Chlorosilanes are used at high temperatures throughout the world’s semiconductor industries primarily as a way to refine and deposit silicon and silicon containing materials. They are most prevalent in the manufacture of solar grade polycrystalline silicon; an industry that has historically used high cost alloys to effectively handle corrosive chlorosilane species. This study focused on understanding the corrosion behaviors of AISI 316L stainless steel, a low cost alloy, in chlorosilane environments at a variety of industrially-relevant times (0–200 hours), temperatures (500–700°C), and hydrogen chloride (HCl) mole fractions (0.0–0.06). It was observed that AISI 316L can form either predominately metal chloride or metal silicide corrosion products depending on the mole fraction of HCl. Increasing temperatures tend to favor metal silicide formation, a trend predicted by thermodynamically generated predominance diagrams. Additionally, metal silicide surface layer growth appears to be diffusion controlled with an apparent parabolic rate at long times and high temperatures. There is also evidence for reaction-limited iron silicide formation at lower temperatures. Improved understanding of metals in high-temperature chlorosilane environments will help guide materials selection processes, and ultimately facilitate cost-competitive deployment of silicon-based photovoltaic systems.

The kinetics of silicide formation when silicon is coated with chlorine in many chemical processing industries.20 Researchers have noted that nickel in pure HCl at temperatures greater than 500°C results in a net mass loss.12 Chromium and nickel also form metal-silicides and metal-chlorides contingent on the environment. It has been reported that CrCl2 scale is only somewhat protective below 600°C, and above 600°C, it readily evaporates.16 There are several chromium-silicon species (CrSi, CrSi2, Cr3Si, Cr2Si3) however, they require extreme temperatures (∼1200°C) to form.17

Metal chloride formation has been studied due to the presence of chlorine in many chemical processing industries.18 Researchers have found that metal chlorides are volatile and will reactively evaporate when formed due to their relatively high vapor pressures at elevated temperatures. Table I shows the temperature that the vapor pressure of the metal chloride associated with many common alloying elements begins to exceed 10^−4 atm (∼10 Pa).19 Depending on the application, this vapor pressure can be used as a “threshold” value, above which a non-negligible amount of vaporization occurs. This demonstrates the need to protect against metal chloride formation. While metal chlorides have not been extensively studied concurrently with metal silicides, there are some potential parallels with chloride formation in oxidizing environments. Jacobson reported that in a mixed oxide and chloride environment at 550°C, iron will follow primarily oxidation behavior with the exception of a condensed metal chloride layer at the oxide/metal interface where the oxygen potential is low.20 Additionally, there is some volatilization of various iron chloride species which must be accounted for. The exception to this trend is at low bulk oxygen partial pressure. In this case, there is enhanced oxidation, likely due to some porosity in the oxide layer caused by chloride volatilization. It is likely that this phenomenon will occur in mixed chloride/silicide environments due to the similar combination of a condensed metal silicide and a partially volatile metal chloride.

Many metal silicides are stable and well adhered to the surface, especially when compared to metal chlorides. Additionally, many metal silicides have a negligible vapor pressures at elevated temperatures as evidenced by the mass gain associated with metal silicide formation. The kinetics of silicide formation when silicon is coated with a metal film has been thoroughly studied due to its importance in the semiconductor industry. For iron and nickel in these conditions, metal diffusion through the silicide layer appears to be the dominant

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transport mechanism that supports silicide growth. This is due to metal diffusion in the metal silicides being much faster than silicon diffusion. Baldwin and Ivey specifically studied the silicon-iron diffusion couple by clamping polished silicon and iron pieces together and annealing them at a variety of times and temperatures. What they found was that a silicon-rich FeSi₂ phase formed next to the silicon piece with a FeSi phase next and an iron-rich Fe₃Si phase nearest to the iron. The atomic concentrations of iron and silicon within each silicide phase was quite constant. This showed that there is limited solubility of either silicon or iron within the metal silicides. Additionally, there was about 4 atomic % silicon in the iron lattice, showing that there is solubility of silicon in iron as predicted by the phase diagram. This type of stratification of silicide layers is also predicted in diffusion limited chlorosilane corrosion.

The behavior of a variety of metals and alloys in a chlorosilane environment has been investigated by Mui using a packed bed reactor to chlorinate metallurgical grade silicon. Samples were exposed to an environment at 500 °C and 2.07 MPa containing 70.6% STC, 28.1% TCS, 0.8% DCS, and 0.5% HCl as measured by an inline gas chromatograph. The metals tested include nickel, copper, Alloy 400, carbon steel, 304 stainless steel, Incollco 800 H, and Hastelloy B-2. Results indicated that many of the alloys tested formed a silicide layer that acted as a protectant from future HCl attack. However, the dependence of silicide formation on time, temperature, or gas composition was not reported. Corrosion rates were calculated based on linear reaction kinetics; however, the author stated that linear kinetics may not be a valid assumption. In order to be applied to industry, it is imperative that chlorosilane users understand how time, temperature, and composition influence corrosion, so that it can be predicted and controlled. Without this knowledge, users risk creating volatile metal chlorides or excessively thick metal silicide surface layers that may spall and consume base metal.

Acker, et al. has also studied the formation of transition metal silicides in chlorosilane environments with their primary focus being nickel. They proposed several reactions in the metal-chlorosilane system that can take place to form metal silicides. The first is the direct reaction of a metal with STC to form a silicon rich metal silicide as modeled by Equation 1. The second reaction of interest is the formation of a metal-rich metal silicide from a silicon-rich metal silicide and a metal (II) chloride as modeled by Equation 2.

\[ xM(s) + ySiCl₄(g) + 2yH₂(g) \rightarrow MₓSiy(s) + 4yHCl(g) \]  
\[ MₙSᵢₙ₋₂ + zCl₂(g) \rightarrow Mₙ₊₂Sᵢₙ₋₂.₅z(s) + 0.5zSiCl₄(g) \]

From these equations, Acker and his colleagues were able to thermodynamically predict several layers of nickel silicide that form when nickel is exposed to STC and then experimentally verify their predictions. In addition to these findings, Acker also studied the behavior of transition metal silicides in anhydrous HCl, although for a different application than what is addressed here. Acker was interested in using HCl to form more metal-rich metal silicides as modeled by Equation 3.

\[ MₙSᵢₙ₋₂ + 3HCl(g) \rightarrow H₃Sᵢ₃(g) + MₙSᵢₙ₋₃(s) + H₂(g) \]

This reaction is applicable in corrosion because it shows that there is some interaction between metal silicides and HCl. This implies that metal silicides are not fully protective, but they may partially impede chloride attack. Additionally, it shows that chloride content can significantly alter corrosion mechanisms in chlorosilane systems.

Acker’s work was aimed at making metal silicides for the electronics industry, not as a corrosion product. A study more focused on the corrosion aspect of these systems is crucial for continued advancement and optimization in industries that use chlorosilanes. Although Acker established a framework for studying other metals in these environments, reported results were limited to nickel. Iron and chromium are arguably more critical structural alloying elements, which further necessitates an investigation in to their behaviors in chlorosilane environments.

**Experimental**

Corrosion testing was performed in a custom tube furnace system constructed in the Montana State University High Temperature Materials Laboratory. This testing system can expose several samples to a controllable chlorosilane environment at a variety of temperatures, times, and gas compositions. The test setup is schematically illustrated in Figure 1.

In this testing system, an adjustable amount of H₂, controlled by a mass flow controller, was delivered via needle through a septum and bubbled into the bottom of a 1 liter bottle containing liquid silicon tetrachloride (STC). As the H₂ bubbles rise through the STC, they become saturated with STC, making the head space a consistent mixture of H₂ gas and STC vapor. This vaporizes the STC at a predictable and constant rate, and forces the H₂/STC mixture to flow out of the bottle through a separate needle in the bottle head space exiting the septum. This H₂/STC stream is combined with a variable amount of hydrogen chloride and makeup hydrogen, both controlled with individual mass flow controllers. The makeup hydrogen permits control of the H₂/STC mole ratio, while the hydrogen chloride is necessary to represent industrial processes. The gas stream is flowed over the samples in the tube furnace, and then to the scrubbing system. The scrubbing system has a built-in pressure relief system that releases if it exceeds approximately 10 psig (~70 kPa). Additionally, line pressure is measured at the hydrogen inlet into the STC bottle, helping to predict STC vaporization rates. The pressure of the STC/H₂ line is not explicitly measured due to the incompatibility of many laboratory scale pressure gauges with STC.

In this testing system, a quartz tube (placed within a tube furnace) with an inside diameter of 26.8 mm is used with flat metal samples placed within. This allows for gas flow on both sides of the samples so that the entire surface area is subjected to the corrosive exposures. The gas composition of the test system was controlled by adjusting the relative amounts of makeup hydrogen and hydrogen chloride to dictate the mole fraction of each component supplied to the system. While the flow rates of hydrogen and hydrogen chloride can be taken

**Table I.** Temperature that common metal-chlorides’ vapor pressure exceeds 10⁻⁴ atm (∼10 Pa).²⁴⁹

| Species       | FeCl₂ | FeCl₃ | NiCl₂ | CrCl₂ | CrCl₃ | CoCl₂ | MnCl₂ | ZrCl₄ | MgCl₂ | ZnCl₂ | PbCl₂ | AlCl₃ |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Temp (°C)     | 536   | 167   | 607   | 741   | 611   | 587   | 607   | 146   | 663   | 349   | 484   | 76    |
| Temp (atm)    | 10⁻⁴  | ∼10   |       |       |       |       |       |       |       |       |       |       |

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directly from the mass flow controllers, the amount of vaporized STC was calculated based on the difference in the STC bottle mass before and after an experiment. For this calculation, the assumption was made that none of the STC leaked through the septum. The amount of STC vaporized in to the hydrogen gas stream can be estimated using Antoine’s equation (Equation 4). The Antoine equation parameters for STC at room temperature are \( A = 4.82892, B = 1616.546, \) and \( C = 5.305.26 \). From this information, at 298 K, the vapor pressure of STC is 0.315 bar. Assuming a total pressure of 1 bar in the head space of the bottle, the hydrogen to STC ratio is 2.17. While this is an important calculation to understand, variations in room temperature and pressure make the previously described STC mass measurements necessary. However, the implication of this relationship is that the assumption of constant STC vaporization is valid. A typical total mole ratio of \( H_2:STC:HCl \) was approximately 0.730:0.252:0.018, with the hydrogen flow rate totaling ~60 SCCM. This leads to a total flow rate of approximately 82 SCCM and an average velocity of 14.5 cm/min through the tube furnace at standard temperature and pressure.

\[
\log_{10} p = A - \frac{B}{C + T} \tag{4}
\]

AISI 316L contains 0.03 max wt% C, 2 max wt% Mn, 0.045 max wt% P, 0.030 max wt% S, 1 max wt% Si, 16–18 wt% Cr, and 10–14 wt% Ni, with the balance Fe. Samples for this testing had a mirror finish prior to cutting and handling steps. They were cut to approximately 12 mm × 12 mm × 1 mm squares, deburred, and cleaned with isopropyl alcohol to remove and cutting fluids. Samples were generally run in triplicate.

Corrosion tests were run between 0 and 200 hours; using this range of testing times, important information regarding the kinetics and thermodynamics of corrosion reactions can be assessed. Exposure temperatures varied from 500–700°C, allowing for temperature dependences to be determined. Finally, the total HCl mole fraction was varied from 0–0.6 while holding the STC and hydrogen mole fractions relatively constant. HCl mole fraction is considered an important variable for several reasons. It is suspected that as the HCl mole fraction increases, the amount of metal silicide formation decreases, and correspondingly, the formation of metal chlorides increases. Because metal silicides may be considered a passivation layer and metal chlorides a volatile product, it is extremely important to understand the amount of HCl that can be present while still forming metal silicides.

Surface and gravimetric analysis were performed before and after chlorosilane exposures. Surface analysis was performed using a Zeiss Supra 55VP field emission scanning electron microscope (FEM) equipped with energy dispersive x-ray spectroscopy (EDS) capable of both spot scans and line scans. Atomic concentrations extracted from EDS scans were done so from spectral analysis without standards. Therefore, the results are semi-quantitative in nature and large composition differences between spots are primarily of interest. Gravimetric analysis was performed using a Sartorius microbalance with 2 microgram precision. Mass change was normalized by dividing by surface area to make the results geometrically independent. Cross section preparation was performed using Allied High Tech cross sectioning and polishing equipment.

The predominance diagrams for this work were generated using FactSage software, a thermodynamic calculation package that is commonly used for condensed phase predictions.\(^{27}\) For this application, FactSage outputs a map of the thermodynamically stable species based on silicon activity, chlorine activity, temperature, and the starting metal. An example of a predominance diagram for the H-Fe-Si-CI system at 550°C is shown in Figure 2a. In this diagram, the vertical axis represents the log of activity of silicon while the horizontal axis represents the log of partial pressure of HCl. There are several species predicted in this system depending on the activities of silicon and chlorine. A few areas of interest include the predicted transition from Fe to Fe5Si at \( \log(Si) = -6 \) and the predicted transition from FeCl2 to either Fe or Fe5Si at \( \log(HCl) = -1.2 \). These represent the compositions necessary to either cause corrosion or change from one type of corrosion to another. One goal of this study is to investigate these two transition areas.

Error bars in all figures displaying gravimetric results represent a 95% confidence interval as calculated from samples run in triplicate. One primary source of gravimetric error was material loss between the exposure and mass measurement. Very thick surface silicide layers occasionally spalled off of the samples during handling steps while surface chloride layers sometimes smeared off. These fragments of broken or smeared layers were included in the mass measurements, however, this was inevitably a potential source of error and the main reason why error bars got larger at higher temperatures, longer exposures, and higher mole fractions of HCl.

**Results and Discussion**

*Composition dependent results.*—The first part of this study was looking at the dependence of corrosion on total mole fraction HCl. Mole fraction HCl was considered the control variable because it directly changes the chloride activity in the system and it is easy to control via mass flow controller. For these tests, the \( H_2:STC \) mole fractions were held approximately constant at 0.73:0.25 while the HCl mole fraction was varied to specified values. The time of exposure was held constant at 100 hours and two series of exposures, one at 550°C and one at 600°C, were performed. The gravimetric results from this
testing are shown in Figure 3. This discussion will first focus on the 550°C results and then move to the 600°C results.

From this graph, it is clear that at 550°C, specific mass change decreases with increasing amounts of HCl. This phenomenon can be explained by suggesting that without HCl in the system, iron silicide formation is the dominant reaction. Iron silicide is stable and well adhered to the sample surface, causing a net mass gain. This reaction is modeled by Equation 5. When a larger amount of HCl is added to the system, iron and chromium chloride formation become the dominate reactions. One type of iron chloride formation in this system is modeled by Equation 6. The chloride resulting from this reaction is volatile at 550°C as shown in Table I. In reality, it is likely that both of these reactions plus many more silicide/chloride forming reactions happen concurrently with the HCl content dictating which are dominant. This helps explain the intermediate values of mass gain with small amounts of HCl.

\[
Fe + SiCl_4 + 2H_2 \rightarrow FeSi + 4HCl \quad [5]
\]

\[
Fe + 2HCl \rightarrow FeCl_2 + H_2 \quad [6]
\]

The presence of chlorine and silicon containing species was verified by FEM and EDS. Figure 4 shows FEM micrographs and EDS spot scan locations for exposures at several different concentrations of HCl. EDS results for all FEM micrographs are shown in Table II. As was predicted by the gravimetric analysis, primarily metals and silicon were detected after exposure at low concentrations of HCl indicating metal silicide formation. As HCl concentrations increase, there is more residual chromium and chlorine on the sample surfaces. This trend continues until very high HCl concentrations at which point there are negligible amounts of detectable silicon species present. It is important to note the large differences in surface morphology between the silicon containing and chlorine containing species. Microscopically, the iron and silicon rich areas appears to have a highly crystalline structure while the chromium and chlorine rich areas are amorphous and friable. This is consistent with macroscopic observations as well. When handling the primarily chloride forming samples, it was clear that the surface chloride layers were wax-like and could be wiped away. The silicide layers were much harder and could only be removed with a considerable amount of force. In surface analysis, presence of chromium chloride was used as an indicator of overall chloride formation due to low vapor pressure at the exposure temperatures (Table I). In addition to using chromium chloride as an indicator of chloride formation, the condensate at the cool end of the tube furnace was collected and analyzed with FEM/EDS. Semi-quantitative EDS analysis revealed an atomic composition consistent with stoichiometric FeCl2.

While the transition from forming silicides to forming chlorides was clear at 550°C, the same shift was not seen at 600°C. This observation was initially counterintuitive, as it was expected that the higher temperature would cause a higher metal chloride vapor pressure, leading to increased reactive evaporation. However, the predominance diagrams were able to help explain this observation. Figure 2b presents predominance diagrams for Fe in a Si-HCl-H2 system 600°C which can be compared to the predominance diagram at 550°C in Figure 2a. These diagrams show that at low chlorine activity, silicide formation is dominant. Within the silicide dominated region, it is also clear that there are several different types of silicides, with iron-rich silicides at low silicon activity and silicon-rich silicides at high silicon activities. As chlorine activity increases, metal chloride formation is dominant. This correlates with experimental results, but what can help explain the results at 600°C comes from comparing the two predominance diagrams.

It is clear that a higher temperature favors metal silicide formation as is indicated by the higher chlorine activity required to form metal

Figure 3. Gravimetric analysis from variable HCl testing at 550 and 600°C. The error bars represent a 95% confidence interval.

Figure 4. FEM micrographs and EDS spot scan locations for several AISI 316L samples after exposure to chlorosilane environments with various amounts of HCl at 550°C after 100 hours of exposure. EDS data is displayed in Table II which shows spots 1, 2, and 4 containing primarily Fe and Si and spots 3, 5, 6, and 7 containing significant amounts of Cr and Cl.

| Atomic % | Fe | Cr | Ni | Si | Cl | O |
|----------|----|----|----|----|----|---|
| Spot 1   | 32 | 1  | 3  | 34 | 0  | 29|
| Spot 2   | 74 | 2  | 6  | 18 | 0  | 0 |
| Spot 3   | 14 | 9  | 0  | 5  | 8  | 65|
| Spot 4   | 70 | 2  | 19 | 1  | 0  | 0 |
| Spot 5   | 1  | 17 | 0  | 0  | 18 | 63|
| Spot 6   | 0  | 9  | 2  | 14 | 16 | 58|
| Spot 7   | 1  | 33 | 0  | 1  | 45 | 20|
| Spot 8   | 30 | 25 | 3  | 12 | 0  | 30|
| Spot 9   | 62 | 16 | 6  | 2  | 0  | 15|
| Spot 10  | 52 | 16 | 6  | 2  | 0  | 24|
| Spot 11  | 59 | 10 | 2  | 15 | 4  | 11|
| Spot 12  | 43 | 5  | 8  | 44 | 0  | 0 |
| Spot 13  | 48 | 7  | 1  | 42 | 0  | 0 |
| Spot 14  | 8  | 2  | 1  | 90 | 0  | 0 |
| Spot 15  | 73 | 13 | 12 | 5  | 0  | 0 |
| Spot 16  | 44 | 7  | 2  | 47 | 0  | 0 |
| Spot 17  | 46 | 6  | 2  | 42 | 0  | 3 |

Table II. EDS results for spots labeled in FEM micrographs in Figures 4, 6, and 8.
Figure 5. a) Raw gravimetric analysis of 316L after 100 hours at a variety of temperatures in a H₂:STC:HCl environment and b) transformed gravimetric data used to indicate changes in corrosion mechanism. The error bars represent a 95% confidence interval.

chlorides. This implies that in the range of 0.03 mole fraction of HCl corresponds to an approximate HCl activity of $\sim 10^{-1.1}$. In this range, iron is transitioning from iron silicide formation to iron chloride formation at 550 °C and is consistently forming iron silicides at 600 °C. This helps to explain why at 600 °C, the mass change appears to be independent of HCl concentration. Based on these results, future work might include much higher HCl mole fractions to attempt to form metal chlorides at higher temperatures.

**Temperature dependent results.**—The next step in characterizing AISI 316L corrosion in chlorosilane environments was to study the effect of temperature on corrosion mechanisms. For these tests, AISI 316L was exposed for 100 hours at a variety of temperatures (500–700 °C) to a H₂:STC:HCl mixture with total mole fractions equaling 0.73:0.25:0.018 respectively. Figure 5a shows the raw gravimetric data and Figure 5b shows the natural logarithm of mass change per surface area plotted against 1000/T. This plot is useful because whether the corrosion is limited by diffusion or reaction rate, the amount of corrosion, represented by mass change per surface area, will follow the form of Equation 7. In this equation, $\Delta m$ is the mass change per surface area, A is a constant, $E_a$ is activation energy, k is Boltzmann’s constant, and T is temperature.

$$\Delta m = A \cdot \exp \left( -\frac{E_a}{(k \cdot T)} \right)$$

[7]

In general, a straight line on a plot with these axes represents a consistent corrosion mechanism with the slope of the line being representative of the activation energy for that mechanism. Because the data from this series of experiments does not form a single straight line in Figure 5b, it signifies that the rate limiting step in the corrosion process changes with temperature. The FEM micrographs displayed in Figure 6 also show a different surface topography for different temperature exposures. For exposure temperatures of 500 and 550 °C, there are areas where EDS detected pockets of Fe and Si that are surrounded by areas consistent in composition with bare 316L. The surface topography is also significantly different for the two regions with the Fe-Si regions being highly faceted and the 316L regions appearing more polished. For the exposure temperatures at 600 °C and greater, only the Fe-Si topography and composition was detected. Based on the gravimetric data and FEM micrographs, one could argue that the lower-temperature exposures resulted in reaction-limited silicide growth while the higher-temperature exposures resulted in diffusion-limited silicide growth. This is primarily evidenced by the discontinuous silicide layer at low temperatures and a continuous silicide layer at higher temperatures. With a discontinuous silicide layer, there is bare metal readily available to react and form silicide, likely making the process reaction-limited. With a continuous silicide layer, the reacting species must diffuse through the silicide prior to reacting, likely making the process diffusion-limited. It is important to recall that these tests were performed for 100 hours. It is likely that for longer exposure times, corrosion layers formed at lower temperatures ($\leq$550 °C) will become continuous and not contain the exposed pockets of bare 316L. Conversely, short exposure times at higher temperatures ($\geq$600 °C) would likely result in discontinuous Fe-Si pockets. It is arguable that two lines could be drawn through Figure 5b, one including the lower temperature exposures and another including the higher temperature exposures. The slope of these lines could then be interpreted as the activation energy for reaction and diffusion controlled mechanisms, respectively. However, this analysis was not done for this study due to the complex reaction mechanisms involving a highly alloyed metal and complex corrosion atmosphere. Therefore, the primary conclusions from this temperature dependent study are that the corrosion rate of AISI 316L in chlorosilane environments is highly temperature dependent, and after 100 hours, the mechanism of corrosion appears to change if the exposure is at, above, or below approximately 600 °C.

**Time dependent results.**—The next step in characterizing AISI 316L corrosion in chlorosilane environments was to determine the effect of time on corrosion. The time dependence of corrosion is extremely important to understand for industrial chlorosilane users because it can help predict service lifetimes and maintenance schedules. Similarly to temperature dependence, time dependent studies...
can help shed some light on transport mechanisms in the corrosion layer. For this series of experiments, AISI 316L was exposed for 7, 20, 98, and 188 hours at 700°C and with H2-STC:HCl mole fraction of 0.73:0.252:0.018. These conditions were chosen because they were shown in the temperature dependent study to promote silicide formation rather than chloride formation, which is more industrially relevant to study. The raw mass change data is shown in Figure 7a.

It is well known that diffusion controlled corrosion follows parabolic growth kinetics. The equation modeling parabolic kinetics is shown as Equation 8. In this equation, x represents the corrosion layer thickness, t represents time, and \( k_p \) is known as the parabolic rate constant.

\[
x^2 = k_p \times t \tag{8}
\]

Therefore, corrosion layer thickness squared can be plotted against exposure time, with the slope being the parabolic rate constant. This relationship, substituting mass change for corrosion layer thickness, is shown in Figure 7b. The nearly linear relationship in Figure 7b suggests that corrosion in these conditions is diffusion controlled. However, as with the temperature dependent study, these results should be interpreted qualitatively rather than quantitatively. This is for a few reasons. First, quantitative analysis would require runs at 75 and 150 hours to add more statistical significance to the parabolic fit. Second, the substitution of corrosion layer thickness for mass change is only a numerically appropriate substitution when the corrosion layer is uniform and non-volatile. Because there are several known forms of silicide species and many chloride species are volatile, neither of these conditions are met.

As with other experiments, FEM analysis was performed on these samples to characterize the corrosion layer. The results are shown in Figure 8. This analysis confirmed that there is primarily formation of iron silicon compounds at these conditions. It is significant that at all times, there is a continuous corrosion layer on the surface. This suggests that the corrosion enters diffusion controlled parabolic growth very quickly in these conditions. This result is consistent with Baldwin and Ivey’s observations of iron silicide growth in a solid-solid diffusion couple.22

In addition to surface analysis, cross sectional analysis was performed on a sample exposed to a STC-H2-HCl environment at 700°C for 100 hours. The FEM micrograph and corresponding EDS line scans are shown in Figure 9. Figure 9 also includes a more macroscopic view of the same cross section. The macroscopic view shows delamination between the bulk metal and the corrosion layer. It is likely that this delamination occurred during the cooling process, primarily because there were no iron silicide species detected at the bulk metal interface. If delamination occurred during exposure, it is very likely that the delaminated layer would contain some pores and cracks allowing the gas stream to pass through. This would cause some metal silicide formation on the bulk metal surface. Also, if the corrosion layer became delaminated during the exposure, it would have cutoff iron transport to the iron silicide growth interface. This would have significantly slowed the corrosion process. Because parabolic kinetics are still present at 100 hours, it is likely that iron could still transport through the iron silicide, meaning that the corrosion layer was most likely not delaminated during the exposure.

The higher magnification image shows the outer interface of the delaminated corrosion layer. An EDS line scan was done along the solid line, and the iron and silicon components are shown below. This line scan shows that there is a silicon rich region at the gas-solid interface, and a much thicker iron rich region through the remainder of the corrosion layer. EDS spot scans in these areas suggest that the silicon-rich region is likely FeSi and the iron-rich region is likely Fe3Si. These phases were both predicted by the predominance diagrams, and the EDS results indicate consistent stoichiometry. FeSi2 was also predicted by the predominance diagrams, but only at very high silicon activity. Because it is not present, either these chlorosilane conditions did not produce a high enough silicon activity to form it, or it decomposed in the time that the cross section was prepared and transferred to the FEM.

Conclusions

In this study, AISI 316L was exposed to a variety of chlorosilane environments as a means to study its corrosion behavior. This study
The metal silicides appeared to adhere better to the surface of the 316L sample when compared to the volatile metal chlorides, so their formation should be preferred in industrial processes. It was found that iron silicide formation in chlorosilane environments is likely diffusion controlled at high temperatures and long times as evidenced by the uniform, continuous corrosion layer and the parabolic growth kinetics. The temperature dependent study found an apparent diffusion-limited iron silicide formation at higher temperatures, which is consistent with other reported studies. At lower temperatures, the data indicated reaction-limited growth of the iron silicide species. Future work in this field could include the study of pure metals in chlorosilane environments in order to more fundamentally understand silicide and chloride formation of different alloying elements.

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