IMPROVING THE RELIABILITY OF ANALYTICAL AND SAMPLING SYSTEMS IN CHALLENGING AND CORROSIVE ENVIRONMENTS

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ABSTRACT

Process analyzers and process sampling systems often times are exposed to challenging environments both internally and externally. Many sample streams are corrosive or contain active compounds that reduce equipment lifetime or require extended preventative maintenance. Some systems are exposed to environments such as sea water, which cause rapid deterioration of equipment, requiring extra costs to keep them operating. For systems that are required to give accurate, reliable and repeatable data in such conditions, the cost of upkeep and maintenance is much larger than systems in more benign environments. This paper reports on data using wear resistant, chemically inactive surface treatment to greatly reduce maintenance cycles and improve analytical reliability.

INTRODUCTION

This paper presents laboratory corrosion and chemical inertness test results for a variety of chemically deposited coatings used by the process analyzer manufacturers. Through improvements in chemical composition, the properties of existing and new coatings will be evaluated in environments common to the petrochemical, refining and off-shore industries.

Process analyzers used in the refining, petrochemical and off-shore environments are exposed to a variety of potentially damaging compounds. Sulfuric acid, hydrochloric acid, caustic streams and salt-water exposure are environments that will be evaluated with stainless steel and stainless steel surfaces treated with silicon and carboxysilane materials.

In addition to corrosion resistance, process analyzers in these applications must also maintain chemical inertness for the sampling of reduced sulfur compounds.

DISCUSSION

In choosing a substrate enhancing coating, selection of material properties is important. Different surface treatments will have different useful ranges of exposure and chemical reactivity. For applications where inertness to reduced sulfur compounds, for example H_2S, is required, modified amorphous silicon treatments are ideal. Applications with particulate and harsh environments requiring part-per-million stability of reduced sulfurs, a carboxysilane material can be used.

Using Auger Spectroscopy, the atomic composition of amorphous silicon (Figure 1) and a carboxysilane coating (Figure 2) are analyzed. The amorphous silicon coatings are usually surface enhanced to deliver low part-per-billion inertness to common active compounds. The silicon substrate, though chemically inactive, has a low level of wear resistance. The carboxysilane surface treatment is a uniform composition of silicon, oxygen and carbon throughout the matrix. Though less chemically inert, it maintains a very corrosion resistant and wear resistant layer. Table I lists the physical properties of both coatings. Both of the coatings diffuse 400 to 500 angstroms into the lattice of the steel which provides for an excellent adherence to the surface.

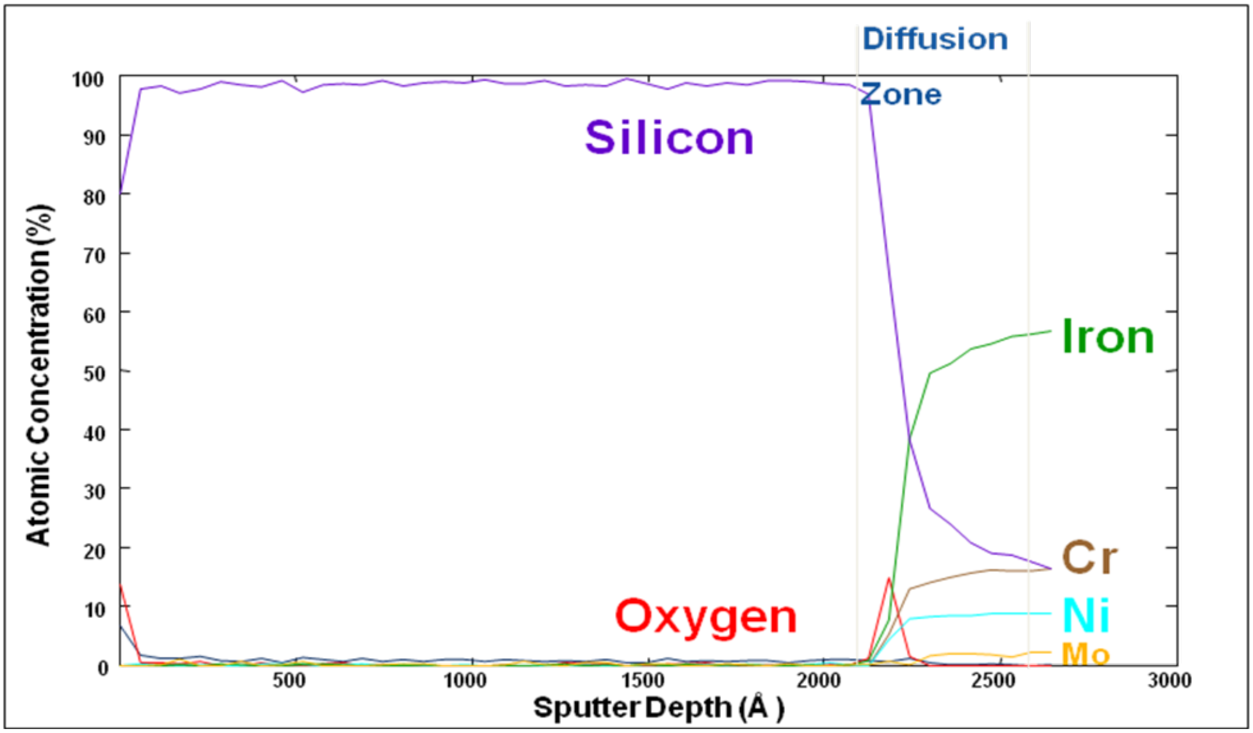

FIGURE 1: AUGER DEPTH PROFILE OF SILICON COATED STAINLESS STEEL

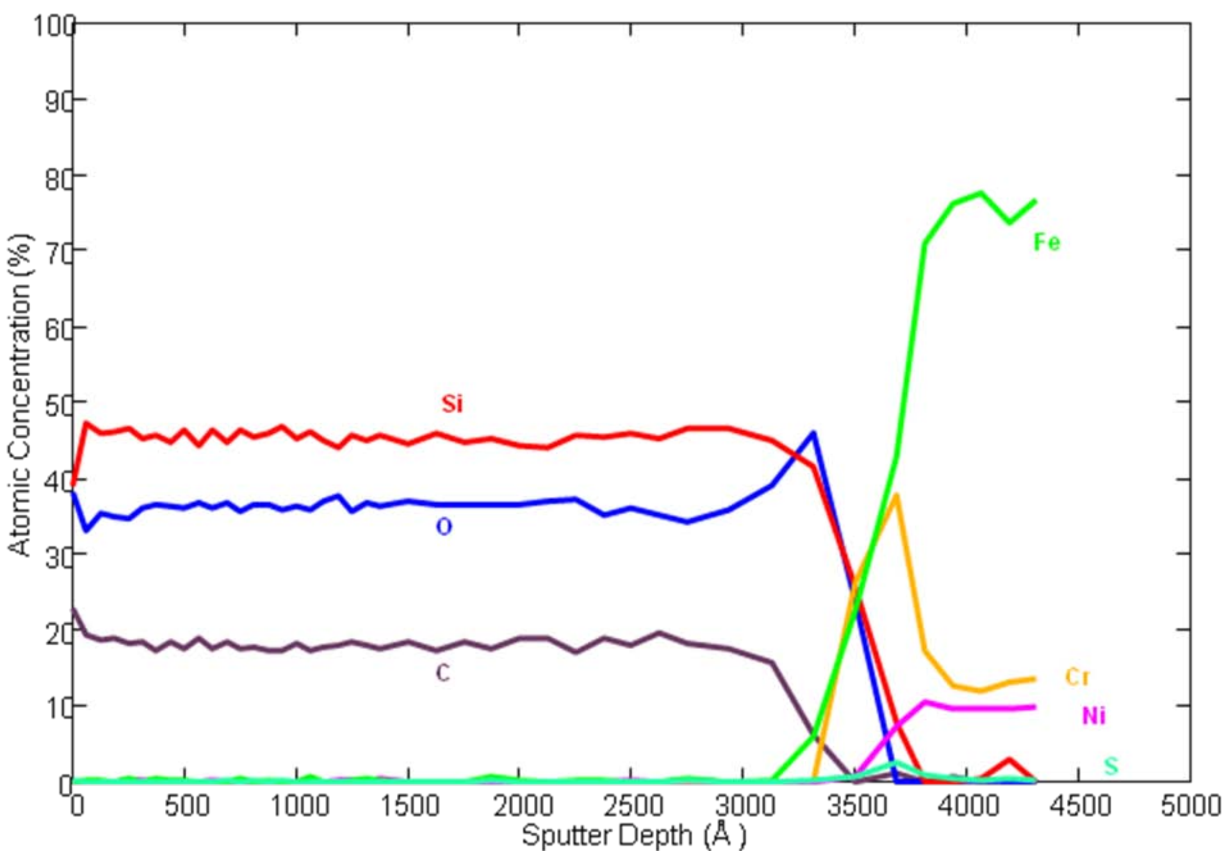

FIGURE 2: AUGER DEPTH PROFILE OF CARBOXYSILANE COATED STAINLESS STEEL

TABLE I: PHYSICAL PROPERTIES OF COATINGS

Coating	Silicon: SilcoNert™	Carboxysilane: Dursan™
Maximum Temperature	1000°C	450°C
Minimum Temperature	-196°C	-40°C
Low pH limit	0	0
High pH limit	7	10
Thickness	500nm	2000nm
Adhesion	Excellent	Excellent

EXPERIMENTAL

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Chloride environments and chloride containing streams can greatly reduce the lifetime of process systems. Coatings, paints and costly super alloys have been used to increase the lifetime of components in salt water and/or chloride containing environments. Table II provides the results obtained from ASTM G31 testing. This method is an immersion test for 24 hours in a 6M HCl (18%) solution at room temperature and pressure. After immersion, differential weighing allows the amount of material loss to be determined. The sample size for each configuration was 3 samples. The amorphous silicon coated stainless steel shows greater than 20 times the resistance of non-treated stainless steel in these environments and the carboxysilane treatment creates greater than 200 times the resistance. Any loss in the coated samples occurred as a result of pitting corrosion. The pitting is an indication that there are still pin-holes present in the surface which allowed corrosive attack to initiate.

TABLE II: WEIGHT LOSS AFTER 24 HOUR EXPOSURE TO 6M (18%) HCL

24hr; 6M HCl; 22ºC	**304 SS**	**Silicon coated**	**Carboxysilane coated**
MPY (mils-per-year)	389.36	16.31	1.86
Improvement Factor	---	23.9	209.8

Another factor for consideration is the wear resistance of coatings applied to analytical sampling equipment. This factor is critical, especially in applications where there mechanical rubbing such as valve movements or physical abrasion like ~~is a great deal of~~ particulates moving through the sampling equipment at high velocity. ~~The~~ Valve seat movements or particulate in these applications can quickly erode a soft coating such as silicon creating sites for adsorption to occur. Table III summarizes the data obtained from wear studies conducted on both non-treated and treated surfaces. Data was generated using a pin-on-disk tribometer (Nanovea, Irvin, CA). The experiment uses a flat plate loaded onto the test rig and the indenter applies a precise force to the surface. The plate is then rotated and forces are measured between the pin and the disc. Results from this experimental method can produce wear behavior and friction coefficients of the plate surface[1]. Results from this study demonstrate that the carboxysilane coatings wear less than untreated steel and silicon coated surface. The improved wear resistance as a result of the coating will lead to longer lifetimes of system components in extreme environments.

TABLE III: PHYSICAL PROPERTIES OF COATINGS

Pin on Disc; 2.0N	**316 stainless steel**	**Carboxysilane coated 316 stainless steel**	**Silicon coated 316 stainless steel**
Wear rate ($x10^{-5} mm^3/N\ m$)	13.810	6.129	2
Improvement Factor over SS	---	2 times	1/3 times

For analytical systems used in sampling and transfer of sulfur containing species, system inertness must be addressed when stainless steel components are used. In most refining and petrochemical streams, analysis in the ppm level they are acceptable. Figure 3, demonstrates that even at concentrations of 50ppm, hydrogen sulfide sampling requires passive surfaces[2]. In this analysis sample cylinders tested were either sourced from the manufacturer, non-coated, or treated with a carboxysilane, commercial name Dursan™. Figure 4, demonstrates the need for coating during the sampling, storage and analysis of part-per-billion levels hydrogen sulfide. In critical applications, the ultimate inertness of components is enhanced using silicon based coatings at the cost of physical durability.

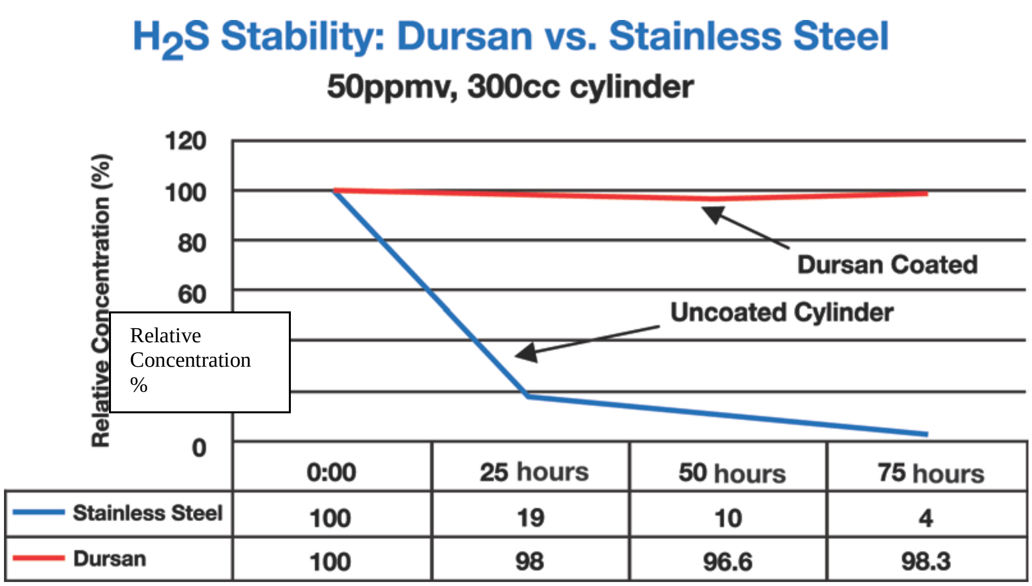

FIGURE 3: SULFUR COMPOUNDS AT 50 PARTS-PER-MILLION IN CARBOXYSILANE TREATED STAINLESS STEEL CONTAINERS VERSUS NON-TREATED CYLINDER

In Figure 3 and 4, the degradation of hydrogen sulfide on bare stainless steel is rapid and irreversible: Both at 50ppm and 17bbp levels, H_2S is lost within 24 hours.

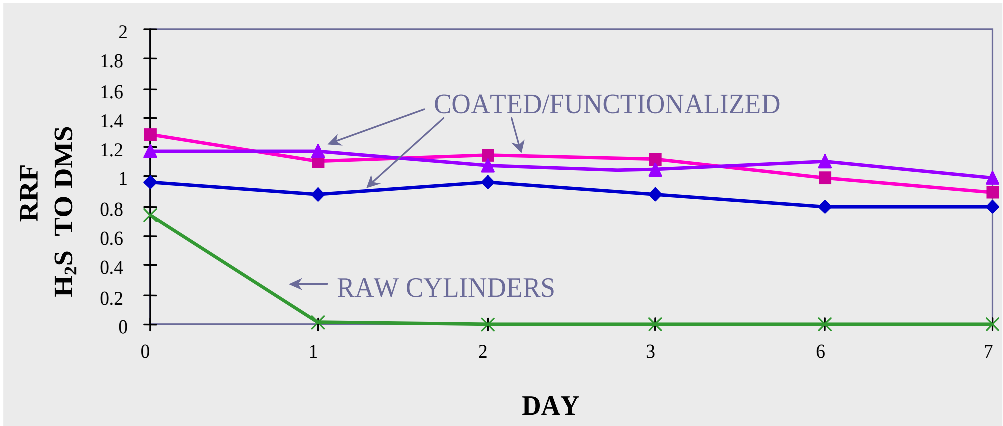

FIGURE 4: SULFUR COMPOUNDS AT 17PPBV IN AMORPHOUS SILICON TREATED STAINLESS STEEL CONTAINERS

Effect of passivation on sulfur storage and transport has consistently been raised. Passivation is a technique that is based on the assumption that if all active areas of a transport vessel or storage vessel are taken up by sulfur compounds, then they are made inert to sulfur compounds. There have been studies to support this at low temperature for gas phase transport through low surface area regulators[3]. It was demonstrated that purging a component with clean gas can reduce the inertness of the passivation with measurable impact occurring within 1 day and complete within 1 week. Additional data in the same study also demonstrate that heated stainless does not passivate and complete adsorption of sulfurs will occur no matter the conditions and previous exposure to sulfur compounds.

In work to test the stability of sulfur compounds during static sampling, as in sample cylinders, the use of gases such as silane (SiH_4) along with multiple day exposure to 5000ppm H_2S was required to create a passive cylinder for storage[4]. Much of the data in these studies was done to demonstrate stability for the use of creating low-level standards.

Commercially available inert coated components have eliminated the need for passivation and are now recognized as a "use out of the box" solution to sulfur sampling and transport. This eliminates the need for working with dangerous materials such as high concentration H_2S or pyrophoric gases such as silane. The value delivered by coating solutions cannot be taken for granted in comparison to passivation techniques which increase the risk of obtaining poor analytical results.

A surface that is hydrophobic is critical in refining and petrochemical applications. Many of the streams are very dry but an upset in process conditions will lead to moisture in the sampling system. This moisture will adversely affect analysis because of the polarity of the water in the system. The faster a system can "dry" of any moisture, the faster the analytical system will begin to generate reliable data. Figure 5, shows images of water droplets applied to 304 stainless coupons as well as coated 304 stainless surfaces. The coatings impart a hydrophobic characteristic to the stainless steel substrate. The hydrophobic surfaces are easier to purge free of water. This is critical in refining and petrochemical operations when upsets occur, as moisture in analyzer systems lead to poor and unreliable data.

FIGURE 5: COATING OF 304 STAINLESS RESULTS IN ABILITY TO INCREASE HYDROPHOBICITY

CONCLUSION

Coatings are well accepted as a means to improve analytical system accuracy and durability in demanding applications. To select the proper coatings, properties such as acid exposure, particulate exposure and the needs for chemical inertness must be know. When coatings are properly matched to the physical and chemical demands of an application, years of accurate and reliable results can be expected.

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