A unique CVD coating for process and analytical pathways

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Restek Performance Coatings

Outline

- Process
- Applications
- Performance data

Chemical Vapor Deposition Process

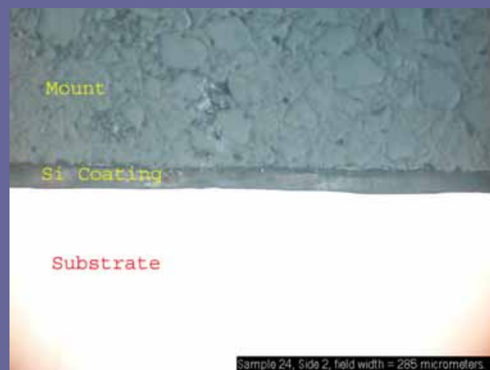
- Thermal decomposition of silanes
- Amorphous silicon deposition
- Functionalization of surface if desired
- Process
  - Clean (caustic surfactant; ultrasonic)
  - Vacuum
  - 400ºC
  - Applied in vessel or oven chamber
- Total 3D coverage, not line-of-sight
- High volume (size dependent)

Photo in lower right shows one of our process ovens. Chamber size is 30” x 24”.

Application Areas

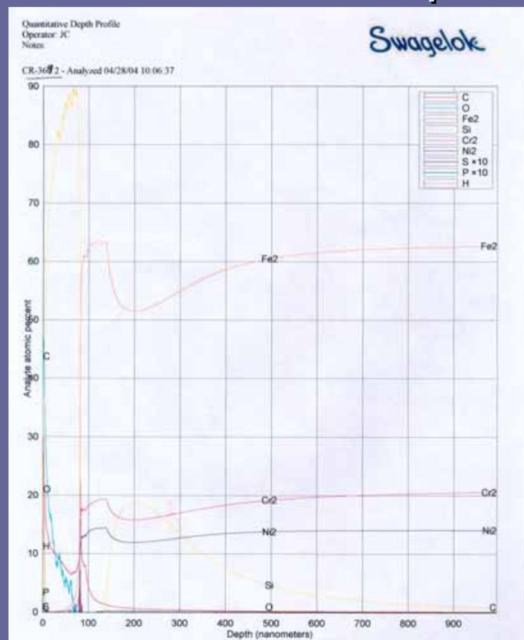
- Anti-Corrosion
- Analytical (passivation)
  - Transfer lines
  - Instrumentation parts
  - GC consumables
- Ultra-High Vacuum
- Anti-Coking

Coating Cross Section



Optical micrograph shows a thicker (ca. 10um) coating on steel cross section. Coating thicknesses can be controlled from 300A to 10um.

Silcosteel GD-OES Depth Profile



Using Glow Discharge Optical Emission Spectroscopy, a depth profile with real-time atomic percentage during the sputter shows atomic mixing of iron and silicon. This intimate mixing explains the absence of delamination with the silicon coatings. This is unlike polymeric coatings and provides a significant advantage over them.

Substrates

- Tubing:
  - 0.004” to 0.5” ID
  - 2000+ ft. continuous lengths
- Complex geometry parts (inside and out)
  - Fittings, valves, frits, custom parts
- Stainless steels, steels, alloys, glass, ceramics

Substrates with Issues

- Nickel (most high-performance alloys will coat)
- Aluminum*
- Copper
- Brass
- Gold, Silver-plated components
- Magnesium
- Elastomers

*heat-dependent

“Rainbow” coatings are approximately 1200A. Blue coatings range from 300-400A. Matte silver coatings are 1-10um. Tubing is generally coated only on the inside, whereas 3-dimensional parts are coated throughout all exposed surfaces, inside, outside, through pores and on fine structure.

Coating Appearances (cont.)

This coated vacuum chamber has an 8” flange and is 18” long. Valve bodies can be coated.

Coating Appearances (cont.)

A six-way UHV cross. 2 ¾” flanges.

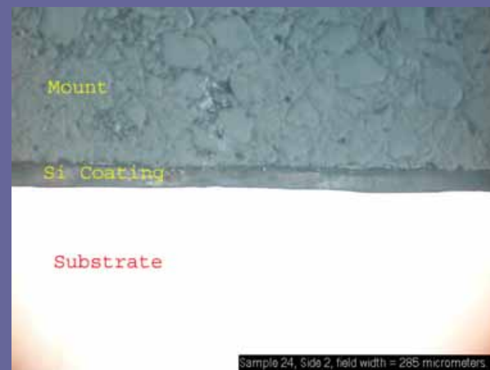
Examples of customer jobs, showing reproducibility between and within lots.

Corrosion Resistance

- Stainless steel surfaces susceptible to attack from hydrochloric acid, sulfuric acid and nitric acid
- Corrosion resistant deposition is a heavier amorphous silicon layer insoluble in hydrochloric acid, sulfuric acid and nitric acid

Corrosion Resistant Data (cont.)

- External Evaluation
  - Certified corrosion engineers (Matco)
  - Spectroscopic analysis
  - Mechanical testing
  - Electrochemical
    Cyclic Polarization in neutral, acidic, alkaline
  - Atmospheric corrosion
    - ASTM moisture condensation
    - Salt spray ASTM B117
  - Stress corrosion cracking ($MgCl_2$; ASTM G36)



We use external experts for most of our data generation. For corrosion, several standardized tests were performed by Matco corporation.

CR Data

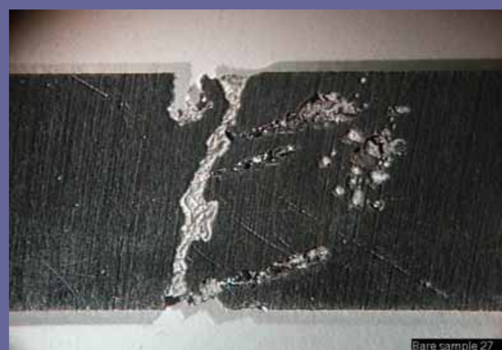
- ASTM G45 method B; Pitting and Crevice Corrosion
  - 6% Ferric Chloride solution
  - 72hrs, 20ºC
  - Gasket wrap

Sample	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Weight Loss (g/m^2)
Silco-CR Sample 17	10.4105	10.3710	0.0395	19
Silco-CR Sample 28	10.1256	10.0743	0.0513	25
Silco-CR Sample 47	10.1263	10.0742	0.0521	25
Bare Sample 27	10.0444	9.5655	0.4789	231
Bare Sample 34	10.1265	9.6923	0.4342	209
Bare Sample 37	10.1007	9.6276	0.4731	228

Using a tight gasket wrap in a corrosive chloride environment, the Silcosteel-CR coating outperformed an uncoated coupon 10-fold.

ASTM G45 B (cont.)

- Bare 316L Stainless Steel coupon showing severe crevice corrosion



The location of the tight gasket is obvious in this photo of the uncoated coupon. Severe pitting corrosion is also present.

ASTM G45 B (cont.)

- Corrosion resistant treated sample showing no crevice corrosion only slight pitting corrosion

This is a Silcosteel-CR coupon after testing.

CR Data (cont.)

- ASTM G-61; Cyclic Polarization Electrochemical Corrosion Testing
  - Acid, neutral, basic aqueous solutions with varying Cl^- ion concentrations (100, 3000, 5000ppm)
  - EG&G VersaStat System, 23ºC
  - 316L vs. Silcosteel®-CR on 316L, 304L

Neutral solution;
3000ppm Cl^-

-CR vs 316L Raw: 50x improvement

Sample	Ec, mV	Ic, uA/cm^2	Eb, mV	CR, mpy
316 L	-418	0.096	370	0.04
Silcosteel-CR 316 L	-533	0.002	1460	0.0009
304 L	-435	0.145	361	0.06

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

CP testing in neutral solution with 3000ppm Cl- gave a 50-fold improvement over an uncoated coupon.

ASTM-G61 (cont.)

Acidic Solution; 1N H_2SO_4; 3000ppm Cl^-

-CR vs 316L Raw: 10x improvement

Sample	Ec, mV	Ic, uA/cm^2	Eb, mV	CR, mpy
316 L	-662	1.920	370	0.83
Silcosteel-CR 316 L	-843	0.123	927	0.05
304 L	-639	2.650	587	1.14

In acidified solution, there was a 10-fold improvement over an uncoated coupon.

Benefits

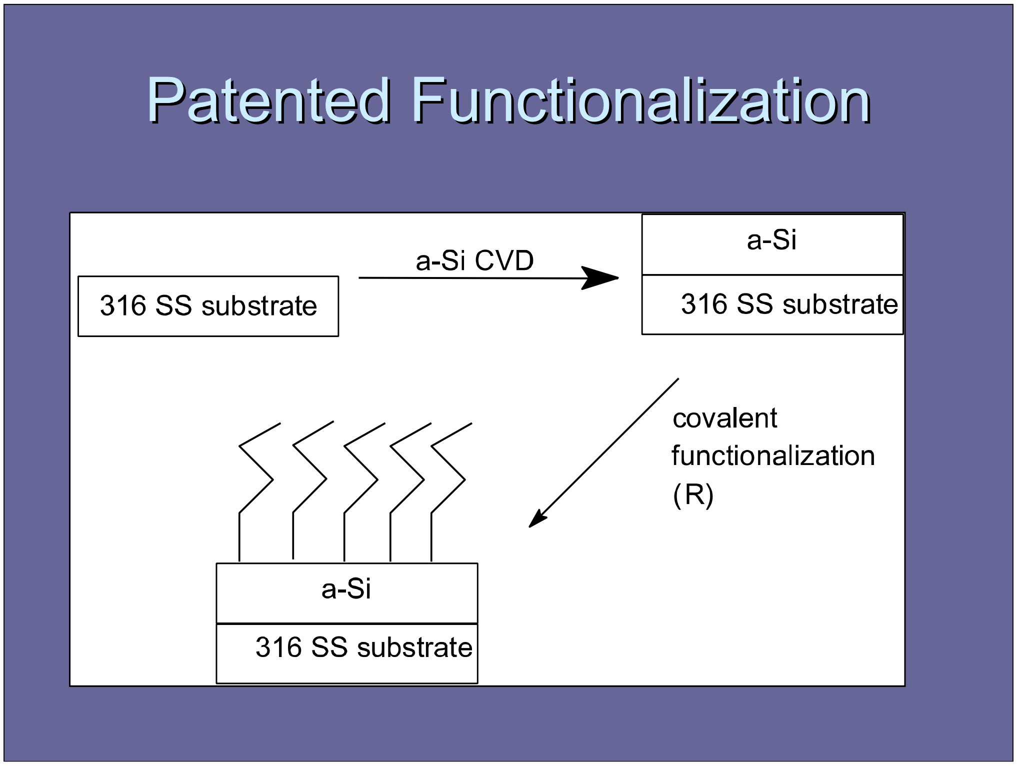
- To extend lifetimes of equipment exposed to corrosive environments and/or process streams
- Protection of high value equipment in corrosive environments

Benefits of improved anti-corrosive performance.

Inertness: Amorphous Silicon and Surface-Functionalized Amorphous Silicon

- Both coatings are based on Chemical Vapor Deposition process. Similar physical properties
- Amorphous silicon (Silcosteel®)
  - recommended if level of active compounds is 10-50 ppm or higher
- Functionalized (Siltek™ / Sulfinert®)
  - ideal for extremely low-level, <1ppb and up, transfer and storage of active compounds

Inertness aspects of a coated stainless steel substrate. Two surfaces are available, Silcosteel and Sitek (also known as Sulfinert), whereby Siltek is the most inert.



The basic Siltek process is sketched out here. An additional bonding to the surface (covalently) can further deactivate the surface. The beauty of this process, however, is that the “R” group can be a wide variety of molecules, thereby allowing tailorability of the surface to a customer’s needs. For example, a fluorinated hydrocarbon can be bonded to increase hydrophobicity.

Current Applications

- Sulfurs: Application areas
  - Natural Gas; LPG
  - Ethylene; Propylene
  - Fuel Cells
  - Petrochemical process Streams
  - Beverage Grade CO_2 (Soda/Beer)
  - Flavor (Wine/Beer)

Current Applications (cont.)

- Sulfur Dioxide (SO_2); Nitrous Oxide (NO_x)
  - Automotive Exhaust (Gasoline/Diesel)
  - Stack Gas sampling
- Mercury/Mercury Oxides
- Alcohols
- Hydrogen Peroxide
- Air Sampling (Environmental monitoring)
- Chromatographic Analyzers

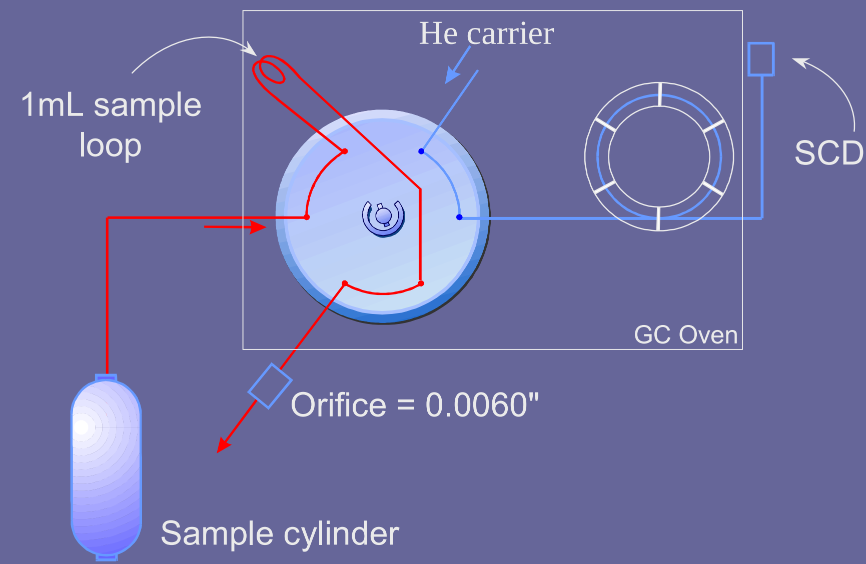
Common Coated Components

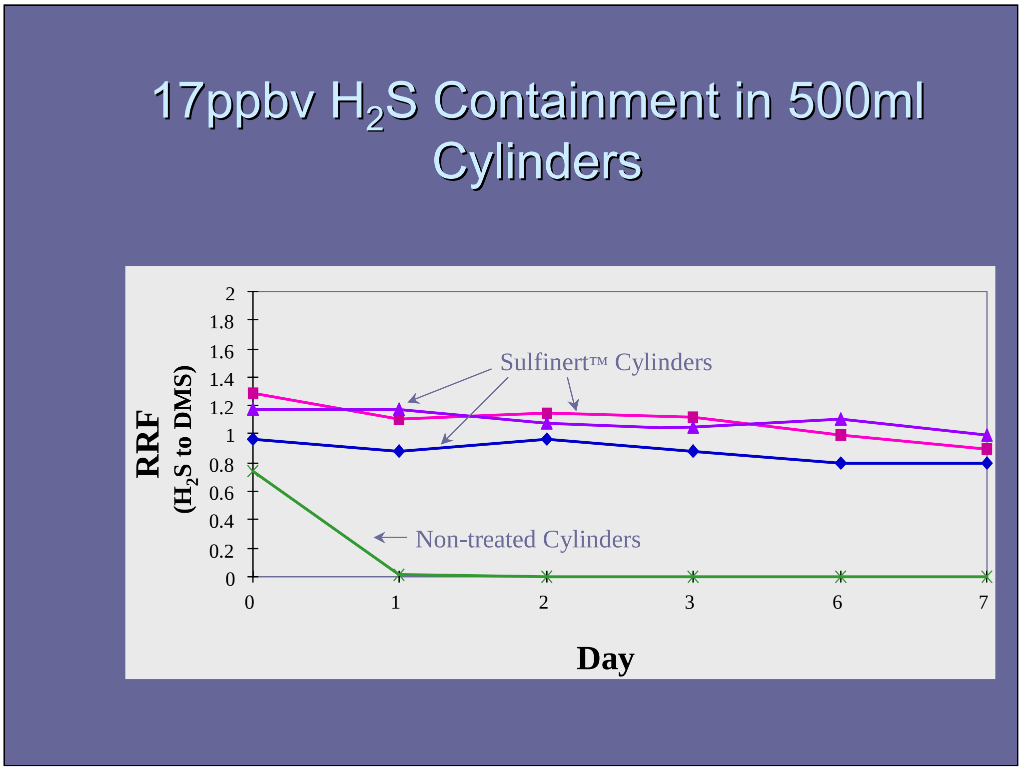
- Sampling Systems
- Transfer Tubing
- Valving
- Particle Filters
- Tube Fittings and Adaptors
- Sample Cylinders; Outage Tubes
- Analyzer components
- Continuous Emission Monitoring (CEM) equipment

Testing System for Sulfur Gas Storage & Transfer

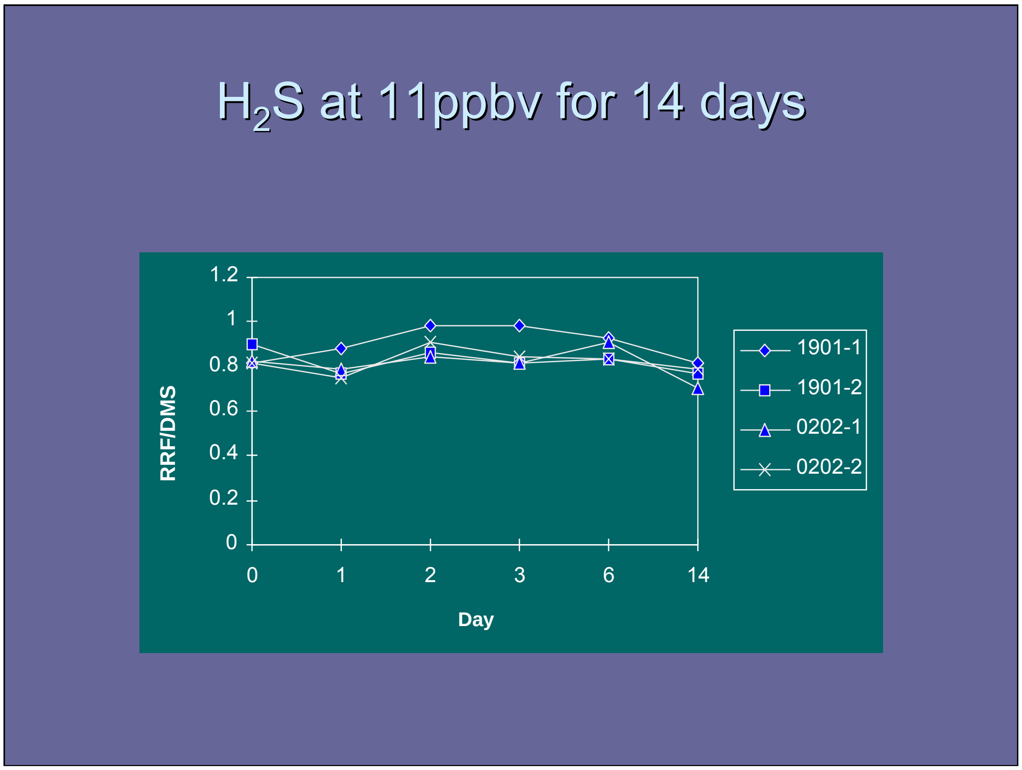
- Sulfinert®-deactivated sample cylinders and sample valves
- Sulfinert®-deactivated sampling system (transfer line, sampling valve, 1mL sample loop)
- 48hr (minimum) containment of dry sample
- 55ppbv reference standard
- Dimethyl sulfide internal standard

Complete Sulfur Analysis System



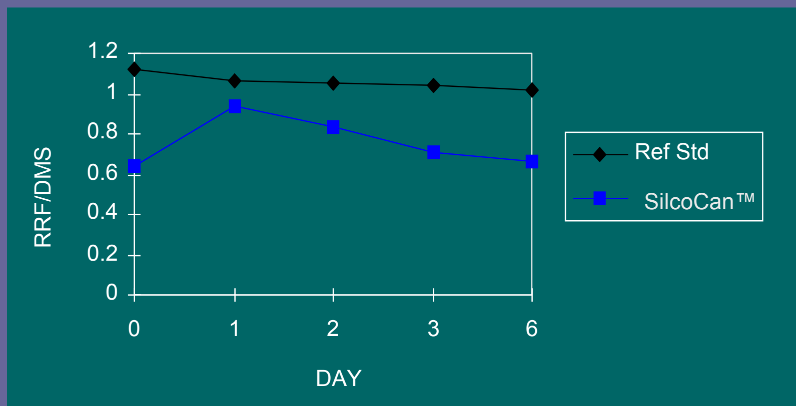


The following slides show data which highlight the inertness of the Siltek/Sulfinert surface. H2S is one of the most difficult sulfur gases for low-level transfer and containment, as it is highly adsorptive and reactive with a stainless steel surface. Here we show zero-to-negligible loss of 11ppbv H2S in a static storage cylinder over seven days.



To push the limit even more, we show storage of 11ppbv H2S over 14 days.

H_2S at 1.5ppbv



And furthermore, 1.5 ppbv H2S over 6 days.

Ultra-High-Vacuum (UHV)

- UHV environments are characterized as having a vacuum of $1x10^{-7}$ Torr or better
- In these conditions, materials trapped to the surface of and inside the steel outgas into the vacuum environment
- The outgassing of material increases pressure in the environment
- Large pumps and long “pump down” times are required to achieve UHV environments
- Silcosteel®-UHV treatment produces a barrier that blocks materials from outgassing into the vacuum environment.

The Silcosteel-UHV studies show the ability of a Silcosteel surface to shed surface contaminants, such as water, CO and CO2 more easily that bare stainless steel. This characteristic translates to lower outgassing in vacuum conditions, quicker pumpdowns, lower base pressures, and quicker drydown in tubing appications.

Theoretical Basis

- Outgassing rate (F) in monolayers per sec:

  $F = [\exp(-E/RT)] / t'$

  t' = period of oscillation of molecule perp. to surface, ca. 10^{-13} sec

  E = energy of desorption (Kcal/g mol)

  R = gas constant

  source: Roth, A. Vacuum Technology, Elsevier Science Publishers, Amsterdam, 2nd ed., p. 177.

- Slight elevation of sample temperature accelerates outgassing rate exponentially
- Basis for comparison measurements

Our experimental design allows us to isolate and directly compare outgassing rates with increasing temperature. By applying heat, the outgassing rates are exponentially increased for the purpose of timely data collection. These comparisons with experimental controls will directly illustrate the differences incurred by the applied coatings.

Treatment / Coating Types

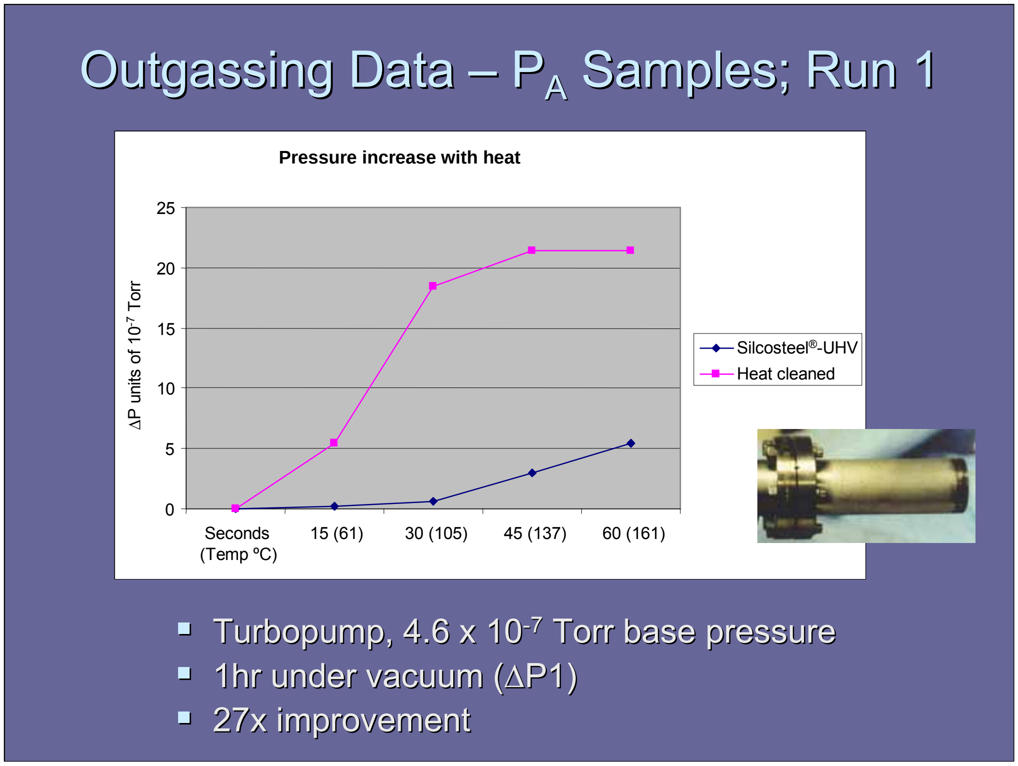
- Heat clean
  - Ultrasonic cleaning in aqueous caustic surfactant
  - Identical process as coated parts, but introduce inert gas instead of CVD gases
- Coatings
  - Silicon-based
  - CVD process
  - Entire surface coverage
  - Manipulation of process parameters key to coating evolution

The only difference between heat cleaned and Silcosteel coatings was the coating itself. Both parts were cleaned the exact same way, only the coated parts were exposed to the deposition gases whereas the heat cleaned parts were instead exposed to inert gas. This allowed for an appropriate experimental control to highlight the performance of the coating itself.

Test Components and Surface Treatments (cont.)

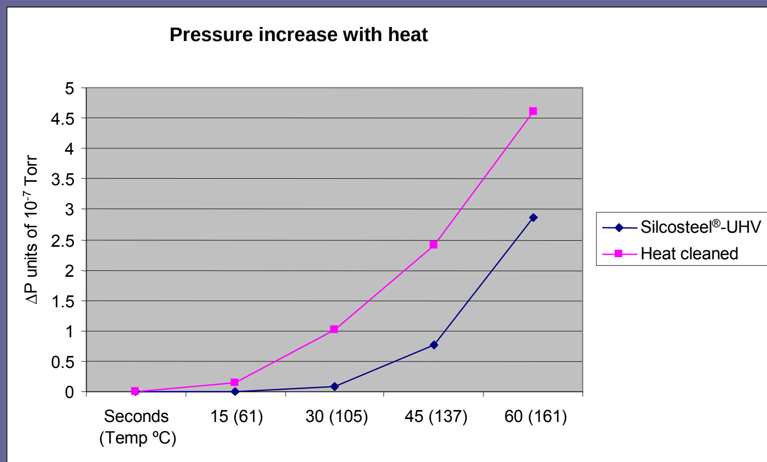
- 2nd Generation “P” samples – 4.5” x 1.5” OD 304 SS closed end thimble
  - Heat cleaned
  - Blue Silcosteel®
  - Silcosteel® Beta and Silcosteel®-UHV

This shows the test set-up whereby each coated thimble was isolated and heated under vacuum, during which outgassing measurements were made via pressure differentials during the heating process. This photo shows an early generation coating (blue) on the same test rig with Silcosteel-UHV coated and heat-cleaned thimbles



The treated parts were tested for outgassing rates after 1hr and 10hrs of pumpdown. This figure illustrates a significant decrease of outgassing rate when comparing the heat cleaned part to Silcosteel-UHV. Note the operating base pressure of 4.6 x 10^{-7} Torr.

Outgassing Data – P_A Samples; Run 2



- Turbopump, 7.5 x 10^{-8} Torr base pressure
- 10hr under vacuum (ΔP2)
- **14x decrease in outgassing**

At hour 10 of pumpdown on a turbopump system, the Silcosteel-UHV coating still shows a significant improvement over a Heat Cleaned part. Base pressure is now in to the 10^{-8} Torr range.

Outgassing increase sample calculations

- For the system (P_A), sample area = 125cm^2, conductance = 12.5 l/sec;
  therefore, $\Delta Q = \Delta P(12.5/125) = \Delta P/10$
- At 1 hour, 61ºC:
  ΔQ_1 (heat cleaned) = 5.4 x 10^{-8} Torr l sec^{-1} cm^{-2};
  ΔQ_1 (Silcosteel®-UHV) = 0.2 x 10^{-8} Torr l sec^{-1} cm^{-2}

  27x improvement
- At 10 hours, 61ºC:
  ΔQ_{10} (heat cleaned) = 0.14 x 10^{-8} Torr l sec^{-1} cm^{-2};
  ΔQ_{10} (Silcosteel®-UHV) = 0.01 x 10^{-8} Torr l sec^{-1} cm^{-2}

  14x improvement

At 61ºC, the figures show a seemingly small difference in outgassing. However, if we compare these results numerically, the differences are impressive. After 1 hour, the Silcosteel-UHV has a 27-fold improvement in outgassing rate (Torr l set^{-1} cm^{-2}) and even after 10 hours under vacuum, the Silcosteel-UHV maintained a 14-fold improvement.

UHV Coating Preliminary Electronic Performance Data

- Resistivity perpendicular to film range 12-60 Ω/cm^2
- Microchannel / pinholes allow conductivity through film to substrate

- Practical applications
  - Comparison of coated vs. uncoated miniature cold cathode gauge housings showed no difference in performance
    - Current density (est.) = 10^{-6} amp/cm^2
      resulting from secondary electron emission from ion impact in gauge
  - Comparison of vacuum tubes with alternative anodes of uncoated vs. coated steel showed no detectable performance difference
    - Internal filament produced 1ma electron current
    - Anode voltage = 200 V
    - Anode area = 23.5 cm^2
    - Anode current density approx. 4 x 10^{-5} amp/cm^2

Initial electronic performance data indicates that although the Silcosteel layer itself is not conductive along a parallel axis, there are microscopic channels that allow the penetration of charge through the thin film and then conductivity along the steel substrate. The “perpendicular” conductivity measurement was performed under vacuum conditions.

Dry-Down Data

- Coatings decrease adsorption of water, hydrophobic
- Leads to quicker removal of moisture through sampling lines
- Faster cycle times and increased accuracy with less moisture hold-up in tubing
- Several coatings and surfaces available

The vacuum measurements translate directly to superior drydown performance for coated stainless steel tubing.

Conclusions / Future

- Reduced outgassing rate by 14x @10 hrs of pumping
- Consistently outperforms cleaned parts
- Eliminates bakeout
- Faster pump down
- Lower base pressure with smaller pumps

The coatings studied have illustrated a decrease in cleaned Stainless Steel outgassing greater than an order of magnitude. Initial studies in electronic and galling characteristics have been favorable and are ongoing. Future evaluation plans include hydrogen permeability and the performance of a completely coated system.

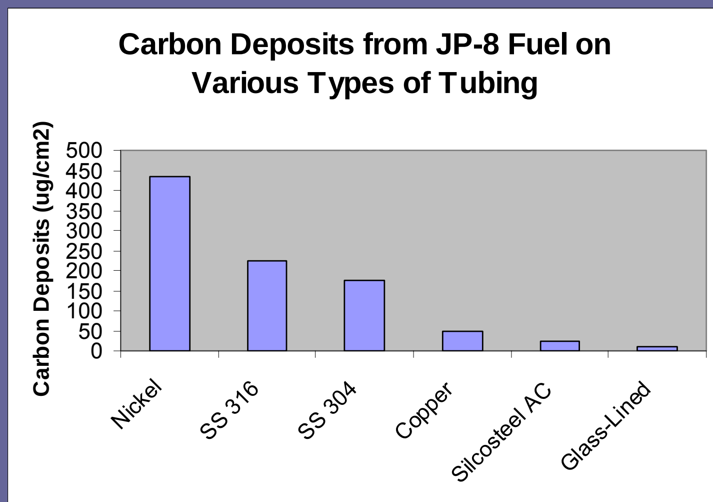
Silcosteel®-UHV is an R&D100 Award winner for 2004

Anti-Coking

- In applications of heated hydrocarbon transfer, carbon deposits can form
- Carbon deposits are catalyzed by nickel, sulfur and carbon in steel lattice
- The Silcosteel®-AC coating produces a barrier that eliminates catalytic carbon buildup

Another coating variation, based on our Siltek functionalization technology, has significantly low coke production for hydrocarbon process streams.

Anti-Coking Data



- Semih Eser; PSU Prof. Fuel Sciences
- 8x improvement over raw 316L

Comparisons of different surfaces shows a significant advantage of a coated substrate over other options.

Example Applications

- Coating fuel injector nozzles to decrease buildup
- Increasing lifetimes of Ethylene and Propylene Plug Flow reactors
- Increasing reliability of valves used in internal combustion engines
- Reduces fouling in heat exchangers

Conclusions/Future

- Continuing research in large systems
- Jefferson Labs conducting H2 permeation studies (XHV)
- System comparison to focus on high vacuum environments
- Continual process improvement and new product development
  - Hardness
  - Improved corrosion resistance
  - Customized surfaces

Acknowledgements

- Swagelok® Company
- Televac

Our gratitude to Swagelok for their assistance with surface analysis and to Televac for supplying and using gauge housings for this study.