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FLAT-PLATE SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

QUARTERLY REPORT

INVESTIGATION OF THE HYDROCHLORINATION OF $SiCl_4$

(Covering the Period January 9, 1982 to April 8, 1982)

JPL CONTRACT NO. 956061
TO
JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

BY

JEFFREY Y. P. MUI

April 12, 1982.

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FLAT-PLATE SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrochlorination of $SiCl_4$"

THIRD QUARTERLY REPORT

April 12, 1982.
by
Jeffrey Y. P. Mui

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ABSTRACT

A research and development program on the hydrochlorination of silicon tetrachloride and metallurgical grade (m.g.) silicon metal to trichlorosilane was carried out as scheduled.

$$3\ SiCl_4 + 2\ H_2 + Si = 4\ SiHCl_3$$

Effects of pressure and temperature on this reaction were last reported. The presence of HCl in the reaction product mixture was successfully analyzed. Approximately 0.1% to 0.5% HCl based on total chlorosilanes were produced by the hydrochlorination reaction. Experiments on the corrosion study were carried out to evaluate a variety of metals and alloys as the material of construction for the hydrochlorination reactor. Material includes carbon steel, nickel, copper, Alloy 400 (Monel), stainless steel (Type 304), Incoloy 800H and Hastelloy B-2. The corrosion test was carried out at reaction temperature of 500°C, pressure of 300 psig and $H_2/SiCl_4$ feed ratio of 2.0 for a total of 87 hours. Results of the corrosion test show that all the test samples achieved a weigh gain. As previously observed, the weigh gain is due to the deposition of silicon on the metal surface to form a silicide protective film. Interestingly, the amount of Si deposition differs greatly between the different metals and alloys. Pure metals, such as, nickel and copper show a much larger silicon deposition than that of their alloys (Alloy 400 with 2/3 Ni and 1/3 Cu). On the other hand, Type 304 stainless steel, Incoloy 800H and Hastelloy B-2 which contain higher melting elements (chromium and molybdenum) show the least amount of silicon deposition.

The silicide films on the nickel and Incoloy 800H test samples were analyzed by Scanning Electron Microscopy (SEM). The composition of the silicide film was analyzed by the X-ray microprobe and the EDAX analyzer. Experimental results obtained from these measurements show that the silicide protective film is formed by a complex chemical and physical process. A plausible mechanism on the formation of this silicide film is discussed. Based on the corrosion test results, the most suitable material of construction for the hydrochlorination reactor is the type of alloys which contain a high level of Ni, Cr and Mo. Further experimental studies on the subject of corrosion is also recommended.

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I. INTRODUCTION

Experimental work on the hydrochlorination of $SiCl_4$ and m.g. silicon metal to $SiHCl_3$ was continued as scheduled. This Quarterly Report is the third one in the series. The objective of this research and development program is primarily designed to generate basic reaction kinetic and engineering data so that the potential application of the hydrochlorination process for the production of high purity, solar grade silicon metal can be fully evaluated.

Activities in this quarter include HCl analysis on the hydrochlorination reaction and a corrosion study on various material of construction for the hydrochlorination reactor. Results are summarized in the following discussion.

II. DISCUSSION

A. The Hydrochlorination Apparatus

The two inch-diameter stainless steel reactor for the hydrochlorination of $SiCl_4$ and m.g. silicon metal is schematically shown in Figure I. The design and operation of the hydrochlorination apparatus were reported in detail in the first Quarterly Report (DOE/JPL 956061-1). The apparatus has been operated satisfactory. Experiments on the reaction kinetic measurements to study the effect of pressure and temperature were last reported. Analysis for HCl in the reaction product mixture and a corrosion test for various materials of construction for the hydrochlorination reactor were carried out.

B. HCl Analysis on the Hydrochlorination Reaction

At elevated temperatures, a reaction system containing a chlorosilane and hydrogen gas is known to produce HCl in variable amounts depending on the reaction conditions. At high temperatures, HCl is highly corrosive toward metals and alloys(1). Thus, the amount of HCl generated by the hydrochlorination reaction is a useful piece of information to know. The small amounts of HCl in the reaction product mixture is difficult to measure. External sampling is not desirable since a trace amount of moisture can react with the chlorosilanes present to produce HCl. This problem was overcome by carrying out the HCl analysis with the in-line gas chromatograph (G.C.). The in-line arrangement avoids any contact of the sample with the atmosphere. Also, contamination of the sample in the sampling procedure is eliminated. The large amount of hydrogen present in the reaction product mixture interferes with the G.C. analysis. This interference was eliminated by using the same hydrogen gas for the hydrochlorination reaction as carrier gas in the G.C. analysis. The G.C. column (SE-30 silicone gum on Chromosorb W) does not separate HCl from other non-condensable gases, such as, nitrogen and argon. Thus, any non-condensable gas in the reactor system must be completely removed. This was accomplished by evacuating the hydrochlorination apparatus with a vacuum pump. Hydrogen gas was used to replace the argon gas to pressure-feed $SiCl_4$ and the m.g. silicon metal into the reactor system.

An experiment for the HCl analysis was carried out at 500°C, 300 psig and $H_2/SiCl_4$ ratio of 2.0. The hydrogen feed-rate was adjusted to give a long residence time of 209 seconds for the hydrochlorination reaction. The long residence time was designed to maximize the amount of HCl. HCl is presumably produced from an equilibrium reaction of chlorosilane and hydrogen gas. After the reactor system has stabilized, the reaction product mixture was analyzed by the in-line G.C. every hour for a period of five hours. Results of the G.C. analyses are summarized in Table I. Data in Table I show that a constant amount of about 0.6% HCl was present in the reaction product mixture throughout the five hours of reaction. Since the amount of HCl remained at a constnat level, there was no interference by any other non-condensable gas in the G.C. analysis. If residual nitrogen or argon gas was present in the reactor system, one would expect the HCl peak to decrease as a function of time.

Another experiment was carried out to study the rate of formation of HCl. The same hydrochlorination experiment was repeated under the same reaction conditions but at different residence times by varying the hydrogen gas feedrate. Results of the HCl analysis are summarized in Table II. Data in Table II show that, as the residence time is reduced, the amount of HCl produced by the hydrochlorination reaction also decreases. For example, the amount of HCl in the reaction product mixture is reduced from 0.6% to about 0.4% and 0.13% at a shorter residence time of 138 seconds and 96 seconds, respectively. The same measurement was repeated at 209 seconds residence time (sample no. 5 and 6). Results of the HCl analysis at 209 seconds residence show good agreement between the two experiments and good reproducible results from the G.C. analysis. These analytical data are indicative of the presence of a small amount of HCl produced by the hydrochlorination reaction.

C. Corrosion Study

In the chloride-rich hydrochlorination reaction enviroment, the operating temperature of 500° C and above post a potential corrosion problem for the reactor constructed with conventional metal alloys. Metals and alloys offer little or no resistence to high concentrations of HCl gas at temperatures much above 450° C (1). Under these conditions, the usual oxide protective film on the metal surface is replaced by a metal chloride film. The covalent nature of the metal chlorides exhibits a much higher vapor pressure than those of their oxide counterparts. At elevated temperatures, the metal chloride film begins to evaporate off. Corrosion becomes a serious problem as the material of construction of the reactor is constantly removed from the reactor wall as metal chlorides.

Contradiction to this corrosion mechanism was noted in the previous corrosion study (2). The previous corrosion test results show that a silicide protective film is formed on the metal surface. The objective of the present experimental work is to provide a basic understanding on the mechanism of corrosion inside the hydrochlorination reactor and to evaluate a variety of metal alloys as the material of construction for the hydrochlorination reactor.

(1) Corrosion Test Results

Samples of material of construction for the hydrochlorination reactor were prepared. Materials include carbon steel, nickel, copper, Alloy 400 (Monel), Type 304 stainless steel, Incoloy 800H and Hastelloy B-2. The approximate compositions of these alloys are given in Table III. The test samples were weighed and their total surface area measured. They were mounted on a stainless steel rack which was fitted inside the 2" hydrochlorination reactor tube. In this manner, all the test samples were exposed to the same reaction enviroment throughout the corrosion test. There are a total of nine test samples of nickel, which were evenly spaced along the entire reactor tube from the grid plate to the top of the reactor. The test sample for carbon steel include six samples. There are two test samples each of copper, Alloy 400, Type 304 stainless steel, Incoloy 800H and Hastelloy B-2. These samples were mounted near the bottom of the reactor tube. The reactor was charged 862 grams of m.g. silicon metal (32 mesh x dust), which formed a mass bed of about 18 inches high. Thus, with the exception of a few nickel and carbon steel samples, all the test samples were buried in the silicon metal mass bed.

The corrosion test was carried out at a reactor temperature of 500°C, pressure of 300 psig and a $H_2/SiCl_4$ molar ratio of 2.0 for a total of 87 hours. After 87 hours of the hydrochlorination reaction, the test smaples were removed from the reactor. Immediately, they were stored in glass bottles containing a drying agent (Drierite). Each of the test samples was cleaned and re-weighed with an analytical balance. Results of the weigh data are summarized in Table IV for nickel, Table V for carbon steel and Table VI for copper, Alloy 400, stainless steel, Incoloy 800H and Hastelloy B-2. Interestingly, the weigh data show that all the test samples achieved a gain in weigh.

Table IV summarized the corrosion test results on pure nickel. The location of each of the nine test samples is given in the second column in Table IV. With an 18 inch silicon mass bed, sample nos. 5,6,7,8 and 9 were buried in the silicon mass during the hydrochlorination reaction while sample nos. 1,2,3 and 4 were outside the silicon mass bed. As the previous corrosion study showed, the weigh gains by the test samples were due to the deposition of silicon on the metal surface to form a silicide protective film. Interestingly, data in Table IV show that the amount of silicon deposition on the nickel samples varies at different locations inside the reactor tube. Test samples no. 5,6,7,8 and 9 appear to show a concentration effect due to the hydrochlorination reaction, since the amount of silicon deposition gradually decreases toward the top of the Si mass bed. On the other hand, test samples no. 1,2 and 3 show very little silicon deposition. This is most likely due to the effect of temperature, since temperature near the top of the hydrochlorination reactor tube is much lower than that of the Si mass bed.

Table V summarizes the corrosion test results on carbon steel. The amount of silicon deposition on carbon steel is less than that of pure nickel (Table IV). Again, a gradual decrease on the amount of silicon deposition is noted on the test samples located upward along the Si mass bed.

Table VI summarizes the corrosion test results on copper, Alloy 400, stainless steel, Incoloy 800H and Hastelloy

B-2. The amount of silicon deposition (last column in Tables IV, V and VI) on the test samples shows large differences between different metals and alloys. In Table VI, the copper sample shows a large silicon deposition of about 15 m.g./cm^2 similar to that of the nickel sample. Interestingly, an alloy of nickel and copper (Alloy 400 with 2/3 Ni, 1/3 Cu) gives a much smaller amount of silicon deposition of about 4 m.g./cm^2 than those of the pure metals. On the other hand, stainless steel (3 m.g./cm^2), Incoloy 800H (2 m.g./cm^2) and Hastelloy B-2 (1.5 m.g./cm^2) show the least amount of silicon deposition in the corrosion test. One plausible explanation is that these alloys contain a third element which has a much higher melting point (chromium, m.p. 1,890°C and molybdenum, m.p. 2,620°C) than that of silicon (m.p. 1,420°C). The mechanium on the formation of the silicide protective film is discussed in Section (3).

The chemical nature of the deposited silicide film on the test samples is also different. For example, the silicide films on stainless steel and Incoloy 800H are reactive toward moisture. These silicide films are readily destroyed when they are exposed to the atmosphere. In contrast, the silicide film on nickel, copper and Alloy 400 are stable toward air and moisture in the atmosphere.

(2) Scanning Electron Microscopic Analysis of the Silicide Protective Film

The silicide protective film on the nickel sample and on the Incoloy 800H sample was analyzed by a Scanning Electron Microscope (SEM). Carbon was used to coat the sample surface in the standard sample preparation procedure for the SEM analysis. To analyze the cross section of the silicide film, the test sample was embedded in an epoxy resin. A cross section was cut and polished. In Figure II, the SEM photographs show the surface morphology of the silicide film on the nickel sample (Sample no. 8 in Table IV) at 500, 1900 and 5000 magnifications.

These photographs show particles of the order of 3 to 10 microns on the surface of the metal. There appears to be two types of particles, one type being rather blocky sections and the other type has a laminated structure. They may be the two different types of nickel-silicon phases formed in the hydrochlorination reaction enviroment. The compositions of these two types of particles are in the process of being analyzed.

Figure III shows the SEM photographs of a cross sectional area of the nickel sample. A well-defined layer of the silicide film is seen on both side of the nickel base metal. At a higher magnification (500x), the silicide film shows a rather porous structure with many void spaces. The thickness of the silicide film was measured directly from this SEM photograph to give 110 microns. The same measurement on the nickel base metal gave 480 microns (0.0189 inch) which is in good agreement with the specification on the 0.02 inch pure nickel sheet from which the test sample was prepared. The composition of the silicide film was analyzed by the X-ray microprobe and the EDAX analyzer. Figure IV shows the X-ray distribution maps of silicon and nickel as well as the EDAX analysis on the four different areas of a cross sectional area of the nickel test sample. The X-ray map of silicon show a rather uniform distribution of Si throughout the silicide film with the exception of a small decrease in Si concentration adjacent to the nickel base metal. As shown by the Si X-ray map, the silicon distribution in the silicide film is well-defined. There does not appear to be a gradual decrease in the silicon concentration across the silicide film-nickel boundary. The EDAX analysis at the four different areas of the test sample show that the bulk of the silicide film has the atomic composition of 40% to 50% Si. This corresponds to the nickel-silicon phases, Ni_3Si_2 (m.p. 964°C) and NiSi (m.p. 992°C), which also have the lowest melting points among the nickel silicides.

The deposition of silicon on the nickel metal surface is primarily a chemical vapor deposition process. Since a chemical reaction on a solid surface does not normally involve surface atoms more than 10 to 20 atomic layers deep, the formation of such a thick nickel silicide film (110 microns) must involve other physical process. Thermal migration of Si and Ni atoms at the reaction temperature of 500°C is a plausible explanation. For example, a θ nickel-silicon phase (38.7% Si, 61.3% Ni) has a melting point range as low as 806°C. The formation of these thermodynamically more stable nickel-silicon phases appears to be the driving force which determines the composition and the physical structure of the silicide protective film. A plausible mechanism on the formation of the silicide film is discussed in Section (3).

The Scanning Electron Microscopic analysis on the Incoloy 800H test sample shows a complex silicide protective film. The Incoloy 800H test sample was obtained from a previous corrosion study carried out at the Massachusetts Institute of Technology (2) (JPL Contract No. 955382). The corrosion test on this sample was carried out under similar reaction conditions at 500°C, 300 psig and $H_2/SiCl_4$ ratio of 2.0 but for a longer duration of 238 hours. The SEM photograph of a cross sectional area of the Incoloy 800H sample is shown in Figure V. The SEM photograph in Figure V shows a well-defined silicide film which was slightly broken off from the base metal. The test sample has been briefly exposed to the atmosphere. The action of moisture on the reactive silicide film might cause the breakage. The test sample was cut from an one inch O.D. Incoloy 800H tubing. Thus, the base alloy does not have a very smooth surface as that of the nickel sample.

Figure VI shows the SEM analysis on a cross sectional area of the Incoloy 800H test sample and the X-ray maps of silicon, chlorine, nickel, chromium and iron. The presence of chlorine in the silicide film is interesting, since no significant amount of chlorine was detected in the silicide film on the nickel test sample. The chlorine, most likely in the form of metal chlorides, appears to concentrate at the boundary between the silicide film and the base metal (see Figure VI, chlorine X-ray map). The presence of chloride in the silicide film may explain the reactivity of this silicide film toward air and moisture. Metal chlorides, $FeCl_3$, $NiCl_2$ $CrCl_3$ and Si-Cl readily react and dissolve in water to form hydrochloric acid which, in turn, can attack the metal-silicide deposits. The X-ray distribution maps also show segregations of silicon and the three basic metallic elements, Ni, Cr and Fe, which make up the Incoloy 800H alloy. For example, Si appears to concentrate more at the outside portion of the silicide film. On the other hand, nickel appears to concentrate more at the silicide-Incoloy 800H boundary. Chromium and iron are distributed more evenly at the middle section of the silicide film.

Figure VII summarizes the results of the EDAX analysis on four different areas of a cross sectional area of the Incoloy 800H test sample. Results of the EDAX analysis are plotted in a graph shown in Figure VII. The graph in Figure VII confirms the high degree of segregations of the elements at different locations of the silicide film. This high degree of segregation is not unexpected. In such a multi-component system, there must be many metal-silicon phases as well as many metal-metal phases. The composition of the silicide film on Incoloy 800H is therefore very complex. A plausible mechanism on the formation of the silicide protective film is discussed in the following.

(3) Corrosion Mechanism Study

a. Chemical Process

The deposition of silicon on the metal alloy surface may be derived from a chemical vapor deposition (CVD) process.

For example, the reversible hydrochlorination reaction,

$$4\ SiHCl_3 = 3\ SiCl_4 + 2\ H_2 + Si$$

is a source for the deposition of silicon. The reaction of $SiHCl_3$ and $SiCl_4$ with hydrogen gas at elevated temperatures to deposit silicon metal is well-established (3,4). At the start of the hydrochlorination reaction, the activity (concentration) of Si on the metal surface is zero. As the reaction proceeds, silicon is deposited until the activity of the Si on the metal surface reaches a steady state concentration. The amount of Si deposition is governed by the system conditions and the equilibria of all the CVD processes. Furthermore, there are other plausible reactions occurring at the metal surface. For example, HCl is known to be present in the hydrochlorination reaction enviroment. It can react with silicon and the metallic elements present at the reactor wall,

$$Si + 3\ HCl = H_2 + SiHCl_3$$
$$2\ Fe + 6\ HCl = 3\ H_2 + 2\ FeCl_3$$
$$Ni + 2\ HCl = H_2 + NiCl_2$$
$$2\ Cr + 6\ HCl = 3\ H_2 + 2\ CrCl_3$$

Metal chlorides are also known to react with silicon metal,

$$4\ FeCl_3 + 3\ Si = 3\ SiCl_4 + 4\ Fe$$
$$2\ NiCl_2 + Si = SiCl_4 + 2\ Ni$$
$$4\ CrCl_3 + 3\ Si = 3\ SiCl_3 + 4\ Cr$$

The free metal atoms generated from these reactions can readily combine with the deposited silicon to form the variety of metal-silicon phases (silicides).

b. Physical Process

If the silicide protective film is produced by the chemical reactions alone, one would expect only a thin deposit on the metal surface, since chemical reactions on a solid surface do not normally involve surface atoms more than 10 to 20 atomic layers deep. The very thick silicide films on the nickel and copper sample suggest that a fast diffusion process is operative under the hydrochlorination reaction conditions. In the case of nickel and copper, some metal-silicon phases are formed at relatively low temperatures, viz., Cu_3Si (553°, 802°), Ni_3Si_2 (845°, 964°) and NiSi (992°), in comparison with the reaction temperature of 500°. Thus, the migration of Si and Ni or Si and Cu to form these low-melting metal-silicon phases can be a rapid process. The kinetics is characterized by a low activation energy. Results of the X-ray microprobe and EDAX analysis of the silicide film on the nickel test sample show that the composition of the silicide film corresponds to those of Ni_3Si_2 and NiSi, which are the thermodynamically most stable nickel-silicon phases. The same argument may be made on the copper sample which also forms a thick silicide film. However, it is interesting to note that, when an alloy of nickel and copper is exposed to the same reaction enviroment, the amount of silicon deposition is much smaller. For example, the Alloy 400 (2/3 Ni, 1/3 Cu) sample in Table VI shows a weigh gain of about 4 m.g./cm^2 in comparison with about 15 m.g./cm^2 for the pure metal, nickel and copper. The kinetics on the formation of these nickel-silicon and copper-silicon phases is characterized by a higher activation energy, since the metal-silicon phases are now formed at the expenses of other nickel-copper phases. This may explain the much smaller silicon deposition on Alloy 400 in comparison with those of pure nickel and copper.

An even slower kinetic process in the formation of the silicide film may be explained by the presence of a higher melting metal component in the base alloys. Stainless steel, Incoloy 800H and Hastelloy B-2 contain chromium (m.p. 1,890°C) and molybdenum (m.p. 2,620°C) which have a melting temperature much higher than that of silicon (m.p. 1,420°C). The metal-silicide phases of Cr and Mo are formed at a much higher temperature, e.g., $CrSi_2$ (1,550°C), CrSi (1,600°C), $MoSi_2$ (1,870°C) and Mo_3Si_2 (2,190°C). The kinetics in the formation of these high melting metal-silicon phases can be expected to be much slower than those of nickel and copper. Therefore, as data in Table VI show, stainless steel (3 m.g./cm^2), Incoloy 800H (2 m.g./cm^2) and Hastelloy B-2 (1.5 m.g./cm^2) have the least amount of silicon deposition.

c. Potential Corrosion of the Hydrochlorination Reactor

The corrosion test results show that all the test samples achieve a weigh gain. Thus, no significant amount of corrosion of the hydrochlorination reactor made by these metals and alloys is expected as long as the silicide protective film is stable. On the other hand, results of the corrosion measurement on carbon steel, nickel and copper show a rather rapid grow of the silicide protective film. If the silicide film continue to grow to a thick scale, there is a potential corrosion of the reactor: (1) a thick silicide scale can weaken the reactor wall due to the poor mechanical properties of silicides and (2) a thick silicide scale can be broken off from the reactor wall due to mechanical and thermal stress - errosion by scaling. For example, if the nickel silicide film on nickel continues to grow at the rate of 110 microns every 87 hours, the silicide scale could penetrate the base metal at an excessive rate of 218 mils per year.

$$\frac{0.5 \times 365 \times 24 \times 110 \times 10^{-4}}{87 \times 2.54 \times 10^{-3}} = 218 \text{ mils/year}$$

Fortunately, alloys with high contents of nickel, chromium and molybdenum appear to have a much slower growth of the silicide film. For example, previous corrosion study on Incoloy 800H showed that about 8.6 microns of the base metal is incorporated into the silicide film (2). Assuming the worse case where the silicide film is erroded from the base metal every 238 hours, the corrosion rate on Incoloy 800H in the hydrochlorination reaction enviroment would amount to only 12 mils per year.

$$\frac{365 \times 24 \times 8.6 \times 10^{-4}}{238 \times 2.54 \times 10^{-3}} = 12 \text{ mils/year}$$

In this respect, alloys containing high levels of nickel, chromium and molybdenum are more suitable material of construction for the hydrochlorination reactor. The subject on selecting material of construction for the hydrochlorination reactor is discussed in Section e.

d. Recommendations for Further Corrosion Studies

A basic understanding on the mechansim of corrosion will not only allow a better choice on the material of construction for the hydrochlorination reactor but also it helps to identify potential corrosion problems. Recommendations for further experimental studies on the subject of corrosion may include,

- Time dependency: growth of the silicide film as a function of time,
- Growth of the silicide film as a function of temperature,
- Upper temperature limits on selected alloys at which corrosion becomes excessive.

e. Optimum Material of Construction for the Hydrochlorination Reactor

The present experimental studies on the subject of corrosion is primarily limited to what happens to the metal reactor in the hydrochlorination reaction enviroment. There are other forms of corrosions which must be taken into account in selecting the proper material construction for the hydrochlorination reactor. In fact, potential problems should be traced all the way back to the manufacturing process of the metal alloy which must meet the desired metallurgical specifications. The mechanical and thermal process (forming, welding, etc.) which fabricates the alloy to form the piece of equipment can effect the final properties of the alloy. A classical example of a potential corrosion problem is the "sensitization" of austenitic stainless steel. The sensitization may be resulted from an uncontrolled thermal cycle, such as, in a welding process. Precipitation of chromium carbide ($Cr_{23}C_6$) can deplete the chromium at the grain boundary. The net result is a sharp reduction in the alloy's resistence to corrosion and make the affected area more susceptable to chemical attack. Contamination of foreign material in the testing procedure, storage and transportation of the equipment could be another potential problem area. The atmospheric enviroment in which the reactor is installed is an important factor in selecting the proper material of construction. The atmospheric enviroment inside a chlorosilane processing plant may be considered as corrosive. The presence of acid chlorides, HCl and chlorosilane vapor contribute the corrosive nature of the enviroment. Interaction of these chlorides with moisture in the atmosphere produces a strong acid. "Chloride Stress Corrosion Crack" is a serious corrosion problem in the presence of high levels of chloride in the enviroment. Austenitic stainless steels are particularly sensitive to this type of structural failure which is generally believed to be the result of a transgranular attack by chloride accelerated by internal stress. The operating temperature of 500°C and above will also subject the outside wall of the hydrochlorination reactor to a high temperature enviroment. Oxidation and the presence of potentially corrosive contaminant (chloride, etc.) at these high temperatures represent still another potential corrosion of the hydrochlorination reactor. After the reactor has been in operation, there will be periods of shutdown for service and repair. Exposure of the inside wall of the reactor to air and moisture can readily destroy the silicide protective film. Hydrolysis of residual metal chlorides and chlorosilanes produces a strong acid which can further corrode the exposed metal alloy.

In the case of carbon steel, the prospect of forming a thick silicide scale is a potential corrosion problem. Furthermore, in the presence of hydrogen gas at high temperature and pressure, hydrogen embrittlement is potentially a serious corrosion problem for carbon steel. Although carbon steel is a low-cost material of construction, it does not appear to be a suitable material of construction for the hydrochlorination reactor. Stainless steel, Incoloy 800H and Hastelloy B-2 produce a stable silicide protective film on the metal surface. The silicide film does not penetrate deeply into the base metal at a rapid rate to form a thick scale. These alloys also show good resistence to the other forms of corrosion such as those in a high chloride level and high temperature oxidative enviroments. Although at a lower cost, stainless steel is somewhat less satisfactory as the material of construction for the hydrochlorination reactor, since it is more susceptable to chloride stress corrosion crack. In general, the type of alloys with high Ni, Cr and Mo contents similar to those of stainless steel, Incoloy 800H and Hastelloy B-2 are suitable material of construction for the hydrochlorination reactor.

Finally, there is the important element of cost. The cost of the base metal alloy, the cost of fabrication and the cost of repair are important factors in selecting the optimum material of construction for the hydrochlorination reactor. In general, the higher the Ni, Cr and Mo contents in a given alloy, the better is its corrosion resistence properties but also at a higher price. Therefore, the optimum material of construction for the hydrochlorination reactor is the choice of a good compromise between the performance of the piece of equipment and the cost of building it.

D. Summary of Progress

Experimental work on the JPL Contract No. 956061 has progressed as scheduled in the attached Program Plan. The analysis for HCl in the hydrochlorination reaction product mixture produces good, reproducible results. Only a very small amount, 0.1% to 0.5% based on total chlorosilanes, of HCl was present in the reaction. The corrosion study provides useful experimental data on the basic mechanism of corrosion of metals and alloys in the hydrochlorination reaction enviroment. The corrosion test evaluated a variety of metals and alloys as the material of construction for the hydrochlorination reactor. Alloys which contain high levels of nickel, chromium and molybdenum similar to those of stainless steel, Incoloy 800H and Hastelloy B-2 are suitable material of construction for the hydrochlorination reactor.

III. PROJECTED FOURTH QUARTER ACTIVITIES

The Program Plan is in the process of being revised for the fourth quarter (April-June, 1982.). More basic research oriented experimental studies are emphasized in future programs. The projected fourth quarter activities may include,

- Milestone checkpoint evaluation, program review,
- Revise Program Plan,
- Basic reaction kinetic studies to expand the range of pressure, temperaure and $H_2/SiCl_4$ molar ratio for the hydrochlorination reaction.

IV REFERENCES

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V. APPENDIX

Program Plan

Tables I to VI

Figures I to VII

SC-1 PROGRAM PLAN JPL/SOLARELECTRONICS CONTRACT No. 956 061

	Year	1981						1982					
	Month of Year	7	8	9	10	11	12	1	2	3	4	5	6
	Month of Contract	1	2	3	4	5	6	7	8	9	10	11	12
I	Program Plan, Baseline Cost Est.	~~1~~											
II	Transfer Reactor form M.I.T.	~~1~~	~~2~~										
III	Reactor Design, Order Equipment Construction of Apparatus	~~1~~	~~2~~	~~3~~	~~4~~								
IV	Safety Review, Start-up Reactor				~~4~~								
V	Reaction Kinetics Measurement							▲					
	(1) Function of T, P, C				~~4~~	~~5~~	~~6~~	~~7~~					
	(2) Impurities Measurement					~~5~~	~~6~~	~~7~~					
	(3) Mass Balance						~~6~~	~~7~~					
VI	Corrosion Study									▲			
	(1) Type 304,316 S.St., Incoloy, Alloy Steel, Carbon Steel etc.						~~6~~	~~7~~	~~8~~	~~9~~			
	(2) Corrosion Mechanism Study								~~8~~	~~9~~			
VII	By-Product HCl Recycle									▲			
	(1) Reaction Kinetics with HCl						~~6~~	~~7~~	~~8~~	~~9~~			
	(2) Corrosion Measurement with HCl							~~7~~	~~8~~	~~9~~			
	(3) Data Evaluation								~~8~~	~~9~~			
VIII	Fluidization Mechanism Study												▲
	(1) Design and Install 4" Reactor								~~8~~	~~9~~	10		
	(2) Safety Review, Start-up									~~9~~	10		
	(3) Reaction Rate Measurements, Fluidized-Bed, Fixed-Bed										10	11	
	(4) Data Evaluation										10	11	
IX	Recommendations									▲			▲
	(1) Optimum Process Parameters									~~9~~			12
	(2) Optimum Material for Reactor									~~9~~			
	(3) Additional Development Work												12
	(4) Final Report												12

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OF POOR QUALITY

▲ Milestone Check Points

Prepared by: Jeffrey Y. P. Mui , Solarelectronics, Inc.
July 22,1981.

TABLE I HCl ANALYSIS ON HYDROCHLORINATION REACTION AT 500°C, 300 PSIG, $H_2/SiCl_4$ RATIO OF 2.0 AND RESIDENCE TIME OF 209 SECONDS

Hourly Sample	Reaction Product Composition, Area %			
No.	HCl	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
1	0.5744	0.3696	31.82	66.91
2	0.5447	0.4007	31.02	68.03
3	0.6134	0.6028	31.85	65.55
4	0.5970	0.7512	32.66	64.04
5	0.5875	0.7611	31.64	66.66

TABLE II HCl ANALYSIS ON THE HYDROCHLORINATION OF $SiCl_4$ AT 500°C, 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.0

Sample No.	Residence Time Second	Reaction Product Composition, Area %			
		HCl	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
4*	209	0.5970	0.7512	32.66	64.04
5*	209	0.5875	0.7611	31.64	66.66
1	96	0.1235	0.4878	26.69	71.98
2	96	0.1388	0.5163	26.75	71.92
3	138	0.3326	0.7961	31.75	66.57
4	138	0.4343	0.3325	31.84	66.80
5	209	0.5962	0.7303	31.95	65.82
6	209	0.5735	0.8337	31.93	66.05

* Sample no. 4 and 5 from Table I.

TABLE III APPROXIMATE COMPOSITION OF THE METAL ALLOYS FOR CORROSION TEST

Metals, Alloys	Approximate Compositions
Carbon Steel	Basically Iron, + 95% Fe
Nickel	Pure
Copper	Pure
Stainless Steel (Type 304)	68% Fe, 19% Cr, 10% Ni, 2% Mn, 1% Si
Alloy 400 (Monel)	2/3 Ni, 1/3 Cu
Incoloy 800 H	45% Fe, 30% Ni, 23% Cr, 1% Mn, 0.6% Si
Hastelloy B-2	68% Ni, 28% Mo, 2% Fe, 1% Cr, 1% Mn

TABLE IV CORROSION TEST ON PURE NICKEL AT 500°C, 300 PSIG, AND $H_2/SiCl_4$ RATIO OF 2.0 FOR A TOTAL OF 87 HOURS

Sample No.	Distance from Grid Plate inch	Total Surface Area sq. cm.	Weigh before Reaction g.	Weigh after Reaction g.	Weigh Gain m.g.	Weigh Gain(1) per Unit Area m.g./cm^2
1	31.3	20.4	4.8807	4.9017	21.2	1.04
2	28.0	20.7	4.9450	4.9676	22.6	1.09
3	23.2	19.7	4.7197	4.7576	37.9	1.92
4	20.0	20.8	4.9888	5.0921	103.3	4.97
5	16.2	20.3	4.8710	5.0639	192.9	9.50
6	13.0	20.4	4.8850	5.1481	261.3	12.8
7	9.5	20.8	4.9808	5.3098	329.0	15.8
8	6.2	20.3	4.8638	5.2190	355.2	17.5
9	2.5	20.8	4.9680	5.2502	282.2	13.6

(1) Milligram per Square Centimeter

TABLE V CORROSION TEST ON CARBON STEEL AT 500° C, 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.0 FOR A TOTAL OF 87 HOURS

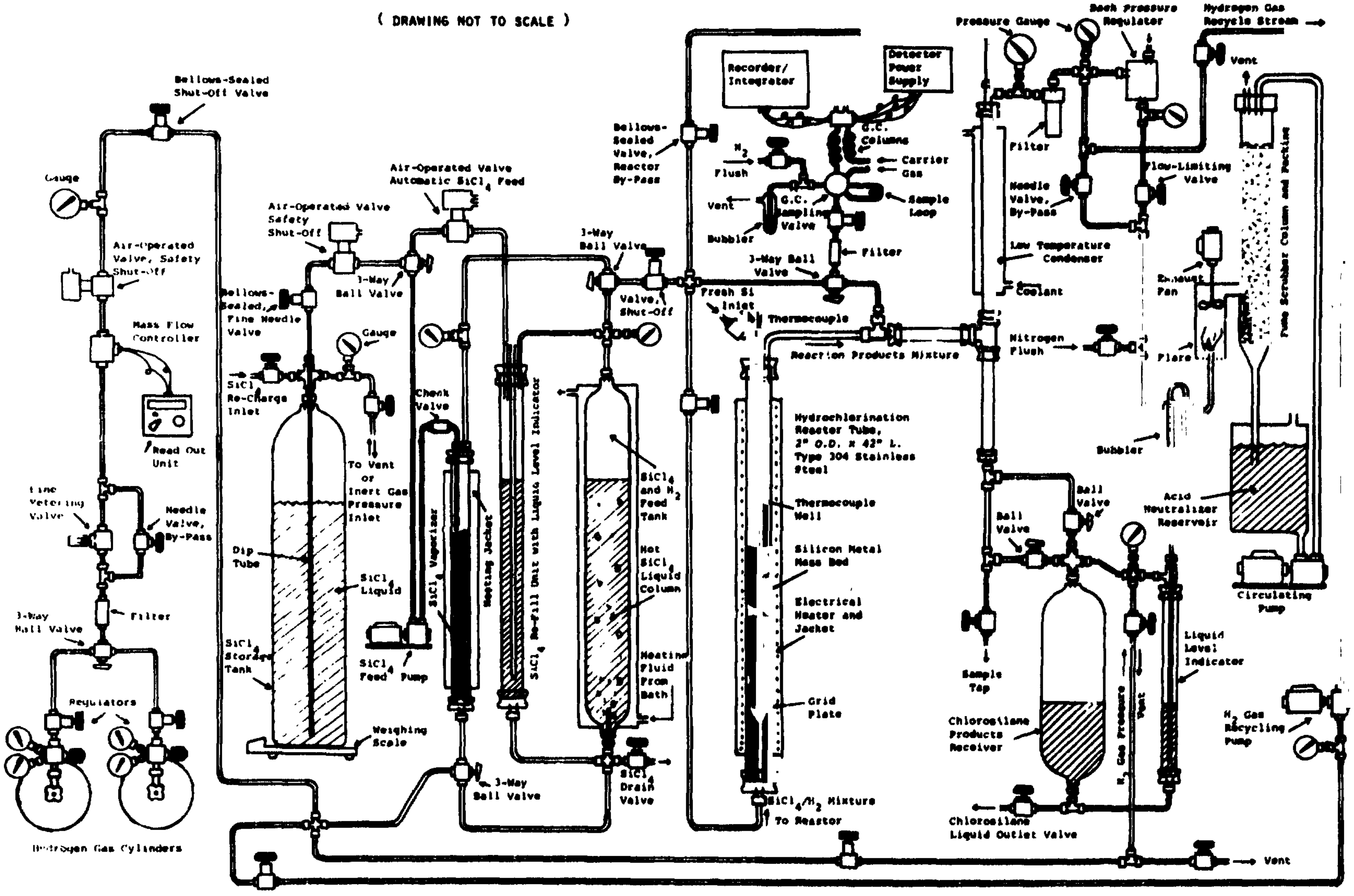
Sample no.	Distance from Grid Plate inch	Total Surface Area sq. cm.	Weigh before Reaction g.	Weigh after Reaction g.	Weigh Gain m.g.	Weigh Gain per Unit Area $m.g./cm^2$
1	21.3	15.9	3.6975	3.7237	26.2	1.65
2	17.2	16.0	3.7114	3.7765	65.1	4.07
3	13.8	16.0	3.7019	3.7938	91.9	5.74
4	10.2	15.9	3.6852	3.8141	128.9	8.11
	6.6	15.6	3.6100	3.7435	133.5	8.56
6	3.0	16.8	3.8900	4.0259	135.9	8.90

TABLE VI CORROSION TEST AT 500°C, 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.0 FOR 87 HOURS

Sample Metal Alloy	Distance from Grid Plate inch	Total Surface Area sq. cm.	Wiegh before Reaction g.	Weigh after Reaction g.	Weigh Gain m.g.	Weigh Gain per Unit Area m.g./cm^2
Copper	15.0	24.3	8.7066	8.9283	221.7	9.13
Copper	8.1	23.1	8.2623	8.5986	336.3	14.6
Alloy 400	11.3	31.2	21.3429	21.4448	101.9	3.27
Alloy 400	3.8	27.8	19.0018	19.1307	128.9	4.64
Incoloy 800H	11.0	28.7	13.4049	13.4561	51.2	1.78
Incoloy 800H	3.6	30.3	14.1411	14.1935	52.4	1.73
Stainless Steel	14.8	19.5	11.9436	11.9923	48.7	2.50
Stainless Steel	7.3	20.0	12.2397	12.2972	57.5	2.88
Hastalloy B-2	11.3	32.2	23.1987	23.2417	43.0	1.34
Hastalloy B-2	5.6	30.3	21.8447	21.9001	55.4	1.83

FIGURE I APPARATUS FOR THE HYDROCHLORINATION OF $SiCl_4$ AND M.G. SILICON METAL TO $SiHCl_3$

(DRAWING NOT TO SCALE)



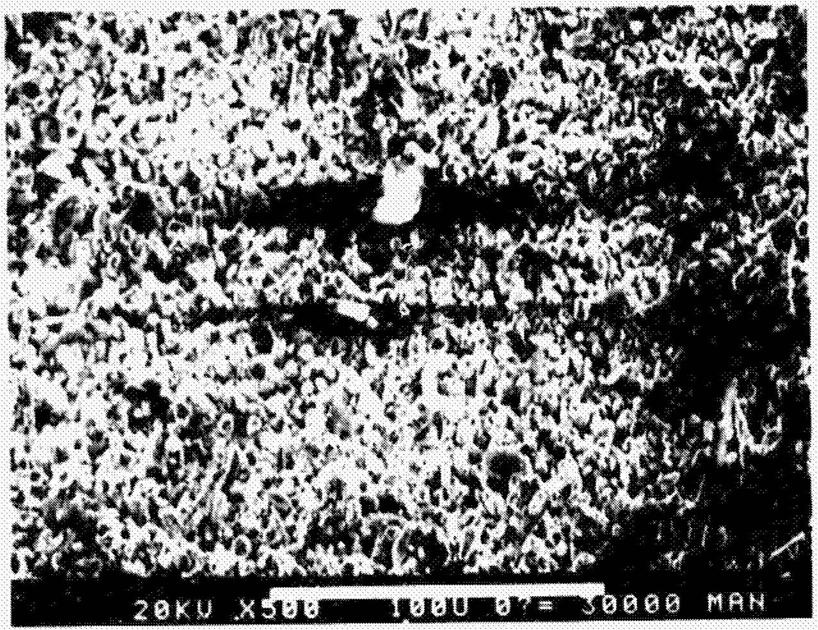


FIGURE II

CORROSION TEST ON PURE NICKEL: 87 HOURS AT 500°C, 300 PSIG AND $H_2/SiCl_4$ RATIO OF 2.0

SCANNING ELECTRON MICROGRAPH OF THE SURFACE OF THE TEST SAMPLE TO SHOW THE MORPHOLOGY OF THE SILICIDE FILM AT VARIOUS MAGNIFICATIONS

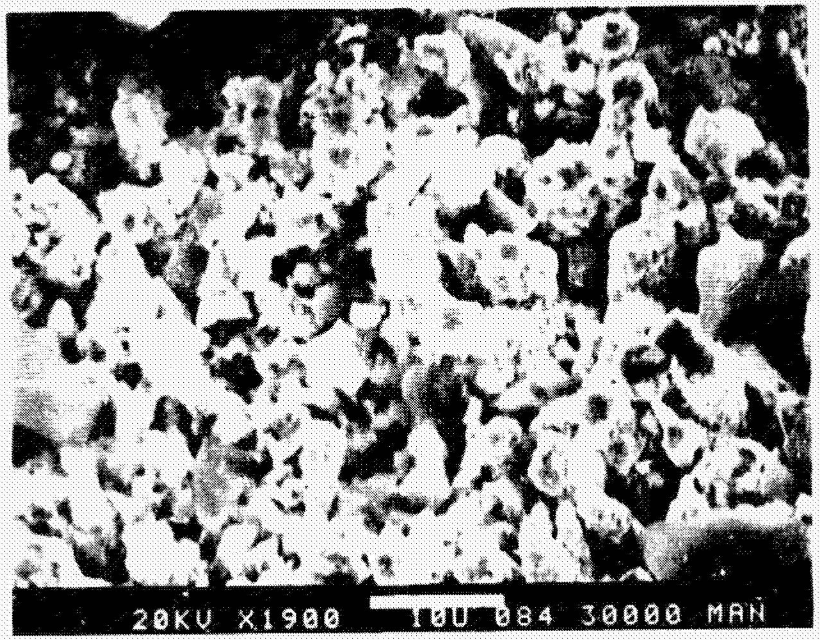
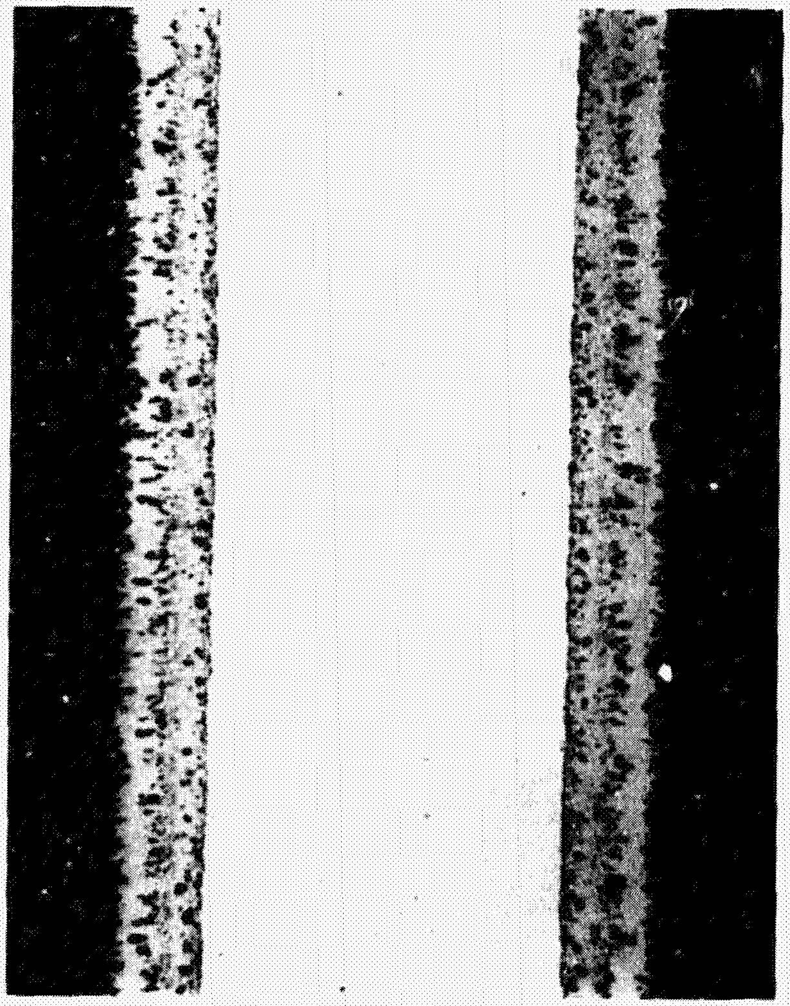


FIGURE III SCANNING ELECTRON MICROGRAPHS OF THE CROSS SECTIONAL AREA OF THE SILICIDE PROTECTIVE FILM ON NICKEL



#3 Silicon on Nickel 100 X

#3 Silicon on Nickel 500 X

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FIGURE IV CORROSION TEST ON PURE NICKEL

500°C, 300 PSIG, $H_2/SiCl_4$ = 2.0

SCANNING ELECTRON MICROGRAPH
AND X-RAY MICROPROBE ANALYSES

AREA	ATOMIC %	
#	Si	Ni
1	46.40	53.60
2	42.88	57.12
3	33.94	66.06
4	0.00	100.00

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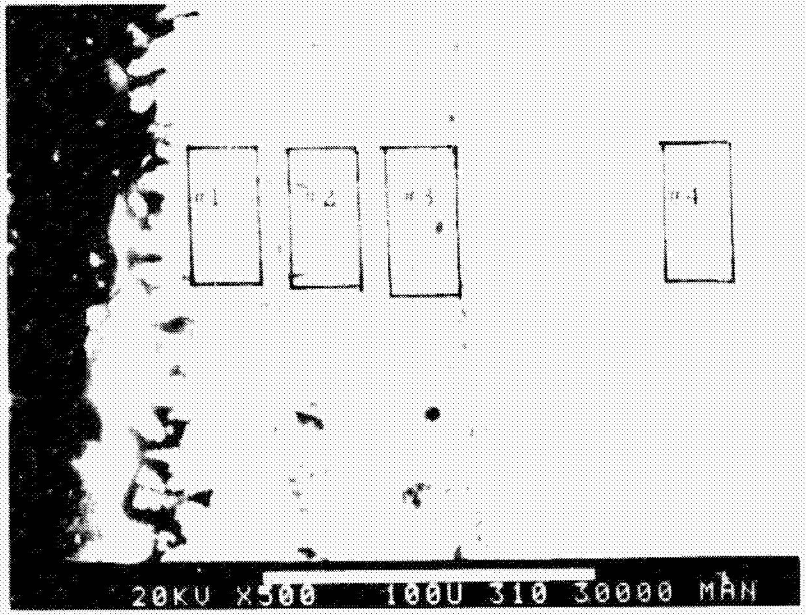
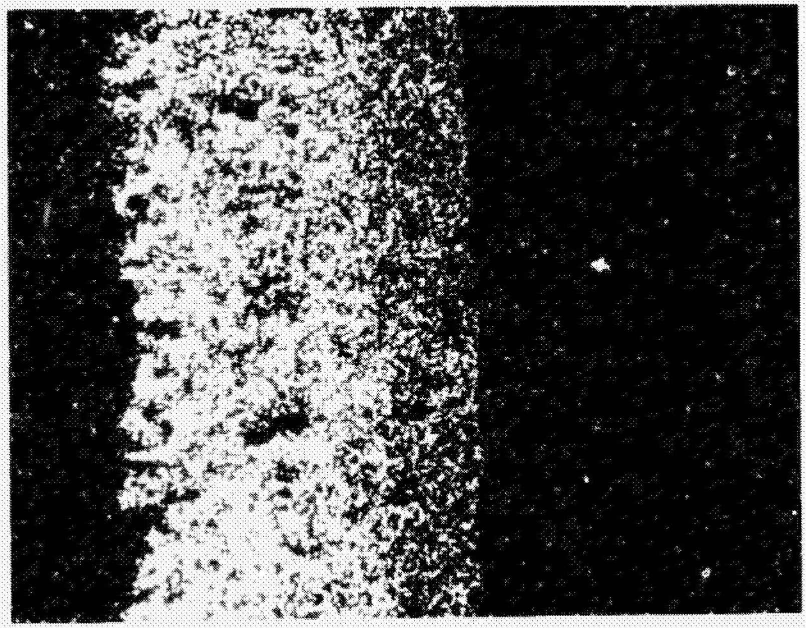
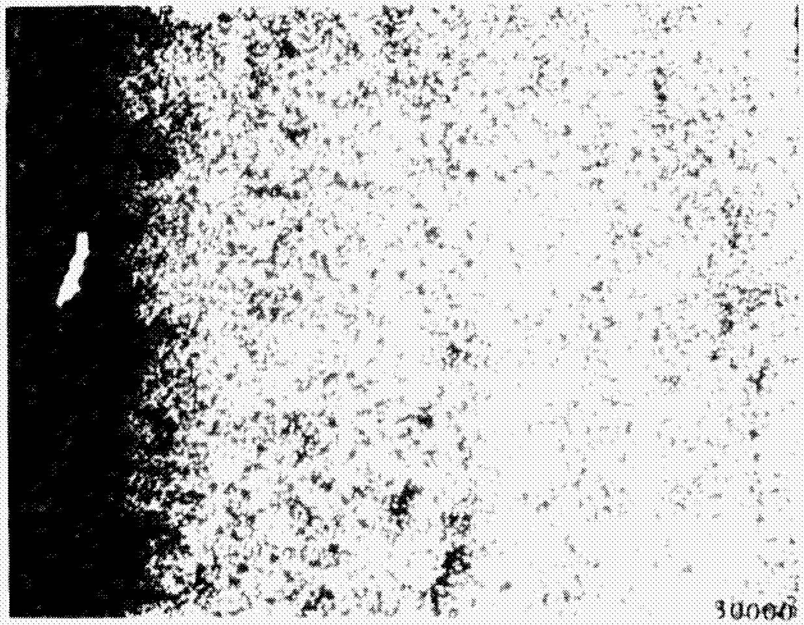



Silicon X-ray Distribution Photo 310 30000



Nickel X-ray Distribution Photo 310

FIGURE V

CORROSION TEST ON INCOLOY 800H

238 Hours @ 500 C, 300 psig, $H_2/SiCl_4$ of 2.0

Scanning Electron Micrograph of
Cross Sectional Area, 500X

Photo 8

FIGURE VI CORROSION TEST ON INCOLOY 800H: SCANNING ELECTRON MICROGRAPH OF CROSS SECTIONAL AREA AND X-RAY MAPS

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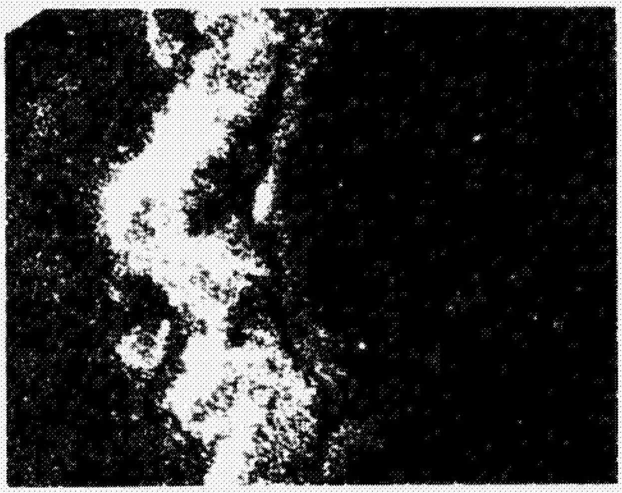

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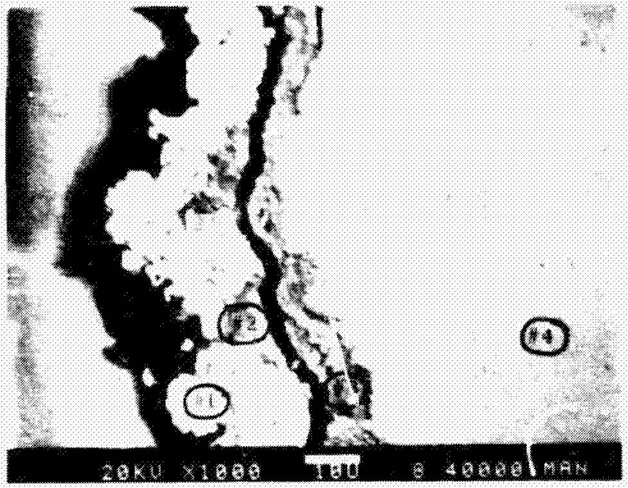
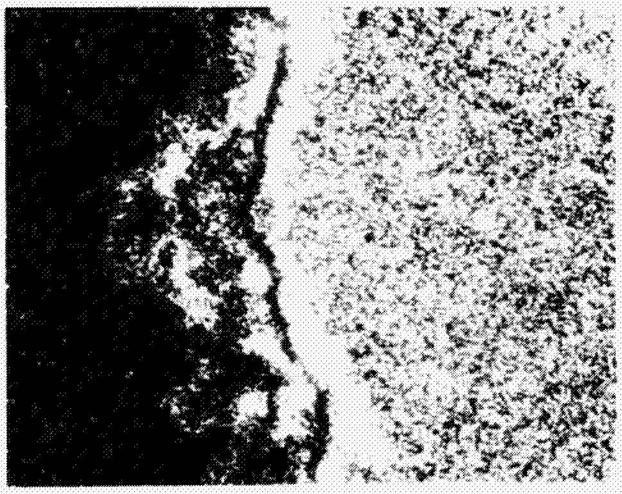
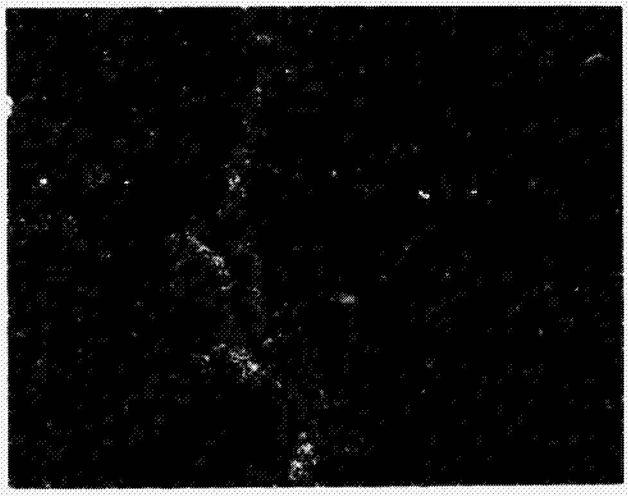




Nickel X-ray Distribution Photo 8 40000



Chlorine X-ray Distribution Photo 8 40000

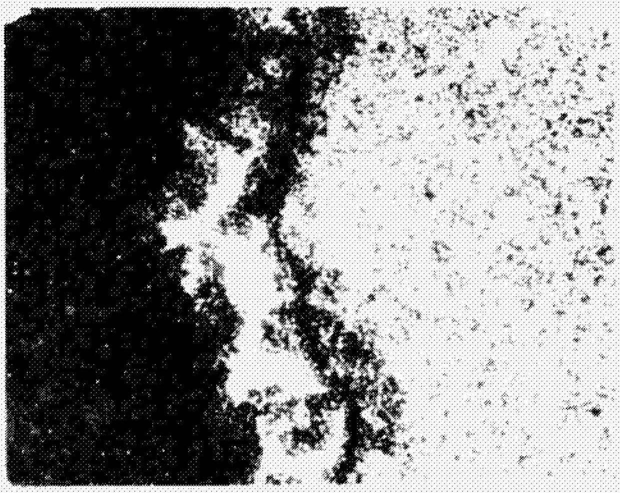


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FIGURE VII

CORROSION TEST ON
INCOLOY 800H

238 HOURS @ 500°C,
300 OSIG, $H_2/SiCl_4$ = 2

SEM ANALYSIS OF
CROSS SECTIONAL AREA