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OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 11/19/96

Project No. E-18-X75\_\_\_\_\_ Center No. 10/24-6-R0076-0A0\_

Project Director HAMPIKIAN J M\_\_\_\_\_ School/Lab MSE\_\_\_\_\_

Sponsor MICROCOATING TECHNOLOGIES/ATLANTA, GA\_\_\_\_\_

Contract/Grant No. AGREEMENT DATED 960815\_\_\_\_\_ Contract Entity GTRC

Prime Contract No. N00014-96-C-0179\_\_\_\_\_

Title CHROME REPLACEMENT & THERMAL CORROSION RESISTANT COATINGS VIA CCVD PROCES

Effective Completion Date 961031 (Performance) 961031 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	_____
Final Report of Inventions and/or Subcontracts	Y	_____
Government Property Inventory & Related Certificate	Y	_____
Classified Material Certificate	N	_____
Release and Assignment	Y	_____
Other _____	N	_____
Comments _____		

Subproject Under Main Project No. \_\_\_\_\_

Continues Project No. \_\_\_\_\_

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

NOTE: Final Patent Questionnaire sent to PDPI.

E-18-X75  
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# Georgia Institute of Technology

School of Materials Science and Engineering

## MEMORANDUM

To: Dr. Andrew Hunt  
President, MicroCoating Technologies  
430 Tenth St., N.W.  
Atlanta, GA 30318

From: Dr. Janet M. Hampikian  
Assistant Professor  
School of Materials Science and Engineering  
894-2845

Date: October 29, 1996  
Subject: Program Final Report (E18-X75), due date: 10/31/96

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Attached, please find the final report for the program. It has been a pleasure to serve as consultant to your company, and also to work with Michelle Hendrick.

Please let me know if I can be of further assistance to you on matters concerning oxidation, and thank you for your assistance on this program.

## Thermal Gravimetric Analysis

### Background:

The thermal gravimetric analysis (TGA) equipment consists of a D-200 Cahn microbalance and a vertically aligned tube furnace capable of temperatures up to 1400°C. The entire system is sealed off during a run, with only one air inlet point (for laboratory grade, dry air) and one air outlet point at the bottom of the furnace reaction tube. This ensures a constant, reproducible environment during each test. A specimen is suspended from a quartz rod into the furnace. The system is designed so that a specimen can be raised and lowered out of the furnace without entering the system once it is sealed. Due to the delicate and extremely sensitive nature of the balance, the specimen size is greatly limited by its weight, which can only be approximately 0.1 grams. In addition, the diameter of the furnace reaction tube is about 2.4 cm, so specimens must be well within this dimension to avoid touching the tube walls once suspended into the tube.

The data collected from the computer interfaced with the balance includes the time of each run and the mass recorded. The mass recorded consists of only the mass gain or loss during exposure to the furnace temperatures. Before the furnace is heated, the sample is suspended into the furnace and its mass is tared to zero. The specimen is then raised out of the furnace to a cool zone of the system, and the furnace is allowed to reach temperature and stabilize at that temperature. The sample is then lowered into the preheated furnace and mass gain or loss is recorded with a starting point of zero mass. Since the sample is originally tared to zero in a cool furnace, and mass gain (or loss) is recorded once the sample enters the hot furnace, the recorded mass is slightly raised due to the effects of buoyancy. The amount of mass increase due to buoyancy should be consistent for similar sized specimens oxidized at the same temperature and gas conditions.

### Results:

Two types of substrates were oxidized: AISI 1010 steel and AISI 304 stainless steel. The behavior of the 1010 alloy is shown in Plot 1, page 15, which displays three curves. Two substrate sizes were investigated: 3 mm x 10 mm x 0.39 mm, and 15 mm x 10 mm x 0.076 mm. Both sample geometries were oxidized at 600°C for 48 hours. The curve showing the greatest amount of oxidation at long time corresponds to the larger sample, and the breakaway oxidation that this curve shows can be understood by scale delamination without spallation. The delamination causes an increase in the amount of metal exposed, resulting in more area for oxide formation and, thus, an increased oxidation rate as seen by the upward curve in the plot. The bottom plot contains the same data as the upper plot, but portrayed instead as the squared mass gain/area. These types of plots will be consistently presented for all the data, for ready comparison.

The first coating which was characterized via TGA was silica. Plot 2, page 16, shows the response of the silica-coated, smaller samples versus their 1010 uncoated control counterpart for oxidation for 48 hours at 600°C. The silica coating reduced the oxidation in two significant ways. The initial, rapid oxidation, corresponding to the formation of base metal oxides that are less protective than the steady state scale, is reduced (for Silica-coated 1) to less than 10% of the transient mass gain of the uncoated alloy. The long term oxidation response, measured at 48

hours, is reduced by over a factor of two. The sample labeled Silica-coated (1) received a higher quality coating than the sample labeled Silica-coated (2), and this difference accounts for the difference in the two curves.

The second coating characterized was a silica-chromia coating in Plot 3, page 17. This sample was of the larger sized substrate. The coating prevented the alloy's breakaway oxidation response from occurring. It also reduced the initial rapid oxidation. The oxidation kinetics is linear, which while being an improvement over the 1010 control alloy, is not "protective" in the long-term. In general, scales which form with linear kinetics are porous to gases. The sample's appearance following oxidation showed no evident spallation or delamination, in contrast with the 1010 control sample, which showed significant scale delamination. This coating performed better long term than the silica, whose kinetics did not achieve steady state.

The remaining oxidation data were taken from the 304 substrate and are shown in Plot 4, page 18. The green curve corresponds to the uncoated substrate. This alloy is a chromia former, meaning it forms a steady-state chromia scale which controls the overall oxidation rate. The three coatings which were investigated for this alloy were silica, alumina and chromia, all shown in Plot 4. The silica/alumina coating consisted of a base coating of thin silica followed by a coating of alumina. All of the coatings reduced the long-time oxidation rates, except chromia. Interestingly, the amount of initial oxidation was not significantly changed by the presence of the coatings. Of all the coatings, silica and silica/alumina were the most effective, by decreasing the overall mass gain by about one and a half times. The bottom figure, displaying squared mass gain/area, shows that the silica and silica/alumina coatings obey the parabolic rate law, which signifies a protective, adherent scale. The coatings are probably causing a change in the oxidation mechanism, although this cannot be determined until several runs at different temperatures have been conducted. The benefit of the silica and silica/alumina coating is that the long time behavior may be reliably predicted, note the "linearity" of the curve, in contrast to the control curve.

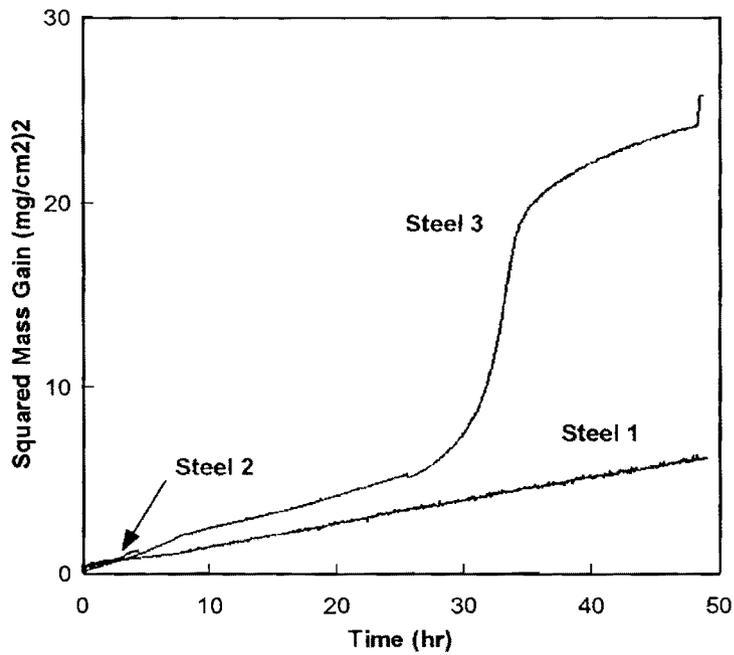
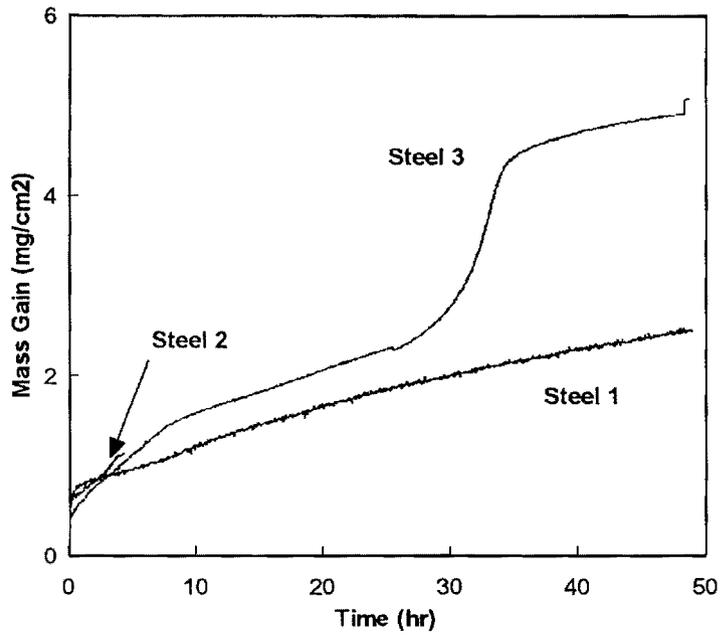
## **Transmission Electron Microscopy**

### **Background:**

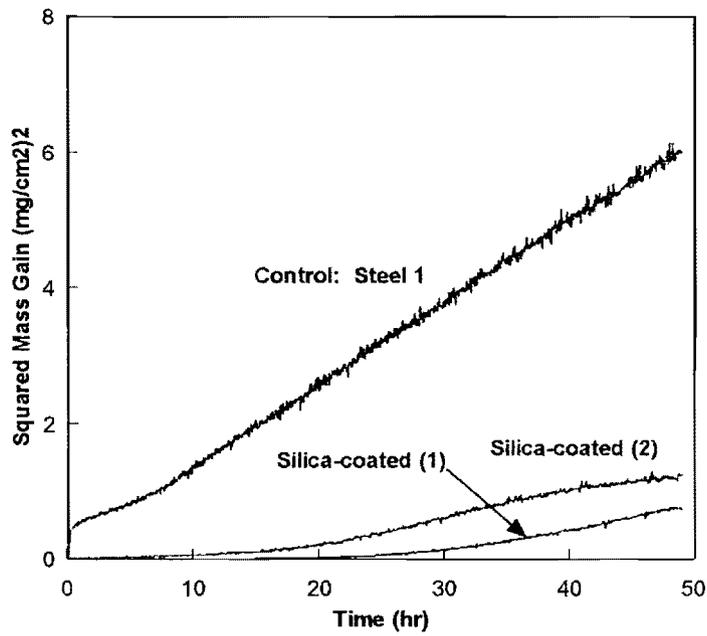
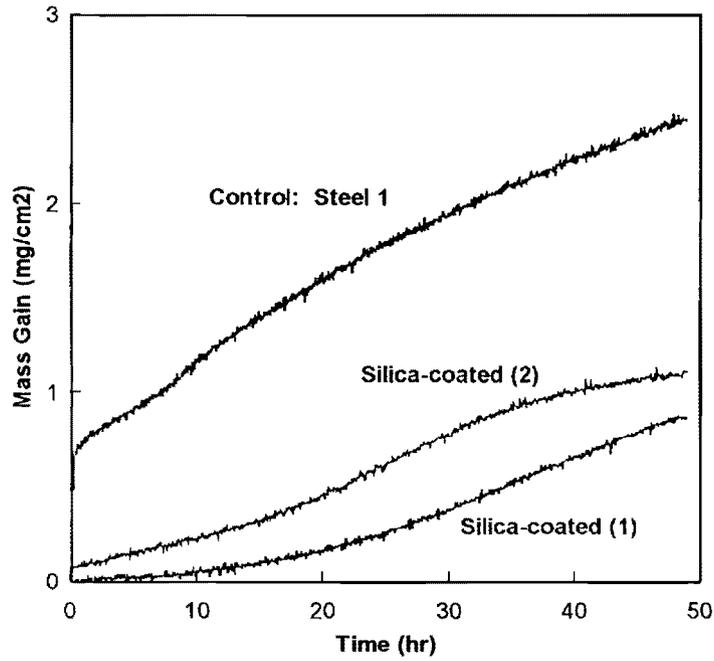
Work continued on characterizing the effects of oxidation of theta-phase alumina coatings, deposited using the CCVD system, on the oxidation characteristics of Ni-20Cr. Michelle Hendrick completed most of the work on this project before joining MicroCoating Technologies, documented in her Master's thesis. Prof. Hampikian conducted transmission electron microscopy on samples generated by Hendrick prior to her graduation. These samples were made using the "old" nozzle assembly. Our kinetic experiments, conducted as part of the Master's thesis, showed that vacuum-annealing the alumina coated samples, greatly reduced the oxidation kinetics. Work continued on this aspect of the research, via transmission electron microscopy, in order to understand why the vacuum anneal in conjunction with the coating caused the reduction in oxidation kinetics.

## Results:

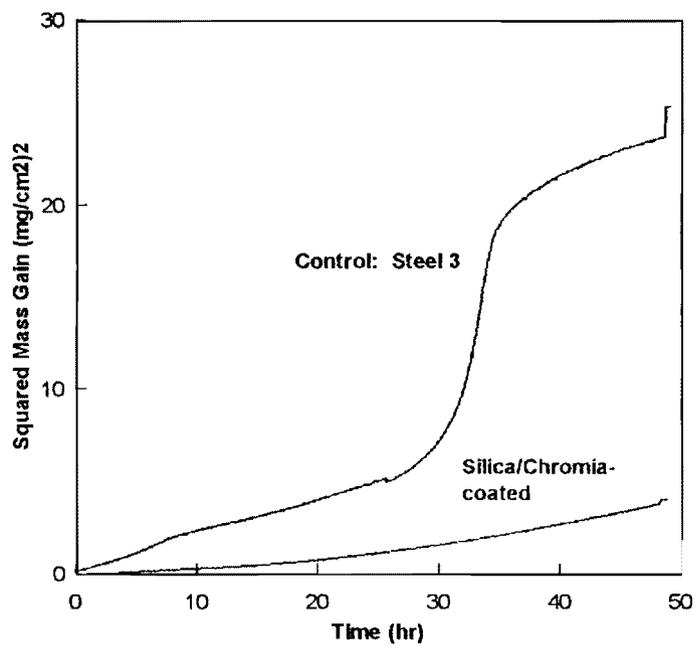
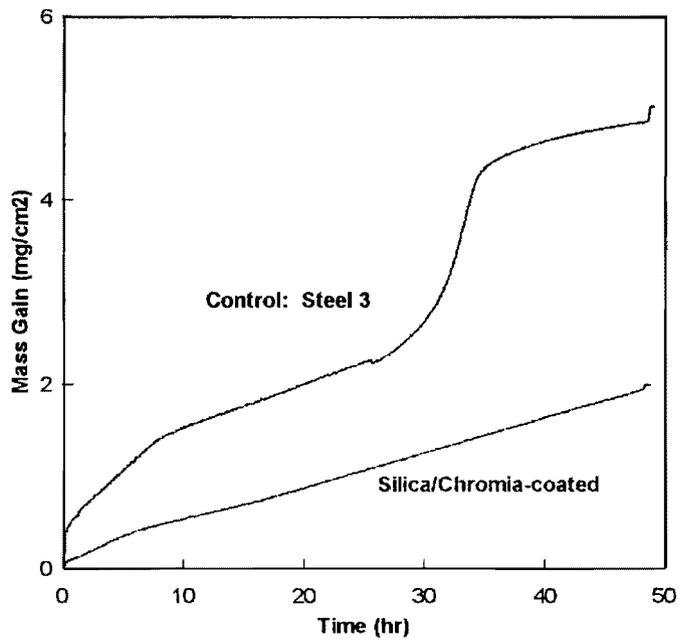
- Theta-alumina phase was found to still be present on alumina-coated samples after four hours of vacuum annealing at 1080°C, indicating relative stability of this phase at high temperatures.
- Vacuum anneal of alumina-coated samples causes the formation of spinel-structured nickel-chromium oxide. Alumina is dispersed within this spinel material.
- Annealed specimens show chromia grains containing aluminum signal present within (not surprisingly, as alumina and chromia are mutually soluble).



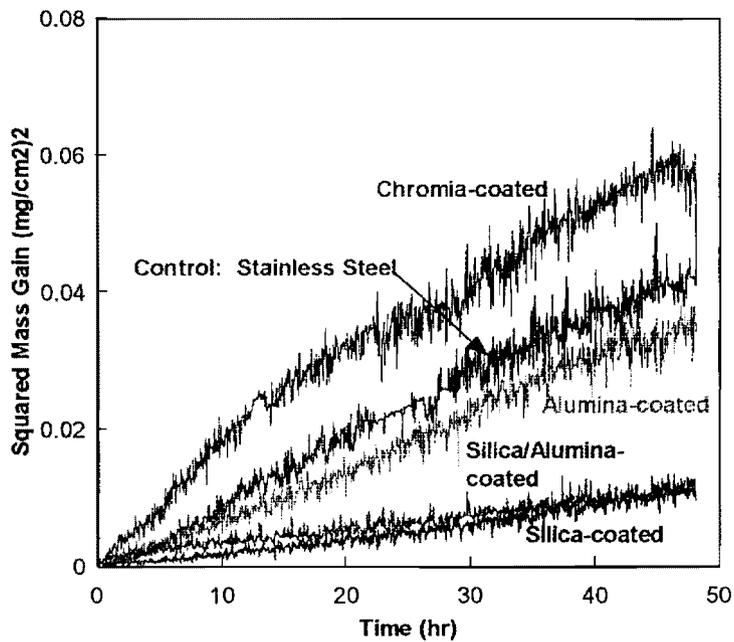
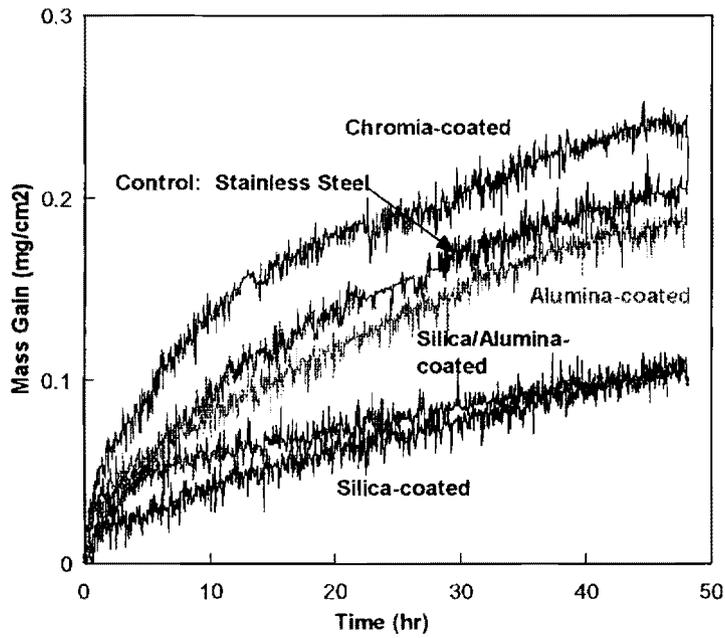
**Plot 1:** Mass gain and squared mass gain curves for oxidation of uncoated AISI 1010 steel substrates at 600°C.



**Plot 2:** Mass gain and squared mass gain plots for oxidation of uncoated (control) and silica-coated AISI 1010 steel at 600°C. Data were corrected for buoyancy by a common value of 0.05 mg/cm<sup>2</sup>.



**Plot 3:** Mass gain and squared mass gain plots for oxidation of uncoated (control) and silica/chromia mixed oxide-coated AISI 1010 steel at 600°C.



**Plot 4:** Mass gain and squared mass gain plots for oxidation of uncoated (control) and chromia, alumina, silica and silica/alumina-coated AISI 304 stainless steel at 800°C. Data were corrected for buoyancy by a common value of 0.05 mg/cm<sup>2</sup>.