

# Corrosion Resistance of Cost Effective Alternative Materials for Semiconductor Gas Distribution Systems

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## Abstract

In a collaboration between Matheson Tri-Gas and Diede Precision Welding, a study was designed to demonstrate the corrosion resistance of two materials commonly used in gas distribution systems. Electropolished 316L SS and Hastelloy® C-22™ were tested under similar corrosive conditions to quantitatively illustrate the differences in performance between these two alloys. Welded samples of both C-22™ and electropolished 316L were exposed to a corrosive HCl environment for an extended period. Corrosion resistance was determined by analyzing particle emissions from exposed surfaces of the materials. As expected, the quantitative results showed a distinct difference in corrosion resistance properties between the two materials.

In an additional study, Matheson Tri-Gas, in collaboration with Sherwood, Harsco Corporation, rigorously tested six alternative materials deemed to be intermediate in both corrosion resistance and cost. In this study, coupons of these materials were exposed to a corrosive HCl environment for a period of one month and visually inspected under magnification for corrosion. One of the six materials tested appeared to exhibit the greatest resistance to corrosion, displaying no adverse effects.

Corrosion results from all the metal alloys studied will be compared and correlations between costs, composition, and corrosion resistance performance will be discussed. Additionally, the feasibility of component fabrication from the different metal alloys will be compared in relation to cost, raw material availability, and producibility to SEMI industry quality standards.

## Introduction

The corrosion of gas distribution systems (GDS) and their components by corrosive process gases has been problematic in the semiconductor industry for many years. Advances in corrosive gas quality and purification techniques have increased the lifespan of gas distribution systems and decreased product contamination. However,

leaks, mishandled cylinder change-outs, component replacements, and other chronic introductions of atmospheric gases are practically unavoidable. These factors can result in the introduction of moisture into the corrosive gas stream and subsequent corrosion. The resultant corroded components of the GDS create not only unwanted particles but also volatile metal halides and moisture from the reaction between HCl with metal oxides [1]. The net effects can cause premature purifier failures, degradation to the tubing and components, and unsatisfactory device yields. It has been reported that the gas distribution system is responsible for 68 % of contamination in a CMOS process [2].

The corrosion of the GDS leads to replacements of costly components and semiconductor processing down time. To reduce GDS replacements, the semiconductor industry has developed methods by which to decrease the corrosion rate in a GDS. One method is to use source gas and point of use purifiers to improve and maintain the purity of a gas or a gas mixture by removing impurity molecules, specifically moisture. Moisture reacts with an anhydrous acid gas to produce byproducts that are much more corrosive than the anhydrous starting material [3]. Therefore, corrosion is reduced significantly by removing moisture from the acid gas stream. A previous study demonstrates quantitatively that components downstream of a corrosive gas purifier were virtually unaffected after being exposed to purified hydrogen bromide (HBr) [3]. The components upstream of the purifier encountered a severe degradation in performance due to corrosion. It was clearly shown that the usage of a purifier dramatically increases the lifetime of GDS.

Another method that has been developed in the semiconductor industry to reduce device contamination due to corrosion is the use of new improved source gas containers. Traditionally, carbon steel cylinders were typically used as a container for corrosive gases. The corrosion that occurs in carbon steel containers produces impurities that deposit into the GDS in the form of volatile metal halides and particulate metal halides. In time, the build up of this metal contamination will cause failures in

components and contamination of wafers, which lead to frequent GDS replacements. Newly developed containers contain wetted parts made from materials that are much more corrosion resistant than carbon steel. Several semiconductor gas vendors have used carbon steel cylinders plated with electroless nickel. The electroless nickel consists of a thin, brittle coating of a nickel-phosphorus alloy that is more corrosion resistant than steel. However, internal Matheson studies have shown this material to be inferior in corrosion resistance to electrolytic nickel (Ni-200, or pure nickel). Electrolytic nickel has been used in various sized cylinders for many different corrosive gases. This technology has also been extended to bulk containers. A highly corrosion resistant bulk container has been fabricated wherein the inner surface consists of polished, electrolytically deposited nickel-200, with externally threaded end connections made from Hastelloy® C-22™. This configuration ensures that all wetted areas of the container are made from corrosion resistant materials [4]. A previous study showed that the electrolytic plated nickel container emitted <13 ppb iron (below the LDL) and 4 ppb nickel after a 60 day HCl shelf life test, and only 18 ppb iron and 21 ppb nickel after 1 year [4]. This demonstrates that newly developed packages are not susceptible to corrosion, and do not contribute in contaminating the GDS.

Even with advances in containers, purifiers, methods, and equipment there are still problems with introductions of atmospheric gases into a GDS, which are essentially unavoidable due to reasons stated previously. Atmospheric contamination will cause corrosion within the delivery lines and components of the GDS. This elucidates a primary problem encountered by many facility engineers. One solution is to use 316L Stainless Steel, the most common material of construction. Although 316L is moderate in price and exhibits acceptable corrosion resistance, GDS constructed of primarily 316L must typically be replaced within 5 years. This requires extensive and valued downtime of the device manufacturing process. The other approach is to use a highly corrosion resistant alloy such as Hastelloy® C-22™. Unfortunately, C-22™ is an expensive raw material and due to the hardness of the alloy, machining or fabrication of parts proves to be extremely cost prohibitive. Based on continually decreasing profit margins throughout the life cycle of a product, neither of these approaches proves to be exceedingly cost effective. Therefore, there is a high demand to find a new metal alloy that is corrosion resistant, easy to work with, and inexpensive.

This paper will discuss the differences and advantages between 316L, C-22™, and six alternative metal alloys. Corrosion from HCl exposure will be discussed qualitatively by visual inspection, and quantitatively by particle counts. Each alloy will be evaluated with regard to cost, raw material availability, and producibility to SEMI industry standards.

## 316L vs. C-22™

### Factors for choosing 316L SS vs. C-22™

There are a number of factors that contribute to the decision making process of choosing 316L SS or C-22™ as a material to be used for the construction of a GDS. Cost, machinability, and weldability of a material can determine if it is even feasible to use a certain alloy. Currently, most parts and components for a GDS are available in both 316L and C-22™. However, the raw material cost and the machining of C-22™ is approximately 3 to 5 times higher than 316L. The process of welding C-22™ is comparable to the welding of 316L, (once the correct weld parameters have been established), but the details of the C-22™ weld procedure are more extensive than those typically required to weld 316L. The time required to weld C-22™ may be slightly longer than the time required to weld 316L. For example, it was found that it takes 10%-20% more amperage to achieve an acceptable C-22™ weld on a square-groove weld joint. However, rather than increasing amperage, it may be more desirable to decrease the speed of the process. Additionally, the appearance of the welded C-22™ is not as appealing as that of the 316L. The weld pool doesn't look as clean with respect to texture and color; however, the weld is mechanically sound. Another important factor is that 316L is much more readily available than C-22™. It has been indicated that there are considerably more vendors of 316L than vendors of C-22™, and a lead time for a part or fitting can be 3 times as long for C-22™.

The dominant factor that makes the C-22™ material more appealing than the 316L material is the corrosion resistance of C-22™. C-22™ is known to be much more tolerant to corrosive gas service than 316L [5,6,7]. For instance, the lifetime of a C-22™ cylinder valve used in corrosive gas service is at least 4 times as long as a 316L SS valve and has been demonstrated to last as long as 12 times the lifetime of a conventional 316L SS valve. It has also been reported in previous studies that C-22™ is very chemically resistant to moisture-laden HBr as compared to 316L [5]. From visual and SEM analysis, an EP316L sample showed extensive corrosion damage from being exposed to oxygen and moisture enriched hydrogen bromide (HBr). A C-22™ sample from the same study displayed little to no effects from the HBr exposure, concluding that the C-22™ should be used for more rigorous applications, where highly moisture enriched acid gases are likely to be present. In other studies where C-22™ was compared directly to 316L under identical corrosive conditions it was shown that 316L had a corrosion rate of 288 times greater than that of C-22™ [6]. In a similar study under a 1% boiling HCl solution, the corrosion rate of 316L was measured to be greater than 200 mm/year compared to a corrosion rate of 0.07 mm/year for C-22™ [7]. This corresponds to an increased corrosion rate for 316L of nearly 3000 times compared to that of C-22™.

Even though C-22™ out performs 316L SS in corrosive gas delivery systems, the semiconductor industry still has not committed to it completely due to the high initial capital

investment. Currently only about 35% of Fabs today chose C-22™ over 316L.

### Experimental

#### Materials

Diede Precision Welding fabricated eight ¼" O.D. welded gas piping samples, four 316L SS (electropolished) and four Hastelloy® C-22™. A gas piping sample, or *sample stick*, consisted of 2, ¼" VCR® glands welded to ¼" tubing of the same material. The sample sticks had a total length of 7 ¾" from gland to gland.

The gases used throughout the study were hydrogen chloride (HCl) and nitrogen. The HCl was ULSI 5.0 purity (99.999%) grade and was obtained from Matheson Gas Products, East Rutherford, NJ. Dry nitrogen was used as the purge gas for the manifold before and after HCl introduction. The nitrogen was obtained from a cryogenic source and was purified using a Nanochem OMX purifier. Use of a purifier reduced the moisture in the nitrogen to <<1ppb. Unpurified cryogenic nitrogen was used during particle count measurements. The moisture concentration in nitrogen was determined to be approximately <1 ppm.

#### Procedures

##### Moisture-in-HCl

An extremely high amount of moisture was introduced to each of the sample sticks by using a glass micro-syringe. 5µL of nano-pure water was dispensed into the upstream side of the sample stick; which corresponded to a moisture concentration of approximately 32,000 ppmv in the sample stick at 614 psig HCl. Each stick, (refer to Figure 1), was then placed and tightened into the test manifold. The sticks were purged individually with 5-8 psig nitrogen for 10 seconds to remove oxygen. The isolation valves were then closed leaving 5-8 psig nitrogen in the sticks. The sample sticks were then heated to 120° Celsius for 30 minutes. This step was taken to ensure that all the water in the sample stick was distributed into the vapor phase. After the sample sticks were allowed to cool to room temperature, the sticks were filled individually with 614 psig HCl by opening the upstream isolation valve for 10 seconds then closing it (the down stream isolation valves remained closed during the fill procedure). The sample sticks were exposed to moisture-laden HCl for a designated period of time. Before sample analysis the HCl was vented from the sticks and then purged with nitrogen. After each analysis the sample sticks were placed back into the test manifold by following the same procedure as above until the experiment was completed.

The sample sticks were exposed to HCl for a total of 590 hours. The sticks were visually inspected and tested for particle emissions at 120 and 590 hours of exposure to HCl.

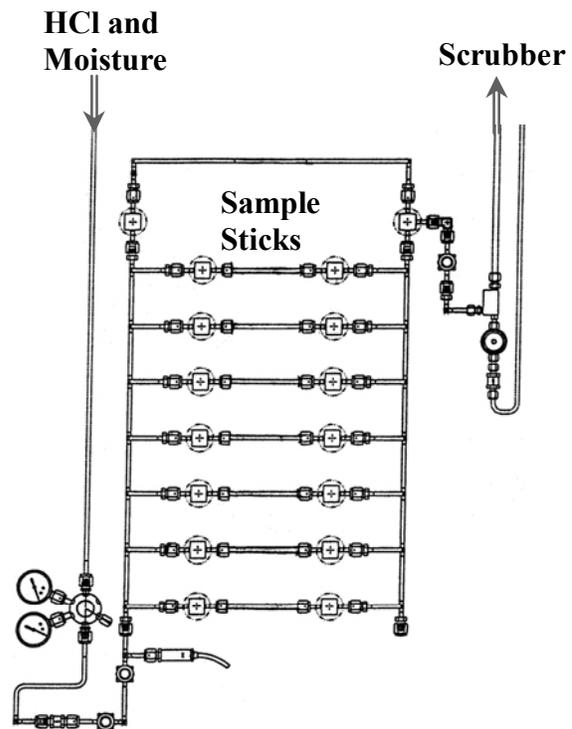


Figure 1: Schematic of the manifold used to conduct experiments.

##### Particle counting of sample sticks

The gas sticks were subjected to two different forms of particle counting: Static and Dynamic particle counting. The particle sizes that were counted were  $\geq 0.1 \mu\text{m}$ . All particle counting tests were conducted based on ASTM Method F 1394-92: Standard Test Method for Determination of Particle Contribution from Gas Distribution Systems. All particle counts were conducted in nitrogen.

Static particle counting was performed on the gas stick by flowing 14 slpm through the test sample and 14 slpm through a bypass leg for a total flow of 28 slpm to the particle counter. Particle counts were recorded once per minute for 20 minutes. The value reported for each individual sample was the average of the particles collected over this 20 minute time period.

Dynamic particle counts were performed similarly with respect to flow rates. However, upstream of the particle filter, on the sample leg, an air-actuated valve was cycled open for ten seconds and closed for two seconds. The valve was cycled five times during a one-minute period for 20 minutes. This action would produce a pressure drop and turbulent airflow within the test sample, causing particles to become dislodged from the test component. The value reported for each individual sample was the average of the particles collected over this 20 minute time period.

##### Data and results

The particle count data reveals that the 316L SS gas piping samples (sample sticks) degraded much more rapidly than the Hastelloy® C-22™ sticks when exposed to wet

HCl. Figure 2 exhibits that after 120 hours of exposure the 316L sample sticks had an average (for all 4 samples) of 221 particles/ft<sup>3</sup> during the static particle test. Whereas the average particle count for the C-22™ sticks was 1 particle/ft<sup>3</sup> after 120 hours of exposure. The data shows that after 120 hours of HCl exposure the 316L sticks emitted more than 2 orders of magnitude higher particle contamination compared to the C-22™ sticks. After 590 hours of HCl exposure both metals displayed high particle counts, 493 particles/ft<sup>3</sup> for the 316L sticks and 351 particles/ft<sup>3</sup> for C-22™, signifying severe degradation for both metals at this point.

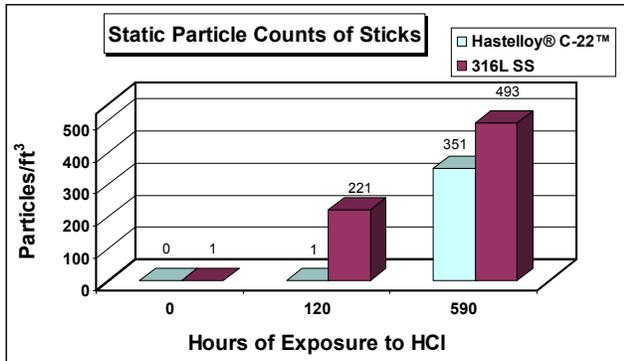


Figure 2: Average static particle counts of the gas sample sticks.

The dynamic particle count results were similar to the static particle count results. Figure 3 displays that after 120 hours of HCl exposure the 316L sample sticks had an average of 131 particles/ft<sup>3</sup> during the dynamic particle test. The C-22™ only had an average of 1 particle/ft<sup>3</sup> during the dynamic test after 120 hours of HCl exposure. After 590 hours of exposure to HCl both metals displayed high particle counts, with an average of 303 particles/ft<sup>3</sup> for the 316L sample sticks and 273 particles/ft<sup>3</sup> for the C-22™ sticks. Both sets of data represent the 316L metal degrading much faster than the C-22™, which in turn proves that the 316L is more susceptible to corrosion. However, the C-22™ did show significant degradation after 590 hours of exposure to high moisture-laden HCl.

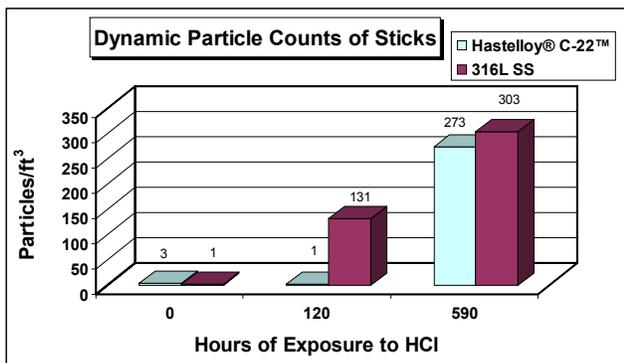


Figure 3: Average dynamic particle counts of the gas samples sticks.

The sample sticks were visually inspected with a boroscope after 590 hours of exposure to the HCl. The 316L sample sticks visually displayed much more degradation than the C-22™ sticks. The 316L samples had large amounts of deposits and debris present, and the C-22™ samples appeared to have a thin film on the surface.

The conclusions obtained from the visual inspection were surprisingly different from the particle counting results. Even though the 316L samples visually displayed significant degradation as compared to the C-22™ samples, the particle data revealed not as much of a difference between the two. One explanation as to why this occurred could be that the high moisture content used during the exposure made the corrosion products in the samples adhere to the tubing walls. This could cause the particles not to shed readily, only allowing the top layer of particles to emit as they dried during the particle testing.

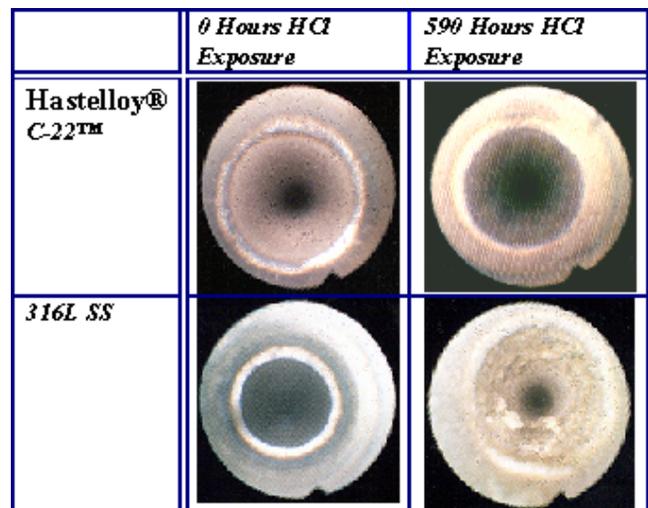


Figure 4: Internal weld of the 1/4" gas sample sticks, before and after exposure to moisture-laden HCl. The circular shape in each photo represents the weld bead of the material.

### Alternative Alloys

#### Material Costs and Workability

Besides studying the corrosion resistance of an alternative alloy it is also important to understand the feasibility of an alloy to be used for components in a GDS. Cost, raw material availability, and producibility are all factors in understanding if a new alloy will be cost effective.

The Sherwood, Harsco Corporation supplied Matheson with 6 different alloys: 20Mo-6®, 20Cb-3®, 2205 Code Plus Two®, 317LMNO SS, 254 SMO®, and 654 SMO®. The raw material costs for 20Mo-6®, 20Cb-3®, 254 SMO® are about 2.5 times the cost of 316L material. The 317LMNO material costs are similar to the 316L costs. 2205 raw material costs are in between the costs of 316L and 254 SMO®. It is unknown what the raw material costs are for 654 SMO® due to the limited amount used in the industrial world. All the materials, except 654 SMO®, are

available in a raw source, (rod material). The 654 SMO® is difficult to find in a rod source, therefore it is presumed to not be readily available. There is minimal amount of information on the machinability of these alloys, but vendors have stated that the machinability for each of these alloys, except 654 SMO®, is not as easy as 316L but easier than Hastelloy® C-22™. 654 SMO® would probably be as difficult to machine as C-22™.

### Materials

The 6 different alloys that the Sherwood, Harsco Corporation supplied were sample coupons measuring roughly ¼”x ¼” x 1”. The alloys tested were as follows: 20Mo-6®, 20Cb-3®, 2205 Code Plus Two®, 317LMNO SS, 254 SMO®, and 654 SMO®. For all the alloys, except for 254 SMO®, the surface finishes had a smooth mechanical polish. The 254 SMO® surface was extremely coarse and appeared to not be mechanically polished. The elemental composition for each metal can be seen in Table 1.

The specifications of the gases used throughout this study were the same as those used for the 316L SS/Hastelloy® C-22™ study.

### Procedures

Two metal test coupons were placed in a ½” 316L sample stick with a 3/8” FEP insert to keep the metal coupons free from the stainless, (which prevented cross contamination of corrosion products from the 316L tubing). This was repeated for six metal test coupons, for a total of three sample sticks. Using a glass micro-syringe, 2.5µL of nano-pure water was dispensed into the upstream and the downstream side of the sample stick for a total of 5µL, this corresponded to a moisture concentration of 18,000 ppmv in the sample stick at 614 psig HCl. Each stick, (refer to Figure 1), was then secured into the test manifold. The sticks were purged individually with 5-8psi nitrogen for 10 seconds to remove oxygen. The isolation valves were then closed leaving 5-8psi nitrogen in the sticks. The sample sticks were then heated to 120° Celsius for 30 minutes. This step was taken to ensure that all the water in the sample stick was distributed into the vapor phase. After the sample sticks were allowed to cool to room temperature, the sticks were filled individually with 614 psig HCl by opening the upstream isolation valve for 10 seconds then closing it (the down stream isolation valves remained closed during the fill procedure).

The sample sticks were exposed to HCl for a total of 710 hours. The test coupons were visually inspected at 250, 475, and 710 hours of exposure to HCl. Before each inspection of the coupons, HCl was released from the sample sticks and the sample sticks were purged with nitrogen. When an inspection was finished the samples were placed back into the test manifold by following the same procedure as above until the experiment was completed. After 710 hours of HCl exposure the coupons were cleaned with a dry paper towel and inspected with a stereoscope. This was done to remove volatile products that were formed

in the highly reactive environment and deposited on the coupons. The coupons were then cut and half and macro pictures were taken.

	20Cb-3® Stainless Steel	20Mo-6® Stainless Steel	317LMNO Stainless Steel	2205 Code Plus Two®	254 SMO®	654 SMO®	316L Stainless Steel	Hastelloy® C-22™
Carbon	0.06*	0.02	0.02	0.03*	0.02*	0.02*	0.03*	0.010*
Chromium	20.0	24.0	18.4	22.5	20.00	24.50	17.0	22
Nickel	34.0	35.0	13.2	5.5	18.00	22.00	12.0	55.5
Molybdenum	2.5	5.5	4.2	3.3	6.25	7.50	2.5	13
Nitrogen	****	0.13	0.16	0.17	****	****	****	****
Phosphorus	0.035*	0.03*	0.02	0.035*	0.03*	0.03*	0.045*	0.02*
Manganese	2.00*	1.00*	1.61	2.00*	1.00	3.00	2.0*	0.50*
Sulfur	0.035*	0.03*	0.00	0.020*	0.01*	0.005*	0.030*	0.010*
Silicon	1.00*	0.50*	0.00	1.00*	0.80*	0.50*	1.0*	0.08*
Copper	3.50	3.00	0.31	****	0.75	0.45	****	****
Cobalt	****	****	****	****	****	****	2.50	2.5*
Niobium	****	****	****	****	****	****	****	0.00
Tantalum	1.00*	****	****	****	****	****	****	0.00
Iron	37	31	62	67	53	42	69	3
Vanadium	****	****	****	****	****	****	****	0.35*
Tungsten	****	****	****	****	****	****	****	3

\*Maximum values.

Table 1: Average Elemental composition of the alloys tested.

### Data and results

From visual inspection, none of the metals displayed any significant degradation after 250 hours of HCl exposure. After 475 hours the 2205 and 20Cb-3® metal coupons exhibited areas of brownish discoloration, or corrosion products. At the same time, 254 SMO®, 654 SMO®, 20Mo-6®, and 317LMNO coupons did not show signs of corrosion at this point. After 710 hours of HCl exposure the 2205, 20Cb-3®, and 317LMNO coupons had a large amount of discoloration and pitting distributed across the surface. The 2205 and 317LMNO coupons developed patches of dark reddish brown, pitted corrosion areas. More corrosion was apparent on the 317LMNO coupon. The 20Cb-3® coupon had a brownish discoloration with large pits scattered across the surface. The third best coupon after 710 hours of exposure was the 20Mo-6®, displaying a small amount of corrosion pitting and discoloration. The 254 SMO® coupon only displayed a small amount of discoloration in some areas of the surface. No significant pitting was found on the 254 SMO® coupon. The 654 SMO® coupon exhibited no adverse effects from the 710 hours of HCl exposure.

It was determined that the 654 SMO® metal alloy exhibited the best performance in corrosion resistance of all the metals. The surface of the 654 SMO® test coupon displayed no effects from 710 hours of exposure to high pressure, moisture-laden HCl. After wiping away volatile oxy-chloride products that were deposited on the coupon, under high-magnification the 654 SMO® surface had a smooth, highly reflective finish with no discoloration or pitting. The 254 SMO® alloy performed almost as well as

the 645 SMO® alloy, displaying a small amount of discoloration from the HCl exposure. All of the other metal test coupons had indications of some type of corrosion, pitting, discoloration, etc. Some coupons exhibited a larger degree of corrosion as compared to other coupons as demonstrated in figure 5.

	<i>Initial</i>	<i>710 Hours*</i>	<i>710 Hours Magnified</i>
<b>317-LMNO</b>			
<b>20Cb-3®</b>			
<b>2205</b>			
<b>20Mo-6®</b>			
<b>254 SMO®</b>			
<b>654 SMO®</b>			

*\*The coupons were cut in half before these pictures were taken.*

*Figure 5: Test coupons of exotic alloys, before and after exposure to moisture-laden HCl.*

**Conclusions**

The research described in this study provides more information on which types of alloys are more resilient to corrosion in a corrosive environment. In the first study it was proven again that Hastelloy® C-22™ is a better

performer than 316L SS when exposed to moisture-laden HCl. This was proven qualitatively by visual inspection, and quantitatively by particle counting the samples. The results showed that after exposure to 120 hours of moisture enriched HCl the 316L samples emitted more than 2 orders of magnitude greater particle contamination compared to the Hastelloy® C-22™ samples (the C-22™ samples emitted virtually no particles). After 590 hours of HCl exposure both alloys displayed comparable particle counts, but from visual inspection it appeared that the 316L samples underwent much more corrosion than the C-22™ samples. The 316L samples had large amounts of deposits and debris present, and the C-22™ samples appeared to have a thin film on the surface.

The second study researched the corrosion resistance of the alternative materials. In evaluating the results, there were two alternative alloys that performed exceptionally well, 254 SMO® and 654 SMO®. In particular the 654 SMO® displayed the best corrosion resistance results. After 710 hours of exposure to moisture-laden HCl, the 654 SMO® alloy demonstrated no corrosion effects. The 254 SMO® alloy performed almost as well, with a small amount of discoloration from the HCl exposure. It should be noted that if the 254 SMO® sample was polished before the experiments, like the other samples, it may have performed as well as the 645 SMO® material. The third best performer was the 20Mo-6® alloy, displaying a moderate level of corrosion resistance with a small amount of pitting and discoloration. The other materials, 20Cb-3®, 2205 Code Plus Two®, and 317LMNO SS exhibited high levels of corrosion with varying degrees of pitting and discoloration from the HCl exposure.

In evaluating the corrosion resistance of the alternative materials on a scale spectrum based on the relative resistance of 316L SS and Hastelloy® C-22™, the 254 SMO® and 654 SMO® are comparable in corrosion resistance to C-22™. 20Mo-6® displayed a corrosion resistance level that would fall in between 316L and C-22™. The other alloys are more comparable to the corrosion resistance of 316L. The level of corrosion resistance that 254 SMO® and 654 SMO® exhibited is acceptable to validate trials of one of these materials in corrosive gas applications.

Based on the results of the corrosion study an attempt was made to correlate the corrosion resistance of a particular alloy with the elemental composition of that alloy. It is currently believed that the nickel percent composition is critical to the performance of an alloy in a corrosive environment. The standard assumption is that the higher the relative abundance of nickel, the higher the corrosion resistance [8]. It has also been well established that pure nickel performs very well in corrosive environments [9].

Figure 6 exhibits the concentration of nickel and molybdenum for all the alloys tested. The graph reveals a trend indicating that higher molybdenum concentration correlates with enhanced corrosion resistance. It appears that when the molybdenum concentration is above 6% the alloy demonstrates excellent corrosion resistance.

Alternatively, the trend for nickel shows no such correlation. Although 20Cb-3® and 20Mo-6® contained 34% and 35% nickel, respectively, the alloys exhibited low to moderate corrosion resistance when compared to the other alloys tested. Furthermore, the 254 SMO® and 654 SMO® alloys only contained 18% and 22% nickel, but demonstrated superior corrosion resistance.

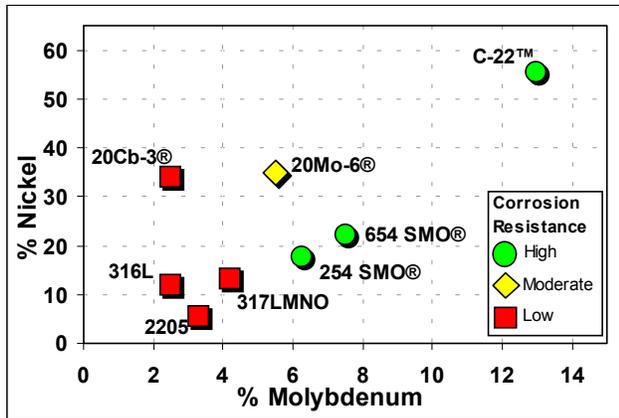


Figure 6: Percentage of nickel and molybdenum composition for all the alloys tested. The relative corrosion resistance level for all the alloys is also presented.

Figure 7 illustrates the concentration of iron and chromium for all the alloys tested. The figure clearly establishes that no correlation exists between the percentage of chromium and iron on the corrosion resistance of the alloys tested. However, in general, a high relative concentration of chromium and low relative concentration of iron has been attributed with highly corrosion resistant materials.

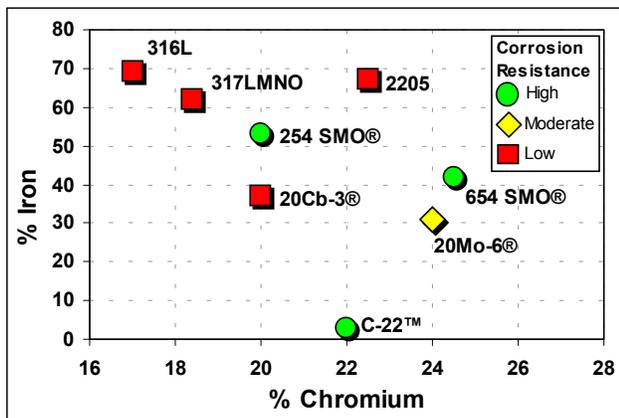


Figure 7: Percentage of iron and chromium composition for all the alloys tested. The relative corrosion resistance level for all the alloys is also presented.

Based on the limited number of alloys tested, the corrosion results indicate that an alloy must contain a minimum of 6% molybdenum in combination with other critical elements such as nickel and chromium to exhibit superior corrosion resistance under the exposure conditions

for the test coupons. Although this statement is an over simplification of the complex and multi-variable system that corrosion encompasses, it does illustrate the importance that molybdenum has on alloys used in corrosive environments.

The feasibility of new alloys to be used within the semiconductor industry for corrosive gas service relies on several factors. First, the alloy must demonstrate superior corrosion resistance relative to 316L SS. Second, the new alloy must be cost effective and offer a lower overall cost of ownership to semiconductor facility engineers. Third, the new alloy must be practical and workable with respect to weldability and machinability. For example, if the alloy hardness is extremely high, then the costs associated with tooling and machining time can be substantial, causing the cost of the final product to be relatively high. The weldability of the material must also be considered since new alloys can take longer to weld, require higher amperage during welding, and exhibit larger heat affected and weld zones. Last, the new alloy must be readily available in a form easily handled by component manufacturers. Multiple component manufacturers must offer many common components manufactured from the new alloy to decrease cost and minimize long lead times.

The relative costs of all the alloys tested, except for 654 SMO®, are shown in figure 8. The raw material cost for 654 SMO® could not be determined because of the lack of available material. The results reveal C-22™ to be the most expensive, while 316L SS is the least expensive. Figure 9 attempts to establish a correlation between elemental composition and relative raw material cost for the alloys tested. The results indicate a higher cost with increasing concentrations of nickel, molybdenum, and chromium. However, iron displays a negative correlation between iron content and raw material cost. Although a perfect correlation does not exist between the concentration in elemental composition and cost, we are able to ascertain that molybdenum and chromium have the greatest impact on the raw material costs for all the alloys tested.

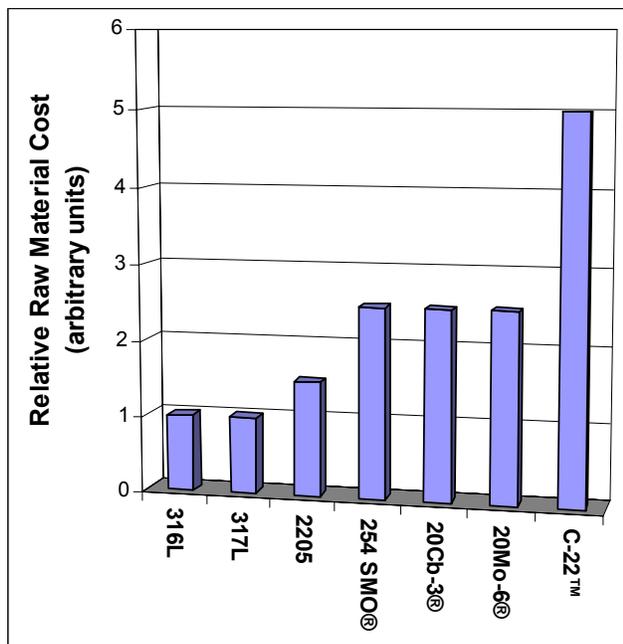


Figure 8: Relative cost of all the materials (based on a scale of 1 being the lowest for 316L and 5 being the highest for C-22™.)

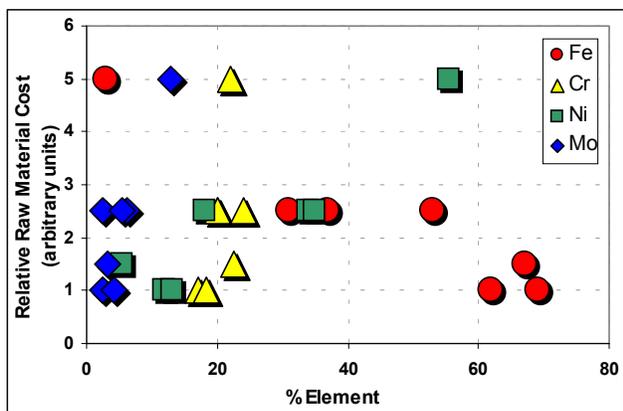


Figure 9: Percentage of iron, chromium, nickel, and molybdenum for all the alloys, (except 654 SMO®), in relation to the cost of the materials.

Since the results demonstrated exceptional corrosion resistance for 254 SMO® and 654 SMO®, consideration must be given to the applicability of these two alloys for semiconductor gas service.

The cost of raw material, (rod material), for 254 SMO® is roughly 2.5 times the cost of 316L. Given that 654 SMO® is difficult to find in rod for forging as a raw material, it is difficult to ascertain an actual cost of the finished material. This leads to the next important factor, availability. 254 SMO® raw material is readily available in rod form. The 654 SMO® alloy, as just stated, is quite difficult to obtain in rod form. Another factor that has an impact on costs is the machinability of the material. According to vendors, the machinability of 254 SMO® is more difficult than 316L but easier than C-22™. 654

SMO® is speculated to be as difficult to machine as C-22™.

From the factors stated above it is quite evident that the 254 SMO® is more feasible economically for use in semiconductor applications than the 654 SMO®. It is unfortunate that the 654 SMO® alloy is not readily available, given that its corrosion resistant characteristics were exceptional. However, the 254 SMO® alloy was positive in all factors discussed, corrosion resistant properties close to C-22™, readily available as a raw material, and a cost factor of ½ that of C-22™. Further tests are necessary on 254 SMO®, particularly for component trials in actual field use with corrosive gas exposure.

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#### References

- [1] R. Paciej, "How to foil the curse of corrosive gases", Chemical Engineering, May 1991, pp. 158-163.
- [2] S.D. Cheung and G.L. Mooney, "Designing, installing, a gas distribution system in a sub 0.5 μm facility", Micro, October, 1995, pp.59-67.
- [3] R. Torres, D. Fraenkel, J. Vininski, E. Hennig, T. Watanabe, & V. Houlding, "High-pressure Point-of-Use Purification of Corrosive Gases: Effect on Gas Distribution Components", Semiconductor Fabtech, 12<sup>th</sup> ed., 2000, pp. 139-145.
- [4] R. Torres, J. Vininski, E. Hennig, J. Felbaun, "Ultra-High-Purity Bulk Specialty Gas Package for 300 mm Wafer Fabrication", Semiconductor Fabtech, 14<sup>th</sup> ed., 2001, pp. 131-137.
- [5] G.H. Smudde, Jr., W.I. Bailey, B.S. Felker, M.A. George, J.G. Langan, "Materials Selection for HBr Service", Corrosion Science, vol. 37, No.12, 1995, pp. 1931-1946
- [6] Haynes International Brochure, "Hastelloy® C-22™ Alloy, Corrosion Resistant Alloys", H-2019D, 1991.
- [7] Mitsubishi Materials Corporation, Okagawa Plant, Research and Development Center
- [8] A. John Sedriks, "Corrosion of Stainless Steels", The Corrosion Monograph Series, 1979, pp. 217-230.
- [9] C.M. Schillmoller, Chemical Engineering Progress, November 1998, pp.49-54.