been explored and excellent wear resistant properties have been shown for all media.

Conclusion

An effective solution to the continuing corrosion problems for the oil and gas industry is described where a thick, hard, corrosion and wear resistant DLC based coating (InnerArmor) can be applied to the internal surfaces of components which are used in the oil and gas industry. This coating can be applied safely due to the benign gases used to grow the coating and it can also be applied extremely fast due to the nature of the vacuum deposition technique utilised. Under various aggressive environments the coating has been shown to be pinhole free, very dense and act as a very good corrosion inhibitor to hostile gases such as H_2S and CO_2.

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