MATHESON Cylinder Technology for Ultra High Purity Materials

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Enabling **D**evelopments in **G**lobal **E**lectronics

Overview

Contamination of Ultra High Purity (UHP) gases and liquefied gases – water contamination in particular – is a known problem with expensive consequences. It has been thought that the use of dried and passivated Stainless Steel cylinders, possibly combined with elaborate purification devices, was the best way to manage the contamination.

MATHESON research has shown that Steel, whether Carbon or Stainless, and whether passivated or not, itself contributes to the problem. The best solution is to use a container whose materials of construction, which come in contact with UHP materials, are non-ferrous.

Nickel plating of the inside of the gas cylinder has proven to be an effective step in minimizing both water and particulate contamination.

Highly polished internal surface of a nickel lined cylinder.

Sources of Contamination

Water contamination of UHP materials can be traced to two fundamentally different types of cylinder contamination:

First, water molecules can bond to surfaces via physisorption and chemisorption mechanisms. Although, dry down and vacuum bake methods can eliminate a large portion of the adsorbed water, these methods are not sufficient to completely remove the surface bonded water. These water molecules become attached to hygroscopic molecules (e.g., Hydrogen Bromide, Hydrogen Chloride, others) that are filled into the cylinder.

Second, all Steel contains some amount of ferric oxide. A simple reduction reaction can occur between these oxides and the corrosive material in the cylinder. Not all gases used in semiconductor manufacturing are oxide reactive, but many are, such as:

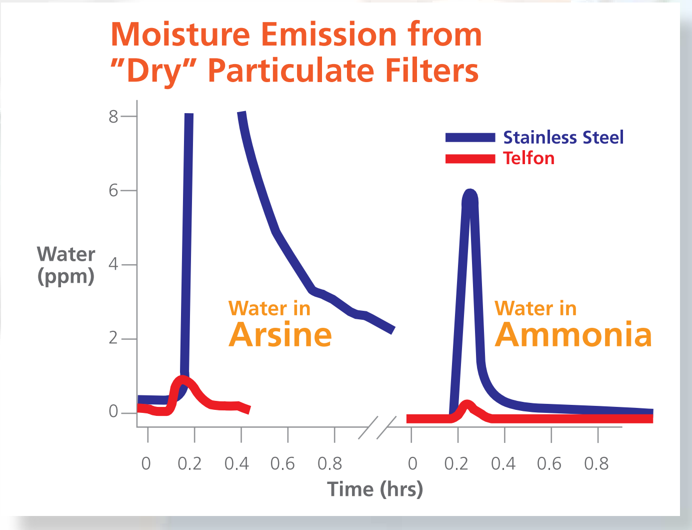
- **Hydrogen Chloride**
- **Hydrogen Bromide**
- **Hydrogen Fluoride**
- **Hydrogen Iodide**
- **Arsine**
- **Tungsten Hexafluoride**
- **Boron Trichloride**
- **Chlorine**
- **Fluorine**
- **Dichlorosilane**
- **Trichlorosilane**

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$

Importantly, the oxide reaction serves not only to liberate water molecules, but also to create particulates. For example, in the reaction with Hydrogen Chloride, water and iron chloride particles are brought into the Hydrogen Chloride supply.

In the cases of both simple water desorption and oxide reaction, the problem is complicated by the surface area of the cylinder walls. The actual surface area of the cylinder walls is very much dependent upon surface roughness. Smoothing of the walls will reduce the problem, but only to the extent that the walls can be smoothed. Water and ferric oxide will always be present in both Carbon Steel and Stainless Steel.

Demonstrating the Impact of Steel on Water Contamination



In laboratory tests, we used Stainless Steel and Teflon filters to look at the impact of Steel on water contamination. In both cases, we flowed Arsine or Ammonia through thoroughly dry filters. Steel harbors both chemisorbed and physisorbed water … this is demonstrated by the larger amounts of water contamination in both Arsine and Ammonia coming from the Stainless Steel filters. The off-scale amount of water in Arsine coming from the Stainless Steel filter demonstrates the additional contribution of the oxide reaction (Arsine is oxide reactive; Ammonia is not).

Why Nickel?

Decades ago, when MATHESON first began working with alternate cylinder materials of construction, Nickel was identified as a material with important advantages over Steel.

One important advantage is that the chemistry of Nickel is such that the formation of oxides is far less troublesome (our data suggest that the threat is near the limit of detectability).

Comparing the Gibbs Free Energy of Formation and the Standard Reduction Potentials of Iron and Nickel, oxides are far less likely to form on Nickel; and those that do form are far more difficult to reduce (i.e., less reactive). The net effect is that water and contaminant formation as the result of an oxide reaction is much less likely to occur on Nickel than on Steel.

Gibbs Free Energy of Formation

ΔG (kJ/mol):
Fe_2O_3 = -741
NiO = -217

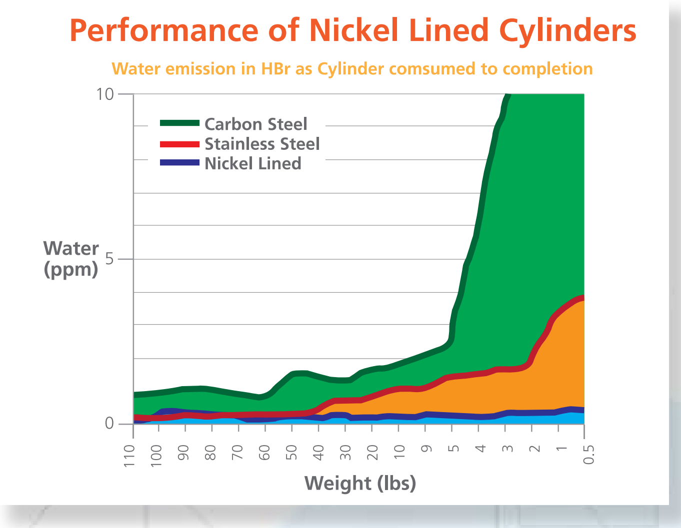
Standard Reduction Potential

E° (V vs. SHE):
Fe = -0.440
Ni = -0.215

A second advantage is that the deposited nickel conforms perfectly to a smoothed and polished steel cylinder. A smooth surface is preferred since this greatly decreases the surface area of the cylinder.

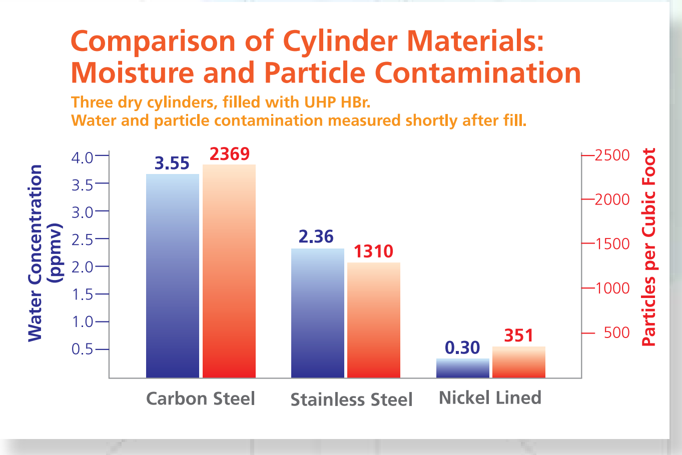
Finally, Nickel is a material that can be uniformly applied to Steel, by plating. Conventional Steel cylinder construction may still be used; but the walls of the cylinder can be plated with a layer of Nickel, effectively containing the UHP materials in Nickel.

Water Contamination to Depletion



It is common practice to take a cylinder off-line before phase break (the point at which all liquid contents are vaporized in the cylinder). In this test, we ran all three cylinders (Carbon Steel, Stainless Steel, and Nickel Lined) until completely empty. Water contamination is significant in both types of Steel cylinders – even long before phase break. Water contamination in a Nickel lined cylinder is far lower, and virtually flat.

Water and Particulate Formation



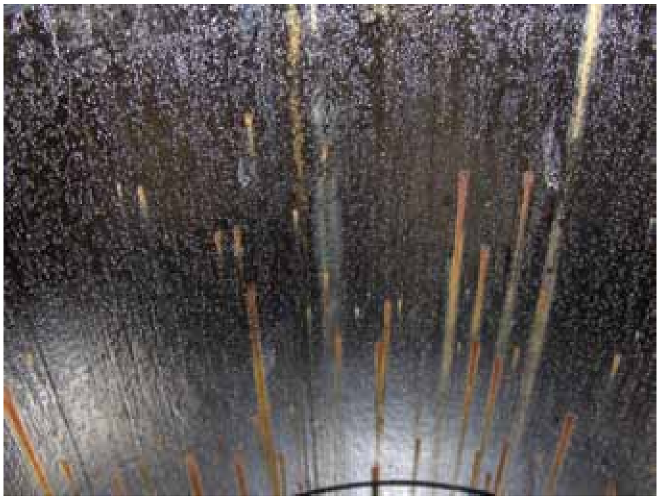
Measured shortly after fill, this comparison shows extreme improvement in contaminant reduction in the Nickel lined cylinder.

All Nickel Plating is NOT the Same

There are two primary deposition methods of Nickel lining. The first is an ***electroless deposition*** where the Nickel is co-plated with Phosphorus to create a Nickel Phosphorus alloy. This alloy typically has a Phosphorus content of 11-15%. Electroless Nickel has tendency to crack and leave pinholes in the plated surface. These disadvantages are intrinsic to the electroless Nickel plating process.

The second method of deposition – ***electrolytic deposition*** - leaves a pure >99.6% Nickel layer. Electrolytic Nickel is more technically challenging to deposit on a cylinder surface, but provides a Nickel lining that is free of cracks and pinholes preventing the contained materials from interacting with the Steel substrate beneath the Nickel surface.

MATHESON has the leading technology delivering electrolytic Nickel cylinders to provide the added benefits over electroless nickel.



Electroless Nickel Deposition

Electrolytic Nickel Deposition

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