Technical Insight

Title: Do thicker coatings provide better corrosion resistance?
Initiated Date: 01-25-17
Submitted Date: 02-20-17
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Background:

Numerous customers use our coating services to solve corrosion issues. The number of unique corrosion environments is infinite, so having a definitive answer for anticorrosive performance in every situation is unreasonable. We have, however, studied a broad range of common corrosion environments, and our Silcolloy and Dursan coatings provide great protection benefits in many corrosive conditions when applied to the proper substrate.

Despite our corrosion tests, which illustrate good performance from our coatings, numerous potential customers consider the thickness of our coatings (which are all less than 2 micrometers) to be too thin for proper anti-corrosive performance. This is from a preconceived notion that to be corrosion resistant, a coating must be thicker. This leads to the question at hand: Do thicker coatings provide better corrosion resistance? As is the case with many questions of corrosion, the answer is complex, but in short, the answer is "it depends". A detailed explanation is provided here.

Goal:

The goal of this Technical Insight is to provide a summary of SilcoTek coating thickness and its relation to corrosion resistance. The intention is not to cover every perceivable corrosive environment, but rather to guide discussion with customers as to why a thicker SilcoTek coating may not necessarily be a better solution for corrosion resistance.

Discussion / Data / Links:

The corrosion process is complex and includes innumerable variables. Luckily, NASA has compiled a wealth of information on the subject on their Fundamentals of Corrosion and Corrosion Control webpage. Corrosion is ultimately defined as "the degradation of a material due to a reaction with its environment". There are numerous ways to combat corrosion from changing the corrosive environment to something more benign (which isn't always an option), to making parts out of expensive, exotic alloys that hold up better to corrosive environments (which is not always practical or cost-effective), or protect the part with a corrosion resistant coating to act as a barrier between the corrosive environment and the substrate.

Where does the idea that "thicker is better" come from?

Many customers that are in the oil and gas, refining, and chemical manufacturing fields are accustomed to paints, epoxies, and wraps that specify the need for a particular coating thickness. These thicknesses can range anywhere from tens to thousands of times thicker than Dursan or Silcolloy, and in general, their belief is that a thicker coating of paints and epoxies will lead to better corrosion resistance. Is this necessarily true? According to International Marine Coatings, a subsidiary of Akzo Nobel, the answer is "yes, however…":

> "*Film thickness can also affect coatings permeability. In general, thicker films delay (but do not stop) the passage of oxygen and water to the steel surface. This is because in all coating films microscopic defects are present which can penetrate to the steel surface and act as conduits for oxygen and moisture. High film thickness can therefore offer a high degree of corrosion protection but this would best be achieved in multi-coat systems rather than in a single coat. High film thickness single coat (or some two coat specifications) also have disadvantages as, subject to coating type and formulation, solvent entrapment may occur which can lead to blistering. Equally, high film thickness may also be a problem on complex structures e.g. ballast tanks and may result in cracking of the coating and subsequent corrosion.*"

With all things equal, a thicker coating provides a longer pathway for corrosive chemicals to penetrate through before reaching the substrate, and therefore more resistance to corrosive environments; however, these thicker coatings can also lead to blistering, cracking, and other issues.

Does thickness influence corrosion with SilcoTek's coatings as well?

We have conducted experiments to investigate the impact of coating thickness on corrosion performance within our coatings' current production thickness ranges. The table below compares our two corrosion-resistant coatings, Silcolloy 1000 and Dursan, at the low end of their thickness output versus the median to high end thickness output, respectively. The test was done by immersing coated coupons in 6M hydrochloric acid under room temperature, for a preset amount of time (ASTM G31 guidelines).

Coating	Thickness range (nm)	Corrosion 24 hours (MPY)	Corrosion 168 hours (MPY)
SL1000 (thin)	250 ~ 320	1.93	65.5
SL1000 (median to high)	750 ~ 1200	0.94	30.8
Dursan (thin)	300 ~ 350	1.18	52.1
Dursan (median to high)	650 ~ 900	1.50	21.5

As can be seen from the table, in the shorter immersion test (24 hours), there was minimal impact of thickness on corrosion rate, whereas in the longer 168-hour test, the thicker coatings showed better performance than their thinner counterparts. The results are not surprising when we consider the role of the coating as a diffusion barrier. With the shorter exposure, both thin and thicker versions exhibit effective barrier characteristics and thus similar resistance; however, as the exposure time increases, the thinner film will be penetrated first, and corrosion will start to accelerate earlier which results in an overall higher corrosion rate.

It should be pointed out that in the study above, the thin and thick films of each coating were produced with the same reaction recipe, and it was only the differences in their CVD micro-environments (shielding effect etc.) that led to the differences in the coating thicknesses. If a thickness increase is achieved through altering a reaction recipe (i.e. temperature, time and/or pressure change), a thicker film may not see the same benefit as the change may affect the intrinsic properties of the coating, and thickness will then no longer be the only factor contributing to anti-corrosive performance.

Why not just go thicker with SilcoTek coatings?

Assuming the deposition parameters have been optimized for the best corrosion resistance available, why doesn't SilcoTek grow even thicker coatings by simply adding more cycles? Theoretically, that would allow us to further increase the corrosion resistance of our coatings. Unfortunately, just like the case with paints and epoxies, there are physical hurdles that must be taken into consideration to deposit thicker coatings.

A trend in CVD thin films is that stresses are induced into coatings that become worse as the film grows thicker.[1] As these stresses, whether tensile or compressive, get large enough, cracks or folds in the coating will occur. This will lead to either substrate exposure and/or delamination issues as shown in Figure 1. Literature shows that in an amorphous silicon deposition onto a silicon wafer, 2 micrometers is an upper limit for film thickness without the introduction of cracks or buckling.[2] Others have painstakingly worked to get amorphous silicon coatings up to 12 micrometers thick on glass.[3] No studies were found to determine the upper limit on steel; however, unlike the thermal CVD coatings we provide at SilcoTek, both studies above utilized PECVD, which allows for more flexibility and better film stress control. With the current design of our CVD reactor, it will be very difficult to grow a single film over 2 micrometers without encountering issues such as cracking, delamination, or dust particle generation.

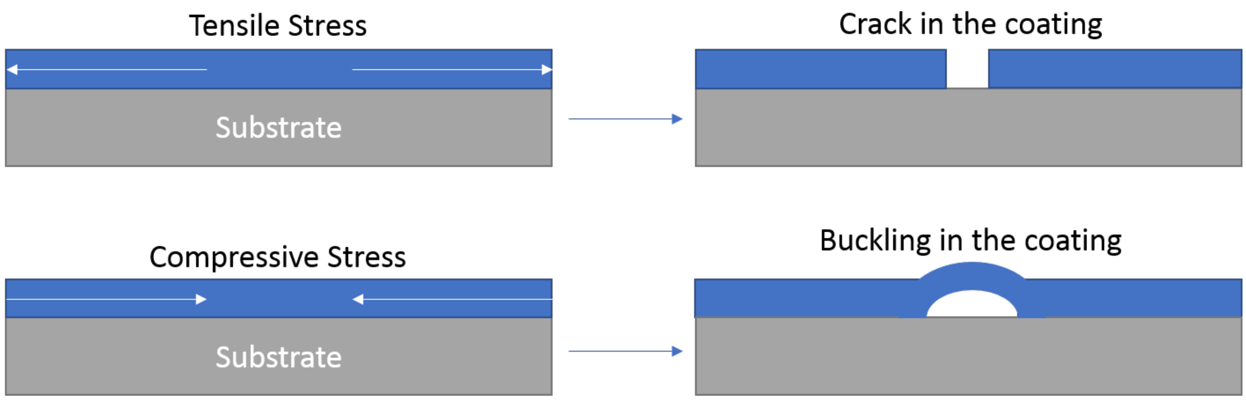

Figure 1 Schematic of the stress relief mechanisms of both tensile and compressive stresses in a thin film.

Figure 2a shows an example of film delamination in a thick Silcolloy coating, as compared to a literature reported PECVD amorphous silicon coating (2b) that has also shown delamination due to high tensile stress. SilcoTek currently has no film stress data for its coatings, but efforts are underway to quantitatively evaluate them. The similarities in structure shown in the optical micrographs reinforce that stress is a real concern when trying to deposit thick films. There are many complex considerations when applying a thicker deposition, and although it seems like a simple solution, thicker film deposition may actually introduce defects that could result in poor anti-corrosive performance.

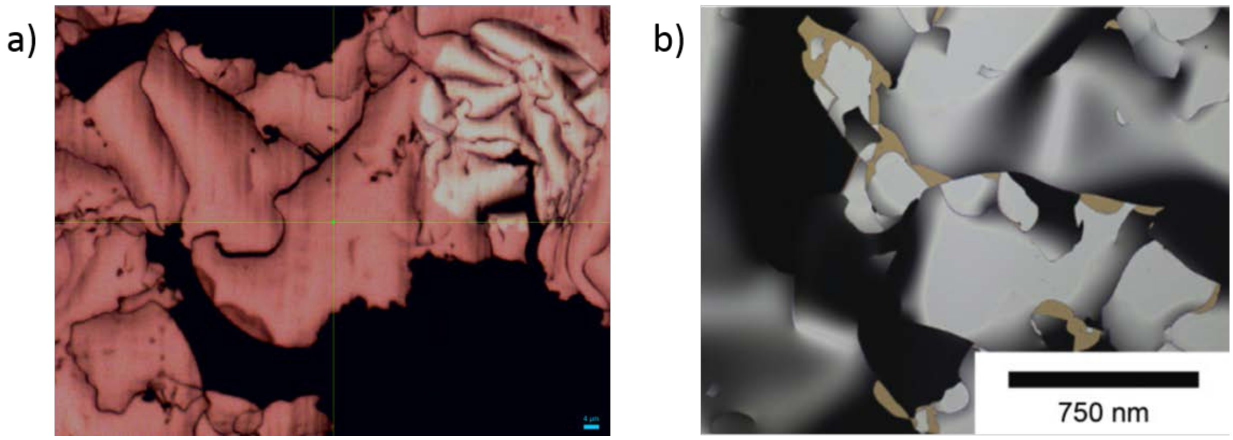

Figure 2: Optical micrograph comparison between (a) a SilcoTek coating that delaminated from the substrate via tape adhesion testing and (b) a high tensile stress PECVD amorphous silicon film that was deposited on a silicon wafer.[4] The black area in the SilcoTek coating and beige area in the PECVD film are voids and cracks in the coating that are the result of film failure due to stress. The coating from PECVD had a measured tensile stress of 450 MPa. The stresses in SilcoTek's coatings are currently being investigated.

Rather than focusing our efforts on growing thicker Silcolloy or Dursan films, SilcoTek's researchers are investigating ways to improve existing film quality, reduce film defects, and further strengthen interfacial bonding integrity. These improvements will help the coatings achieve higher corrosion resistance without necessarily making them thicker. Think of the coatings as a corrosion barrier wall. If the wall is constructed of lower quality materials, you can make it bigger and thicker and it will serve its purpose, or you can upgrade your construction materials and have a better, denser wall to accomplish the same goal. With a focus on fundamental film deposition optimization, we have been applying the approach of process optimization which has already led to several upgrades to the Dursan and the Silcolloy coatings in the past two years. This work will continue, and please look out for our future Technical Insights to keep informed.

Conclusion:

Do thicker coatings provide a better corrosion resistance to the surrounding environment? With all things being equal in the coating, it can. It will create a longer diffusion barrier and restrict corrosive compounds from interacting with the substrate causing corrosion to occur. However, creating a thicker coating has numerous technical hurdles including:

- Stresses induced as the film grows thicker which can lead to film cracking and delamination
- Creation of potential interfacial failure sites and the possibility of more stresses throughout the coating
- Dust particle generation
- Growth mechanisms that may impose an upper limit on coating thickness
- Extended deposition time that leads to metallurgical property change and cost increase

While overcoming these issues to develop thicker coatings is an option to achieve better corrosion resistance, the approach we have taken and will continue is to deposit a higher quality and more consistent coating to further improve the corrosion resistance of SilcoTek coatings.

References:

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