

PROTECTIVE CHEMICAL VAPOR DEPOSITION COATINGS FOR STAINLESS STEEL SURFACES

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ABSTRACT

A growing application area is the use of protective coatings to reduce corrosion of stainless steel components exposed to hydrochloric acid (HCl) and sea water. In this presentation discussion will be focused on chemical vapor deposition (CVD) coatings for protection against corrosion caused by HCl and salt environments.

Initial discussion will be on the process of applying CVD coatings. The CVD coatings discussed in this presentation are amorphous silicon coatings developed specifically for stainless steel. Examples will be shown of application of CVD coatings to a wide variety of geometries and steels of varying composition.

The importance of the ruggedness and durability of the CVD coatings will be evaluated. Advantages and disadvantages of CVD coatings to solve corrosion problems versus metallurgical solutions will be discussed.

Data comparing the resistance to corrosion by HCl and sea water of a coated stainless steel surface versus non-coated stainless steel will be given. Discussion will focus on using the CVD coatings for reducing maintenance costs and lowering materials cost by using a coated stainless steel versus expensive high nickel alloys of stainless steel in HCl and salt service.

Keywords: silicon, chemical vapor deposition, coating, hydrochloric acid, sea water, corrosion, stainless steel

INTRODUCTION

The annual cost of metallic corrosion in the U.S. totals \$276 billion¹, or more than 3% of the US gross domestic product. Corrosion impacts many sectors of the economy, from infrastructure, utilities, and transportation to government and industry. Industry is especially susceptible to high corrosion costs, due to exposure of facilities and equipment to both aggressive process chemicals and ambient weather conditions. The total annual direct cost of corrosion to U.S. industry is \$17.6 billion¹. Figure 1 breaks down costs of corrosion by industry.

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Figure 1
Costs of Corrosion to U.S. Industry
(\$ billion)

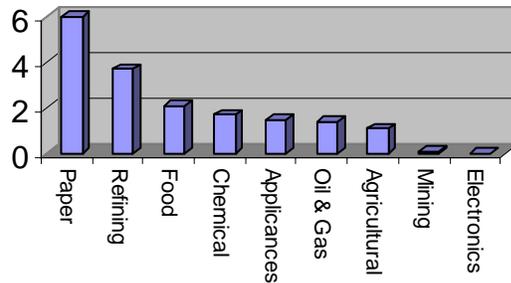


FIGURE 1 - Cost of corrosion to Industry in the United States

Methods available to control industrial corrosion are limited to corrosion-resistant alloys, barrier coatings, cathodic protection, and corrosion inhibitors. When properly applied, each method can be effective in slowing corrosion, but each has limitations as well. For example, some coatings are inexpensive, but require rigorous inspection and/or frequent reapplication. Corrosion-resistant alloys can provide exceptional corrosion protection, but can be prohibitively expensive. Some alloys require significant process redesign, increase operating cost, or generate hazardous waste.

Silicon based coatings are a new class of performance coating offering up to an order of magnitude improvement in corrosion resistance, relative to existing processes. Silicon maintains high dimensional tolerances, demonstrates extreme heat capability, and exhibits leak-tight system performance in steel, stainless steel, and alloy systems.

This study presents laboratory corrosion test results and potential cost savings of applying this alternative corrosion-resistant barrier coating technology. Silicon was applied using a chemical vapor deposition (CVD) process, designed to improve corrosion resistance of steel, stainless steel, alloys, glass, and ceramics. The unique non line-of-sight CVD process produces a flexible amorphous silicon layer that diffuses into the base metal lattice. The layer will conform to the most intricate surface while maintaining high dimensional tolerances. The amorphous silicon will deform with tubing surfaces, allowing leak-free seals or radius bends.

EXPERIMENTAL METHODS AND RESULTS

Deposition of the silicon layers described in this study were achieved through the thermal decomposition of silane. In this process, items to be treated are cleaned to remove any oils and materials that may outgas during the process. Items are then loaded into a vacuum chamber, heated to 400C under vacuum. Once vacuum and heat in the chamber are uniform, silane is backfilled into the chamber. The silane then decomposes into silicon which diffuses into the lattice of items to be treated and grows into a layer over the surface. Figure 2 is a graphical representation of chemical composition achieved through Auger Electron Spectroscopy. The silicon layer is present as an abundant surface coating over the steel substrate used in this example. At the interface of the steel substrate the silicon can be seen decreasing while the iron, chrome, nickel and steel increase as the sputter enters the substrate. The silicon diffusion into the surface creates a very strong physical adhesion of the silicon coating on the substrate surface.

The silicon deposition technique can be applied to a variety of metals such as stainless steels, high chrome nickel “superalloys” and even aluminum. Materials such as copper, brass and bronze cannot be used in the process as outgassing and poor deposition of silicon occur.

The process of application can be applied to items of various geometries as long as they are manufactured of an acceptable material and can be held in the vacuum chambers. Common items such as coils of tubing, fittings, valve bodies, regulator bodies have been coated using similar deposition processes.

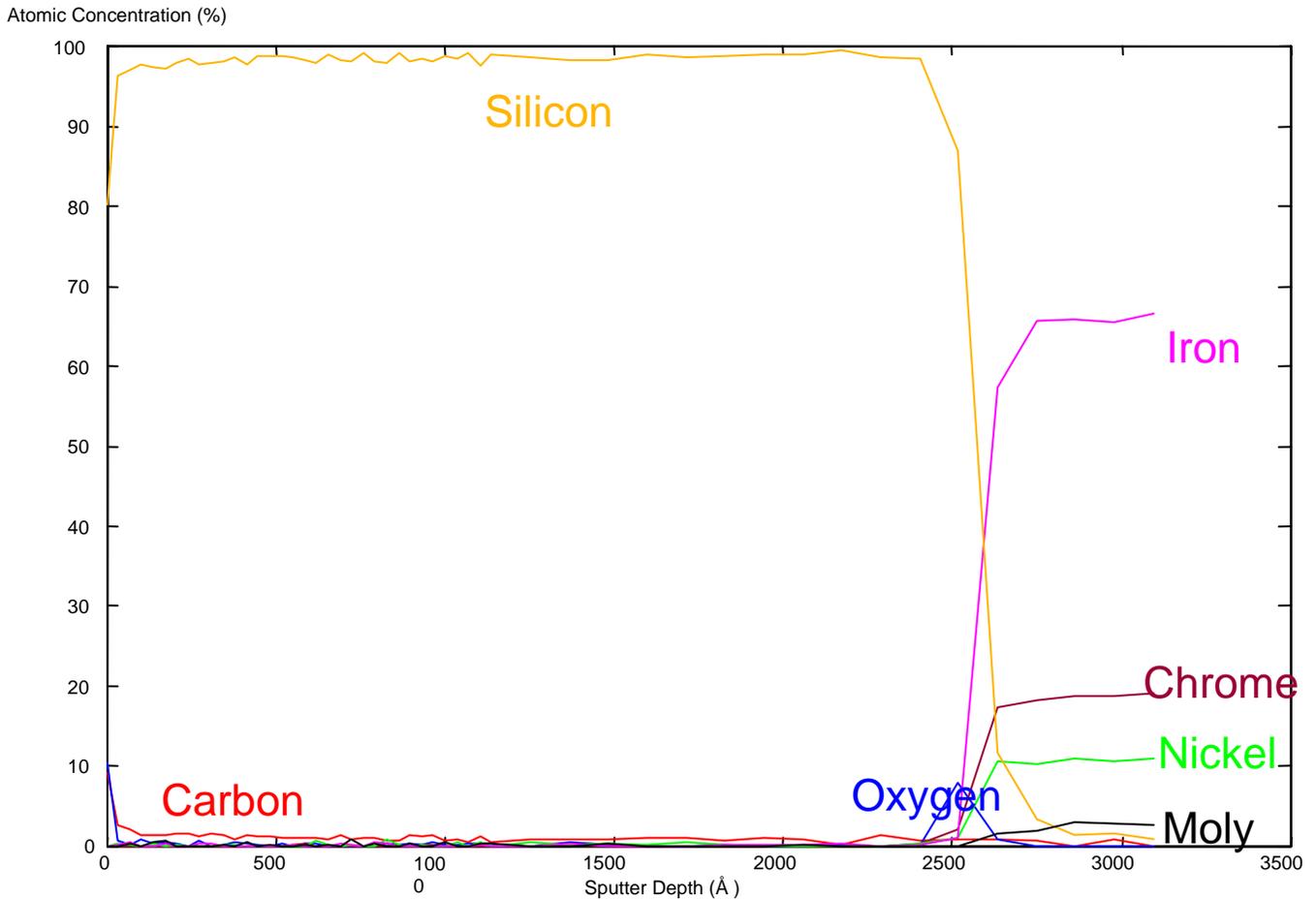


FIGURE 1 – Auger Electron Spectrograph of silicon coated 316L stainless steel

ASTM G48, Method B: Ferric Chloride crevice corrosion

Corrosion testing was conducted on the silicon treated 316L stainless steel and untreated type 316L steel according to ASTM G 48, Method B (72-hour ferric chloride crevice corrosion testing²), demonstrates corrosion of the treated stainless steel is reduced by an order of magnitude, as measured by weight loss. Figure 3 displays the differences in corrosion rate for silicon treated 316L stainless steel and untreated 316L stainless steel coupons. Figures 4 and 5 are photographs of treated and untreated coupons respectively after exposure to the test conditions and environments. 316L stainless steel shows significant crevice corrosion while the silicon treated coupon shows only minor pitting after 72 hour ferric chloride exposure (ASTM G 48, Method B)²

Figure 2
ASTM G48, Method B

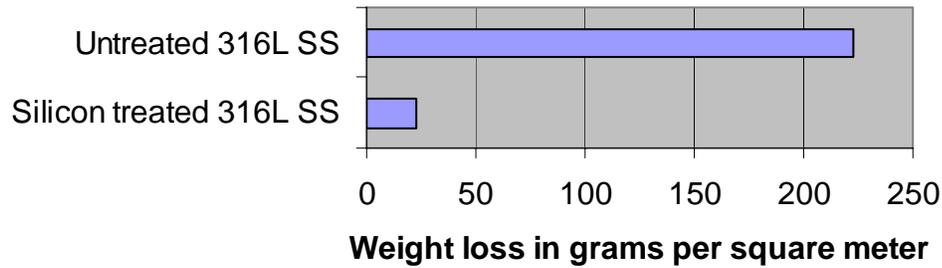


FIGURE 3 – Weight loss of samples on exposure to 6N ferric chloride solution for 72 hours



FIGURE 4 – Photograph of Silicon Treated 316L SS after 72 hour exposure to 6N ferric chloride

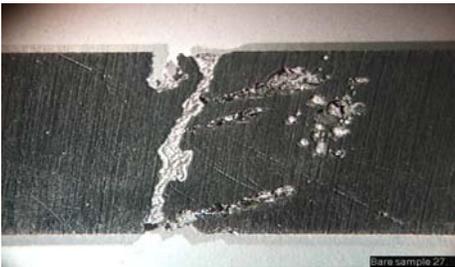


FIGURE 5 – Photograph of Untreated 316L SS after 72 hour exposure to 6N ferric chloride

ASTM G61: Cyclic Polarization

Table 1 summarize electrochemical data produced from testing of Silicon treated coupons in neutral and acidic solutions, (according to ASTM G 61)². The silicon treatment reduces corrosion rates by up to 50 fold over untreated 316L stainless steel and 304 stainless steel.

**TABLE 1
CYCLIC POLARIZATION DATA OF DIFFERENT PH SOLUTIONS**

Ec = corrosion potential
Ic = current density at Ec
Eb = pitting potential
CR = corrosion rate

Neutral solution; 3000ppm Cl-				
Sample	Ec, mV	Ic, uA/cm ²	Eb, mV	CR, mpy
316 L	-418	0.096	370	0.04
Silicon Coated 316 L	-533	0.002	1460	0.0009
304 L	-435	0.145	361	0.06

Acidic Solution; 1N H ₂ SO ₄ ; 3000ppm Cl-				
Sample	Ec, mV	Ic, uA/cm ²	Eb, mV	CR, mpy
316 L	-662	1.920	370	0.83
Silicon Coated 316 L	-843	0.123	927	0.05
304 L	-639	2.650	587	1.14

ASTM B117: Salt Spray Testing

4000-hour salt spray testing demonstrates no impact on the silicon coated 316L stainless steel while there is some oxidation and rusting on a non-treated 316L stainless steel coupon². Figures 6 and 7 are photographs of exposed coupons after the 4000 hour salt spray exposure.



FIGURE 6 - Photograph of silicon treated 316L SS after 4000 hours salt spray exposure



FIGURE 7 – Photograph of untreated 316L SS after 4000 hours salt spray exposure

SUMMARY

A silicon treatment extends the lifetimes of existing steel and steel alloy systems, while maintaining high dimensional tolerances, high temperature capability, and leak-free conditions, making it an ideal treatment for: Process tubing and fittings; Valves; Reactors; Gas transfer and delivery systems; Nozzles; Stack gas monitors; Analytical testing equipment.

A silicon treatment is effective in acidic or salt corrosive environments, in which the user demands extended service life for an existing process without using high-priced alloys. Silicon is highly effective protection for stainless steel exposed to hydrochloric acid, nitric acid and corrosive marine environments.

A silicon treatment has extended the life of process systems in oil and gas production, oil refining, petrochemical processing, aerospace equipment, food & beverage processing, and laboratory testing.

Figure 8, a relative comparison of lifetime costs in a typical process system, shows silicon treatment can reduce the overall lifetime cost of the system by hundreds of thousands of dollars. While the initial cost of an unprotected stainless steel system is lower than a comparable Silicon system, the overall lifetime cost, considering replacement cost due to corrosion, is nearly double a silicon treated system. Conversely, high performance alloy systems offer superlative corrosion performance, but the initial material cost can be up to 10 times greater than a comparable stainless steel system.

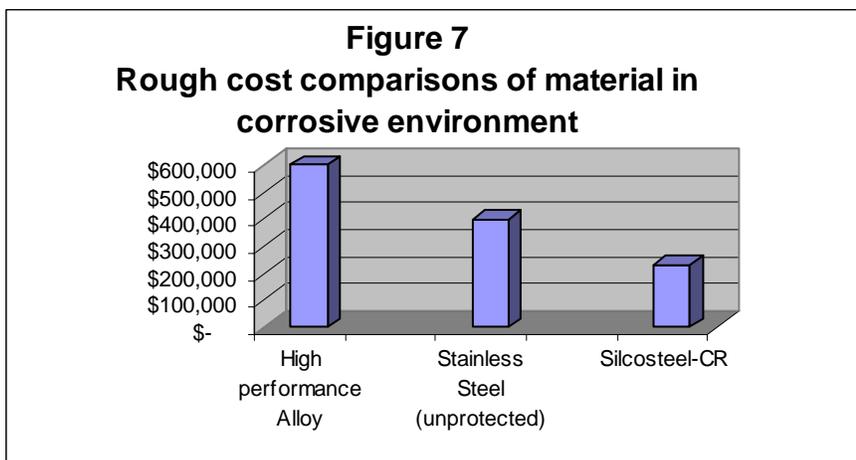


FIGURE 8 – Comparative costs of different materials applied to corrosion prone application

CONCLUSION

Test data has shown that a silicon CVD treatment is effective in extending the corrosion resistance of stainless steel process systems while reducing overall system maintenance cost. Because silicon treatments can be applied to existing process components, process equipment life is extended without significant re-engineering.

REFERENCES

(1) Koch, Gerhardus; Brongers, Michiel; Thompson, Neil; Virmani, Y; Payer, Joe; Report # FHWA-RD-01-156, "Corrosion Cost and Preventive Strategies in the United States"; Office of Infrastructure Research and Development, Federal Highway Administration, McLean, VA. 2001

(2) Zamanzadeh, Mehrooz; Bayer, George; Rhodes Geoffrey; Smith, David; Higgins, Martin; "Laboratory Corrosion Testing of a Chemical Vapor Deposited Amorphous Silicon Coating"; Matco Associates, Inc. Pittsburgh, PA; Restek Corporation, Bellefonte, PA. 2005