# Coking and Carburization Resistance of an Engineered Oxide Nanofilm for the Petrochemical and Refining Industries

Arvid Pasto[1], James Keiser[2], Chaitanya Narula[2], Evan Hyde[1], Morgan Spears[1], Mark Deininger[1], and Michael Pozvonkov[1]

An engineered nanofilm of ceria-stabilized zirconia, applied to an industry-standard alloy for use in coker heaters, is shown in a 1000 hour/900°C test performed at Oak Ridge National Laboratory (ORNL) to reduce the extent of coking and internal metal carburization. Weight gain from the coke deposit and the internal carburization is reduced by approximately 50 %. Data from scanning electron microscopy of the external surfaces, and optical metallography and electron microprobe analysis of cross-sections, show that the several hundred nanometer-thick film remains intact, although there appears to have been chromium migration through it. Other compositions of nanofilm were not as successful at blocking coking and carburization, however.

---

(1) C3 International, LLC, Alpharetta, Georgia
(2) Oak Ridge National Laboratory, Oak Ridge, Tennessee
(3) Coker Coaters, LLC, Alpharetta, Georgia

## INTRODUCTION

Carbon deposit fouling and carburization cracking of steam or ethylene cracking furnace tubes are portions of the most severe fouling service in all petrochemical applications. Total worldwide production of ethylene and other basic petrochemical monomers via this process was 119.6 million tpy as of Jan. 1, 2008, with an expected growth of 2% per year for the next five years. Ethylene is a key basic chemical element in the production of many types of plastics, surfactants, detergents, and agricultural ripening agents. The critical step in the production of this product is the rapid heating of a feedstock, less than 1 second to more than 900° C, in a furnace. Carbon buildup, or fouling, can limit the production runs to as short as a few weeks before cleaning is required. The cracking issue is a large safety concern and requires the producers to routinely replace equipment and use exotic alloys where possible.

The feedstocks for the ethylene or steam cracking process range from very light hydrocarbons, such as ethane, propane, and mixed butanes, to heavy hydrocarbons, such as gas oils. However, the problem of carbon fouling and carburization affects all types of cracker feedstocks. It is only the extent to which these problems are seen that vary by feed component. The operational strategy to deal with each problem can be quite different.

Currently, the industry can only design around the issue of carbon fouling. The problem of fouling within cracker heaters is that coke attaches to the inside walls of the heating tubes. Carbon is an effective insulator and its buildup inside the heater tube is measured in part by the tube temperature increase that is necessary to maintain the temperature required for the thermal cracking. Once a maximum skin temperature is reached, which varies by the metallurgy in-service, the furnace must be taken offline for cleaning. After repeated high temperature cycles or a single incident of isolated extremely high temperatures, the tube can fail, sometimes catastrophically, resulting in a fire and potentially other serious safety incidents.

Similar safety issues can arise from the problem of tube metal carburization. At the extremely high temperatures seen in the tubes, elemental carbon can diffuse into the tube metal, called carburization. Carburization weakens the materials to the point of failure. Carburization is typically monitored via destructive testing methods with sample tube segments being taken when the furnace has been offline for cleaning. Recent techniques to monitor carburization using non-destructive methods have been developed but still require the furnace to be offline. Once the carburization has extended sufficiently deep into the parent material, the tube must be replaced. The replacement requires additional lost product and significant material and labor costs. The retubing of a cracker furnace can exceed $10 million, with weeks of additional lost production valued at more than $50 million. The rate of internal carbon fouling can be monitored online while carburization cannot.

A typical cracker will employ multiple furnaces in parallel with excess capacity so that one can be taken off line, cleaned, and repaired with limited throughput penalty. The frequency of cleaning varies but can range from 3-8 weeks between offline cycles. A typical example of a world-scale cracker is on the U. S., Gulf Coast, consisting of 7 furnaces in parallel with an average run length of 6 weeks. The net result globally is that significant portions of the production capacity are continuously in a state of cleaning or decoking. If the time between decoke or tube replacement can be extended, significant capacity expansions could be realized with little or no cost.

## EXPERIMENTAL

The phenomenon of coking has been quite well-known in heterogeneous catalysis, where supported catalysts become inactive due to a build-up of carbonaceous residues. This phenomenon is quire reaction specific [P. Albers, J. Pietsch, and S.F. Parker, J. Mol. Catal A: Chemical, 173 (2001), 275; Ostrovskii, N.M.; Kinetics and Catalysis, 42 (2001) 317].

Our initial efforts to manipulate the surface acidity of coating materials were not successful. We embarked upon an approach to modify the chemical and structural properties of zirconia materials. Such materials, applied on the surface with C3 solution methods described delow, modify the metal surface and also prevent the bonding of unsaturated hydrocarbons and partially oxidized hydrocarbons. Since the initial bonding of unsaturated hydrocarbons and partially oxidized hydrocarbons with the stabilized zirconia modified surface does not occur, there remains a weak interface between coking materials and metal. As a result, no substantial coking is observed.

Sample Preparation: Incoloy 803 was chosen as the substrate material for this high temperature fouling test as it represents a median of the high quality materials used in steam cracking applications. Dozens of samples were ordered from Alabama Specialty Products Inc. of Munford, Alabama, with Certificates of Analysis for each batch. The material was cut from a 25 mm rod stock to a thickness of about 1.6 mm each. Each sample was then polished to a “lapped” surface finish by the supplier prior to shipping to C3.

Upon receipt, the samples were visually inspected to ensure consistent surface finishes across the lot. After inspection, the samples were cleaned in a 60 kHz ultrasonic bath heated to 60ºC filled with a mild industrial soap for approximately 1 hour. The samples were then removed and thoroughly rinsed individually with warm water to remove any soap residue. After rinsing, the samples were washed in a heated alcohol bath, and then allowed to cool in a clean, dry place.

A special sample holder was fabricated using SS304 mesh to minimize contact points during the treatment process. The clean samples were then placed in this holder and heated in an infrared quartz tube furnace constructed by Infrared Heating Technologies of Oak Ridge, Tennessee, to a temperature of approximately 300ºC under inert atmosphere to burn off any residual contamination.

Once cool, the samples were ready to accept the MIST surface treatment. C3's patented metalorganic solution was applied on the entire sample surface before placing them on the furnace fixture.

Once all samples are wetted, the furnace was sealed and an inert atmosphere was introduced. Once the air was displaced, the furnace was heated for a time less than 1 hour to a temperature of approximately 450ºC. Several type K thermocouples were placed in different locations within the furnace to ensure temperature uniformity. The furnace and samples were allowed to cool back to close to ambient conditions, and the process was repeated several times.

A random set of the samples was inspected after each treatment with a Hitachi TM-1000 tabletop scanning electron microscope at magnifications ranging from 50x to 10,000x to check for surface defects. The final treatment thickness was estimated at less than 1 micron, based on prior characterizations of the treatment at the Oak National Laboratory using Scanning Auger Nanoprobe analysis.

Control samples were cleaned in a similar manner. Each sample was individually catalogued, packaged, and shipped out for testing.

Testing: ORNL's Corrosion Science and Technology Group has a test facility designed for study of the interaction of carbon with materials. The facility has two pieces of test equipment; one for testing in low velocity gas and one for testing at gas velocities that approach those used in ethylene cracking furnaces. The low velocity system was used for the studies described in this report.

The low velocity test system is shown in Fig. X and utilizes a three zone electrical resistance heated furnace that is capable of operation at temperatures up to 1200EC. Each zone of the furnace is approximately 28 cm (11 inches) long, and an alumina furnace tube about 9.5 cm (3-3/4 in.) OD and 8.6 cm (3-3/8 in.) ID is used to contain the atmosphere.

The gas composition in the low velocity system can be varied over a fairly wide range, but the gas composition used in a test is primarily determined by whether it is desired for the environment to be such as to create the conditions for carburizing, coking or metal dusting. Gas flow is controlled by three mass flow controllers which generally are used to control flow of argon, hydrogen and a hydrocarbon such as methane or pentene. If desired, steam can be included as a component of the atmosphere by injecting a controlled amount of water through a metering pump. Because of the flammability issues associated with the hydrogen and the hydrocarbon components, the gas leaving the system flows through an electronic flowmeter just before being fed into the exhaust system. If the flow of gas through the flowmeter drops below a preselected level, the furnace is turned off, the supply of the combustible gases is stopped and the system is purged with argon. In addition, gas detectors sensitive to hydrogen are located near the furnace, and detection of a preselected level of hydrogen outside the test system will also terminate the test and turn off the gas supply.

For these coking studies, the tests were conducted at 900EC with an atmosphere that was approximately 97.9 volume % hydrogen and 2.1 vol % methane. This resulted in a carbon activity slightly greater than 1.0 so that coke would be expected to form on the more susceptible samples.

The studies conducted at ORNL involved exposing samples of a selected group of materials in a coking environment for ever-increasing periods of time. The first exposure was for 100 hours, and this was intended to be followed by successive exposure periods of 200, 300 and 400 hours. However, problems resulted in the subsequent exposures being for 176, 324 and 400 hours. After each exposure, samples were removed for weighing and photographs were taken to document the visual appearance.

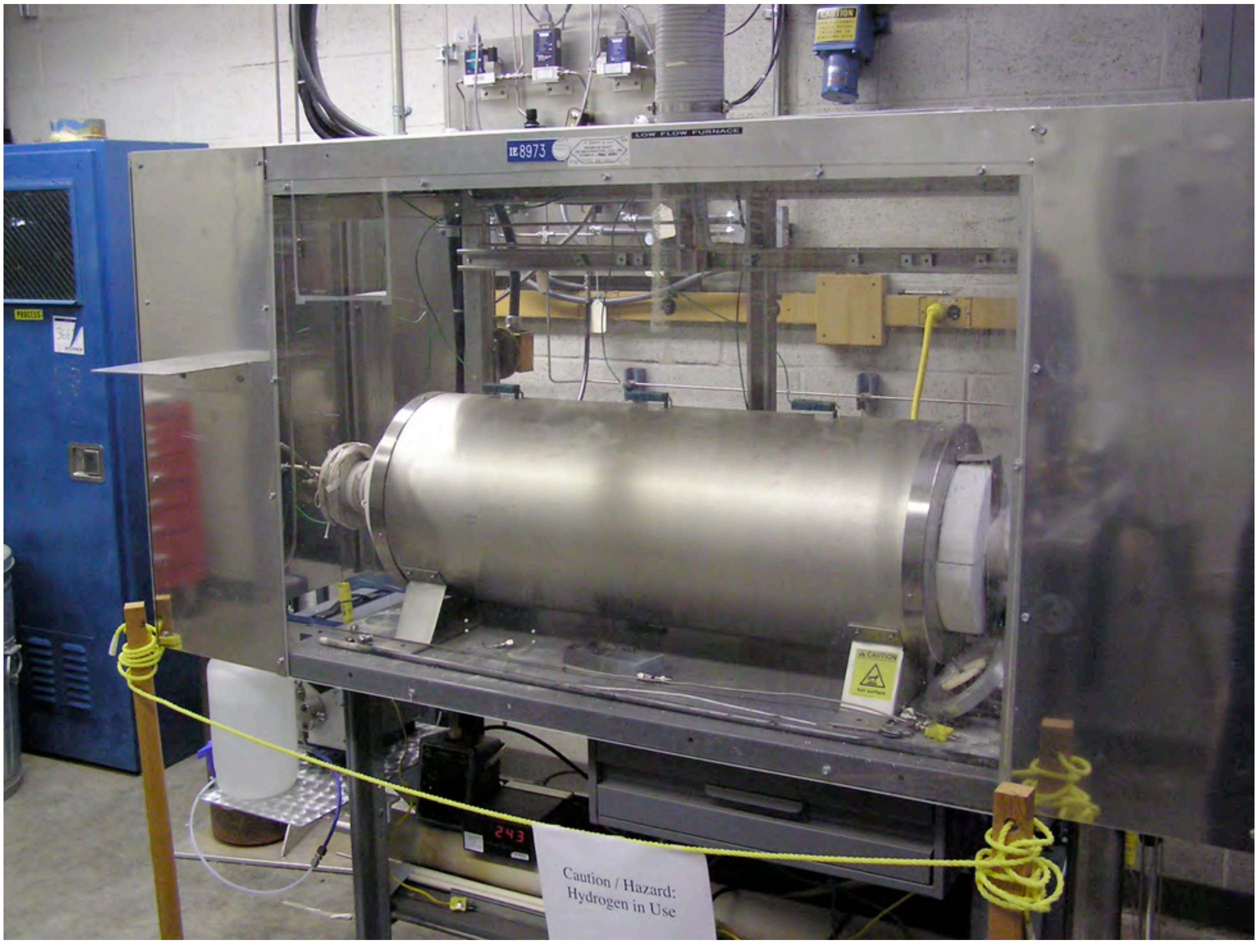


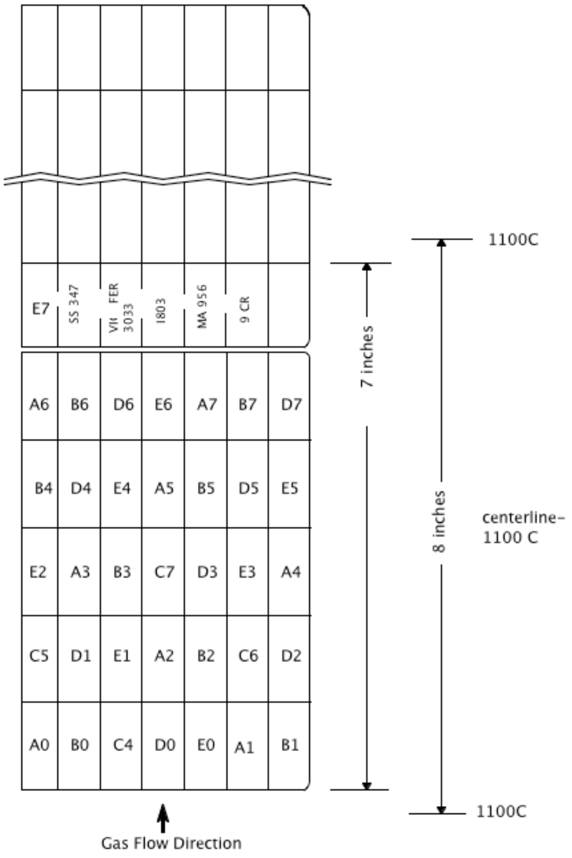
Figure X. Low velocity test system used for coking and carburization studies. The three zone furnace is in the foreground, the three wall-mounted mass flow controllers are visible above the furnace enclosure and the gas cabinet used for the cylinders of combustible gas is on the left.

Scanning electron microscopy (SEM) was performed on the surfaces of selected specimens using an Hitachi Model S3400 Variable Pressure SEM fitted with an EDAX

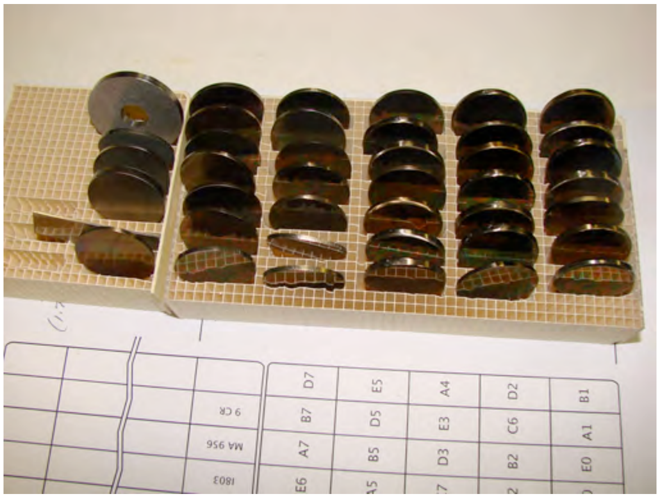
Energy Dispersive X-ray Spectrometer using EDAX Genesis Software. Specimens were not coated prior to examination. Electron microprobe analysis was performed on polished cross-section specimens using a JEOL 8200 WD.ED Combined Microanalyzer with JEOL Software. Metallographic and microprobe analysis specimens were prepared by abrasive cutting, mounting in epoxy, ground with decreasing grit sizes, then polished to approximately a 0.5 micrometer finish using standard metallographic techniques.

## RESULTS

The coated specimens were distributed in a ceramic carrier in a non-serial fashion as illustrated in the figure below, in order to allow specimens of each film type to be exposed to potential variations in the gas flow environment.



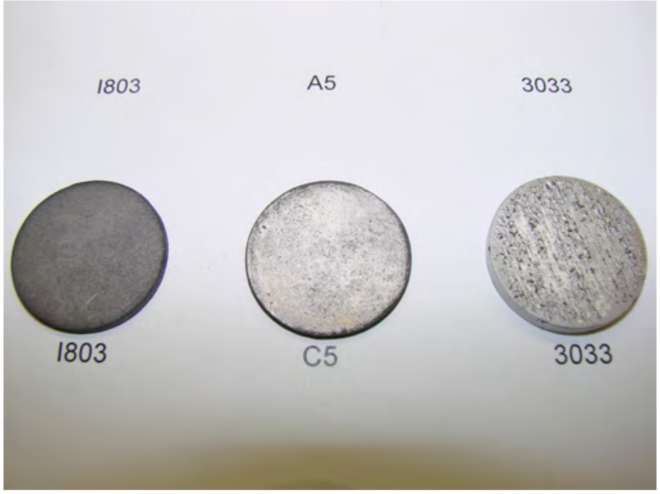
Photographs of the specimens in their carrier, both before and after the 1000 hour exposure, are provided below.

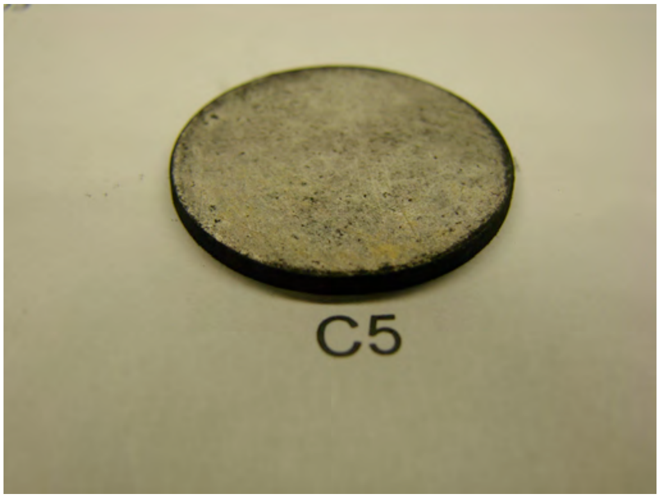


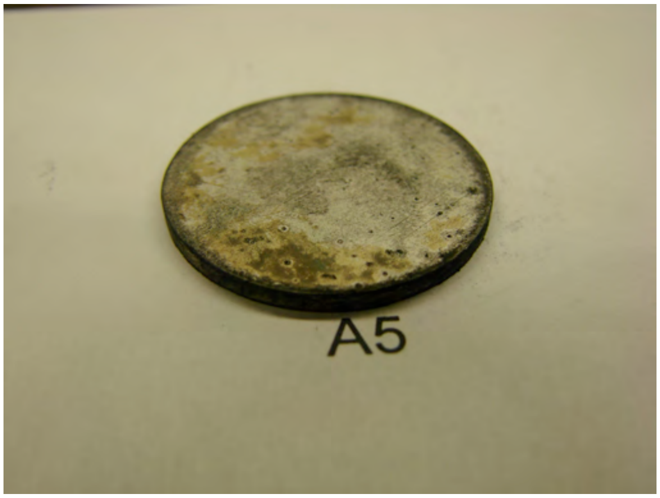
A photograph of all of the specimens after removal from the test is provided below, in which distinct differences in their appearances are observable. These variations arise from the carbon deposited on them. There were not large observable differences between the ceria/zirconia-coated specimens and those of the other types coated onto alloy I803, in general. Specimens A5 and C5 are shown below in a closer view, and it is apparent that there has been more deposition on the edges of the specimens than the faces, and some of the coatings had pin-hole defects in them.


A0
C5
E2
B4
A6
E7
B0
D1
A3
D4
B6
SS 347
C4
E1
B3
E4
D6
3033
D0
A2
C7
A5
E6
I803
E0
B2
D3
B5
A7
MA956
A1
C6
E3
D5
B7
9 Cr
B1
D2
A4
E5
D7

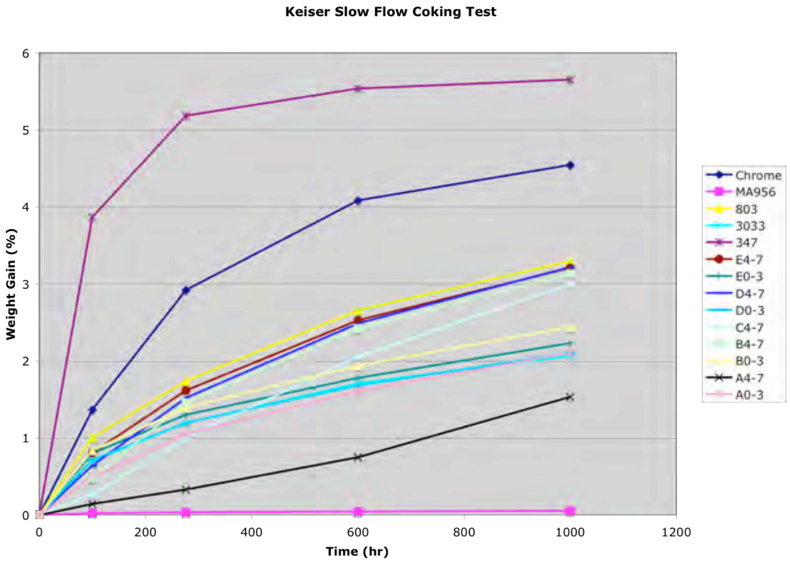

I803
A5
3033



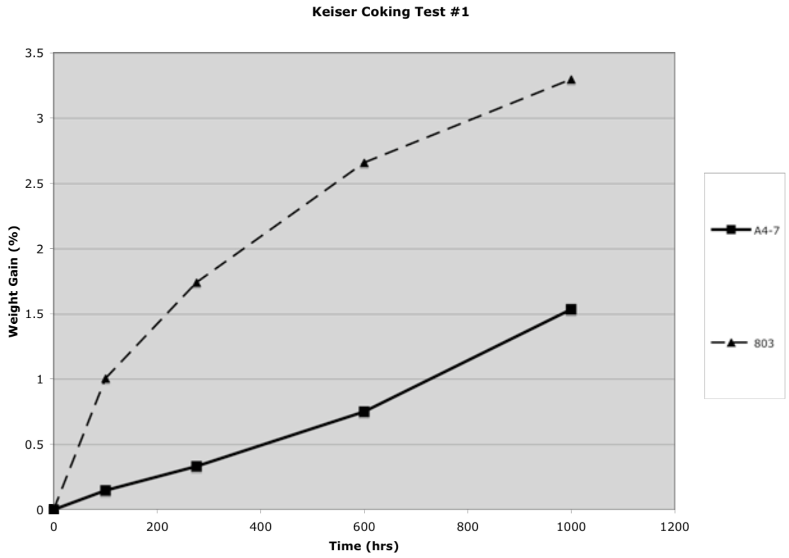




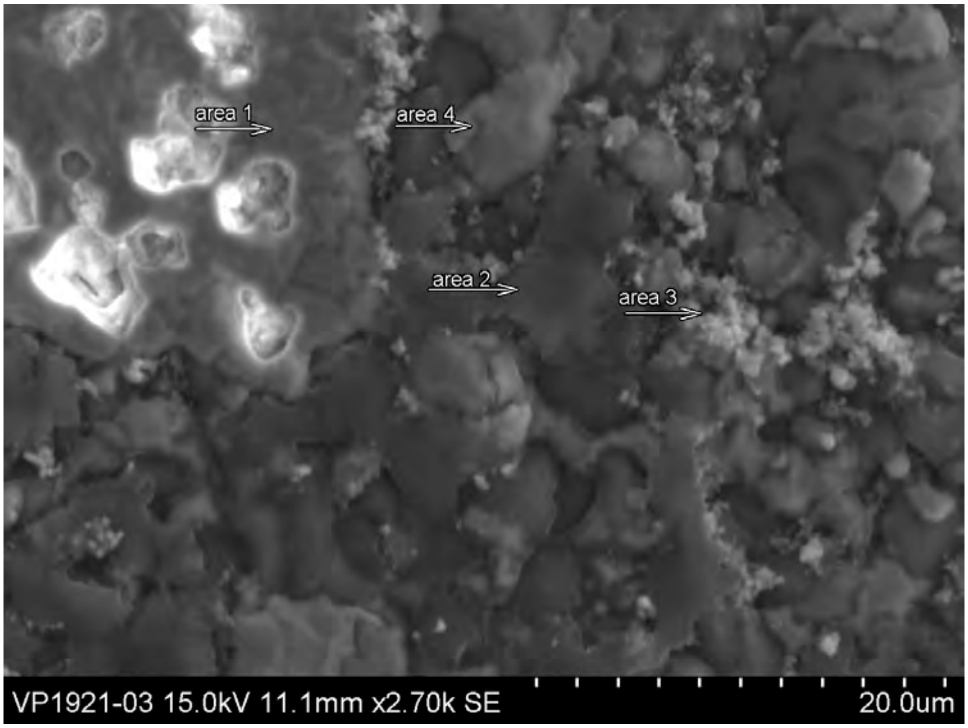
Weight gain data for all of the materials is plotted in the following figure, showing that most of the materials exhibit a rapid initial weight gain followed by a diminishing rate of change. Alloy MA956, known for its low coking and carburization rate, is the slowest at gaining weight, followed by the A4-A7 specimen set. This latter set of materials also exhibits an unusual behavior, staring off slowly then gaining weight more rapidly. Evidence to be presented later suggests that this is due to the initially-protective zirconia film ultimately becoming breached by the outward migrating chromium from the I803 alloy.



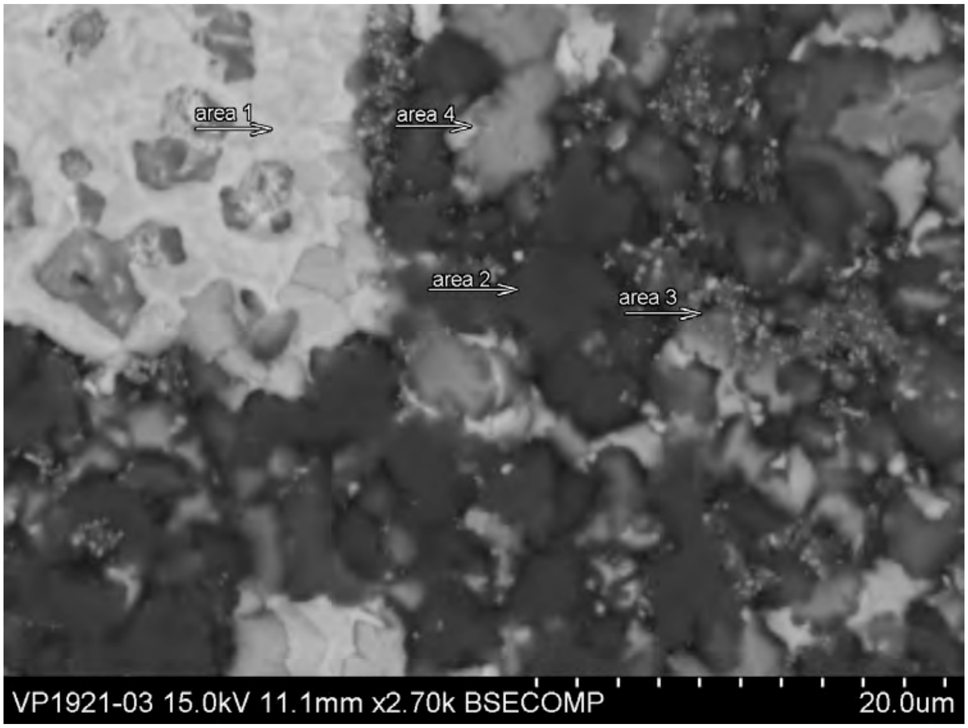
The performance of uncoated alloy I803 is plotted along with that of the A4 – A7 specimen set in the following figure, where the weight pickup of the latter is seen to vary from about 80% less at 200 hours to about 50% less at 1000 hours.



Scanning electron microscope examination of the external surfaces of I803, specimen C5, and specimen A5 all showed a granular carbonaceous deposit. Energy dispersive x-ray (EDX) analysis was performed at several locations on each type of specimen. The following two figures present first secondary electron (SE), and then back-scattered electron (BSE), images of the uncoated alloy. The BSE image clearly shows several different regions of composition, denoted areas 1 through 4, which were EDX analyzed.



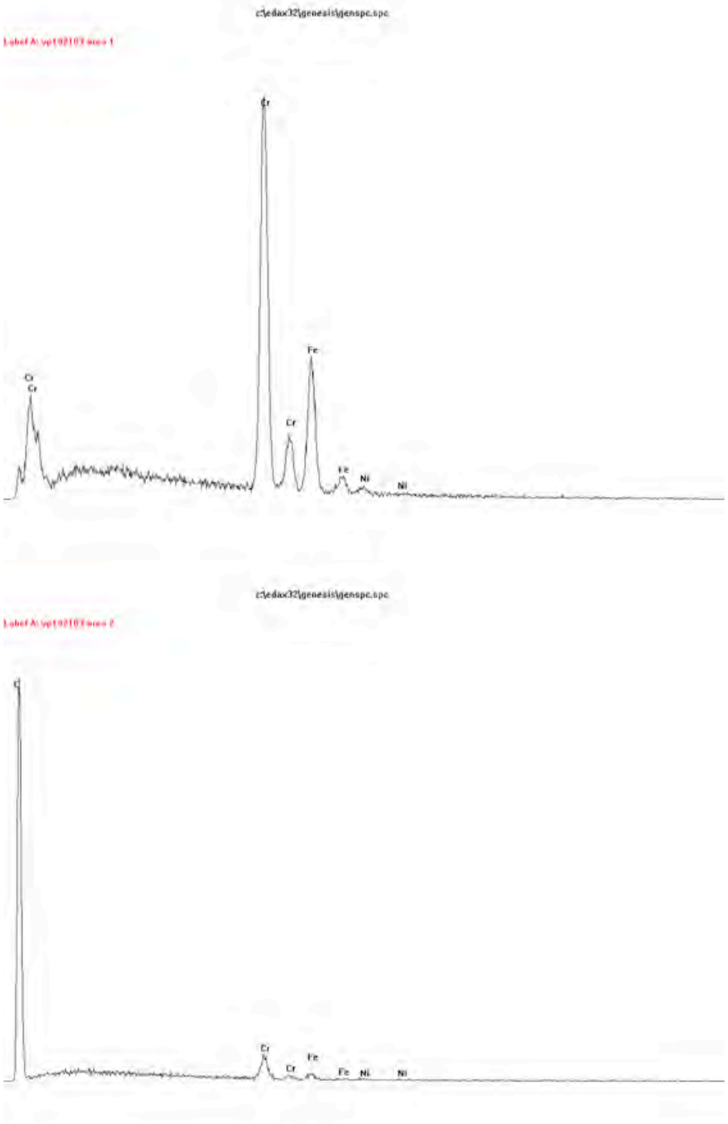
Secondary

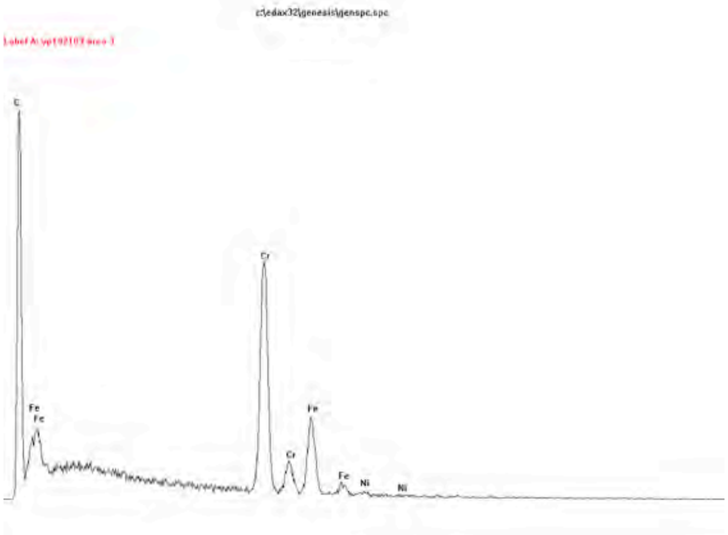


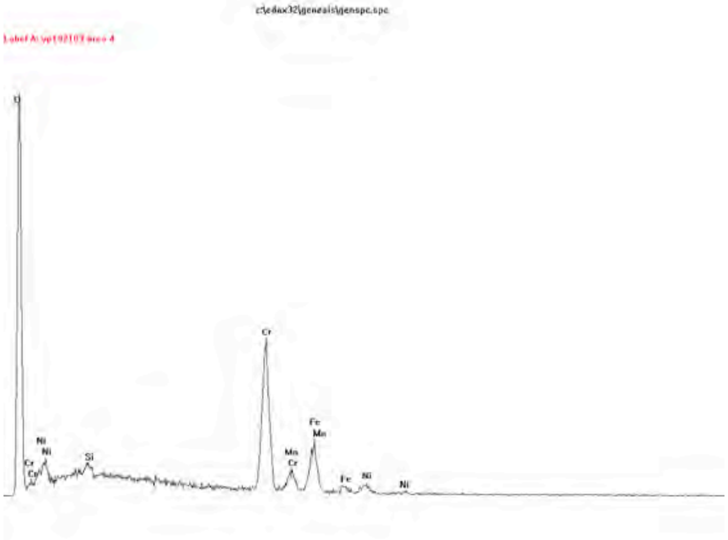
Backscattered electron image of I803

The brightest area (1) is chromium-rich, but contains little measurable carbon. The next-brightest area (3) is again rich in Cr, but this time with significant carbon. A similar dark area (4) again shows a preponderance of Cr and C. The darkest region (2) is largely C, likely as coke.

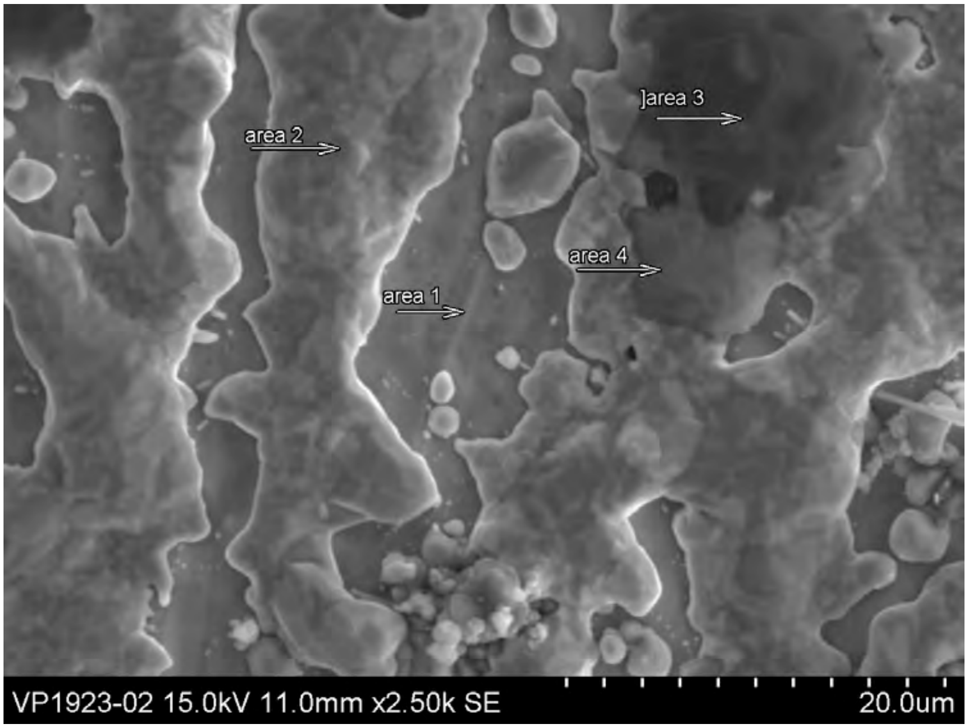
EDX I803



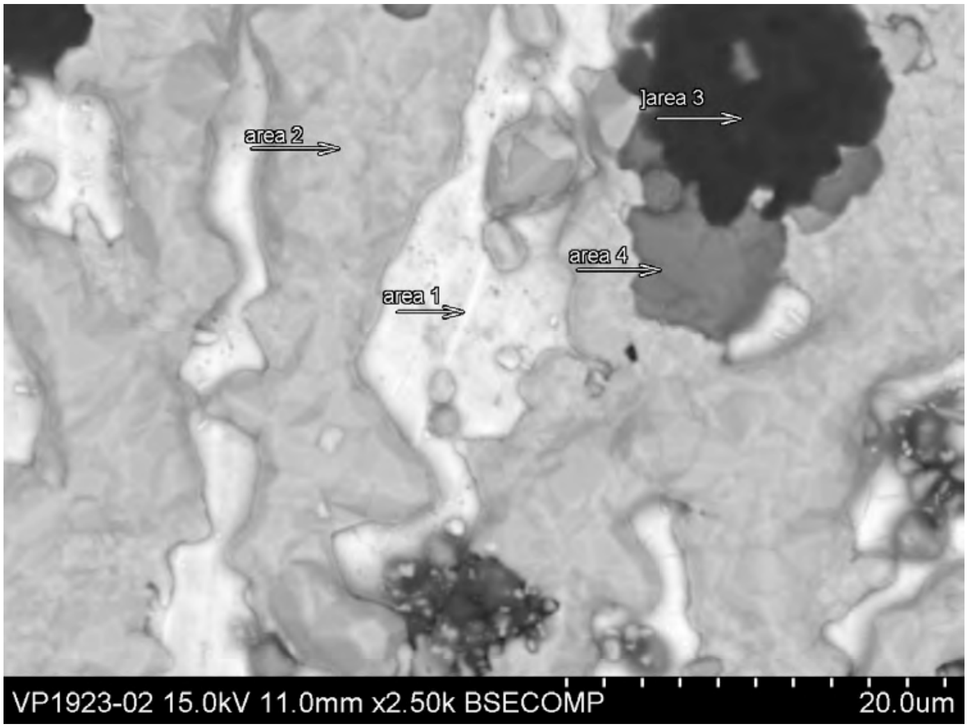




Specimen A5 (CeZr type) also exhibits a dark granular deposit, thicker at the rims and edges of the specimen than on the faces. The SE and BSE images following illustrate the morphology of the surface coating and deposit.

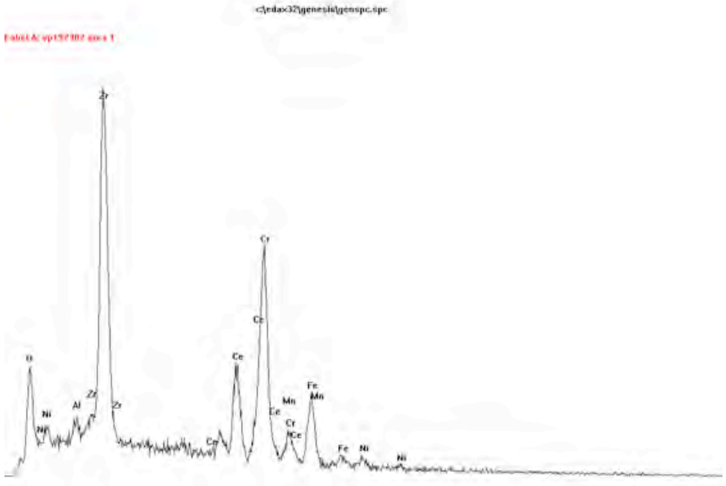


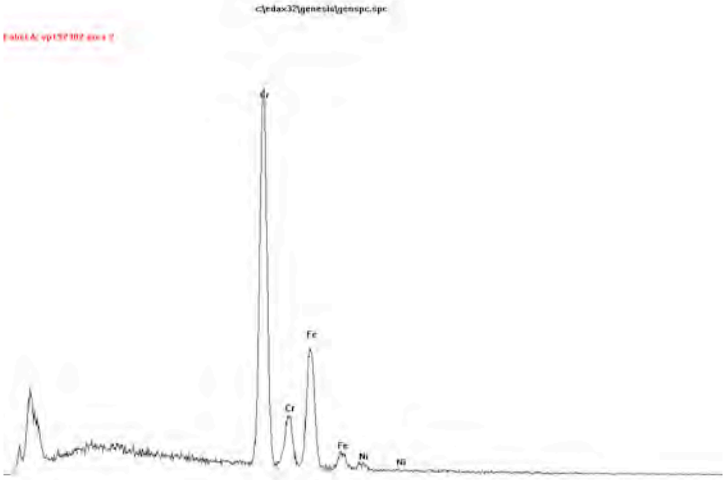
Secondary

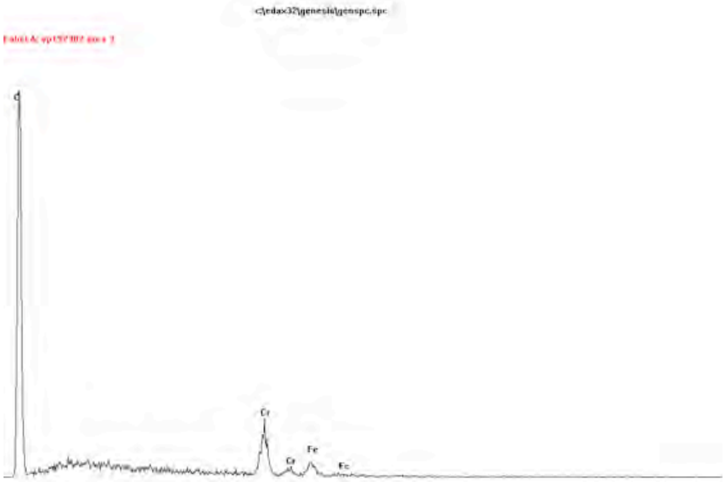


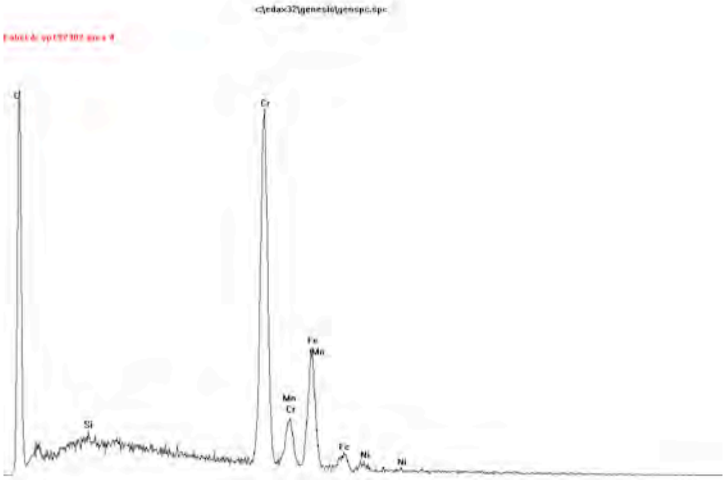
Backscattered

EDX analysis of four regions (areas 1 – 4) is presented below. The brightest region (1) yields a preponderance of Zr, with Ce, Cr, Ni, Fe, and O, showing that the CeZr oxide coating remains. The Fe-Ni-Cr alloy underneath is also detected, meaning that either these elements have migrated through the film, or the electron beam has penetrated the film and excited x-rays from the underlying material, or the film has begun diffusing into the alloy. Electron microprobe results to be presented later argue against the last possibility. The second brightest region (2) is preponderantly Cr, with small Fe and Ni. The third brightest area (4) is mainly C and Cr, with no evidence of the nanofilm apparent. This could be taken to mean that the film has been breached by outwardly migrating metal atoms. Similarly to the uncoated alloy, there are regions (3) that are mainly C, and these are likely the coke deposits.

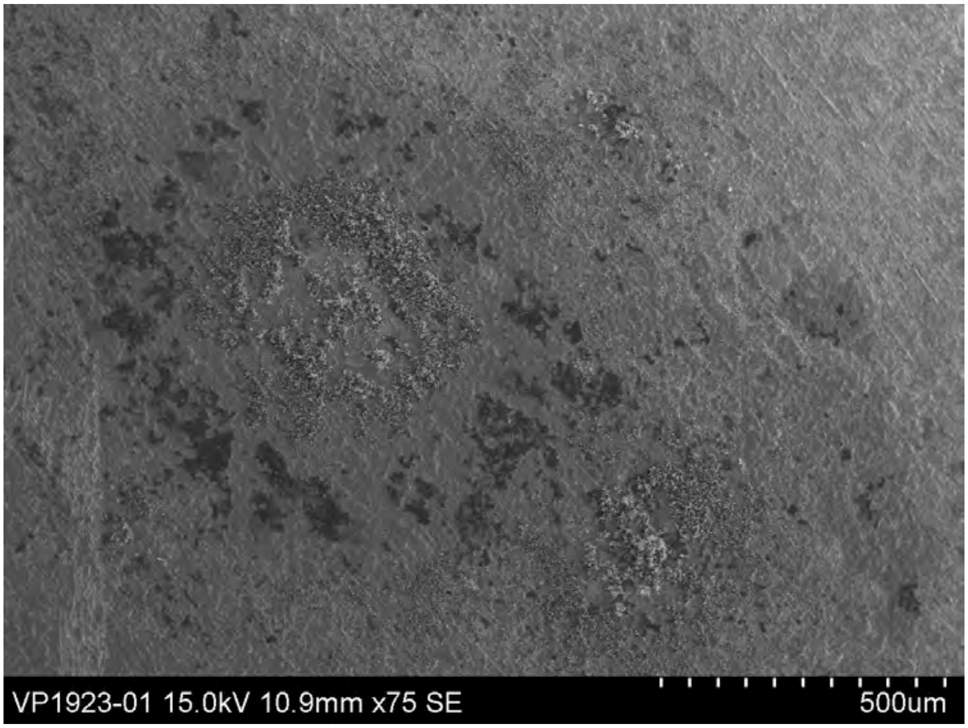




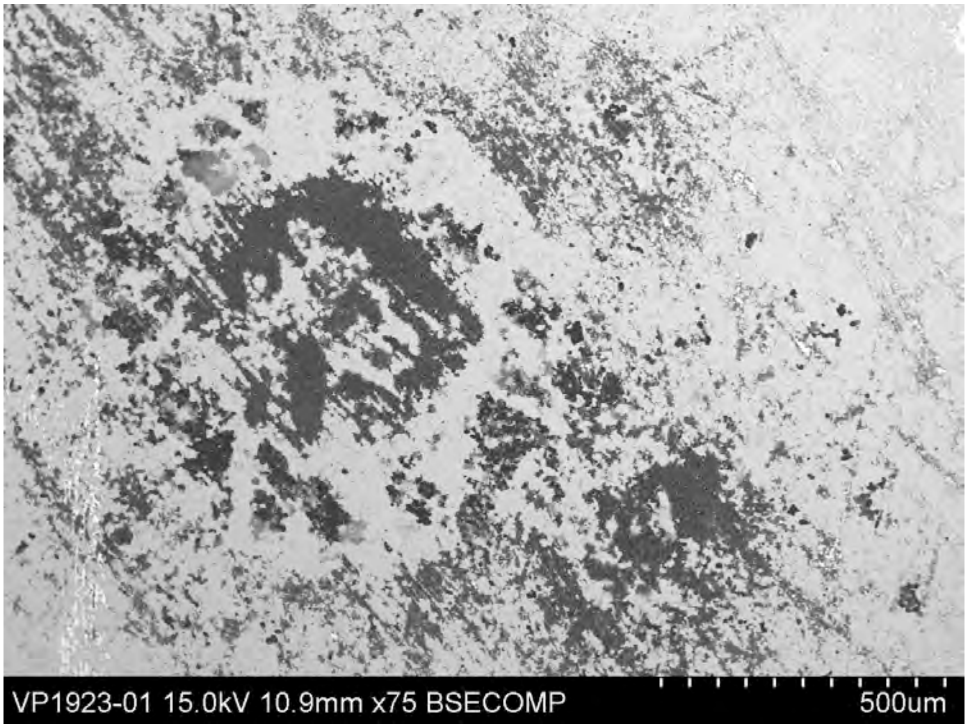




SEM examination illustrates the pinhole-defects present in the films/ The following two figures show a defect on specimen A5 in SE mode, where a deposit is clearly seen to be thicker in the center, and the BSE image shows that it is the dark variety described above, likely the coke deposit.



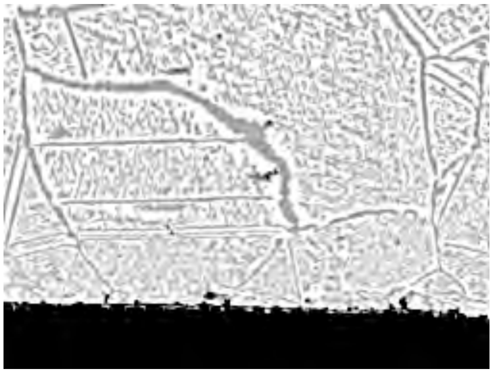
SE image A5

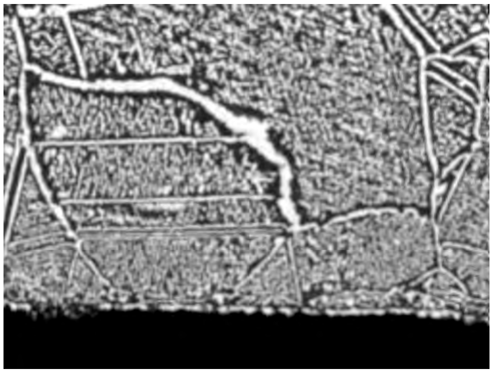


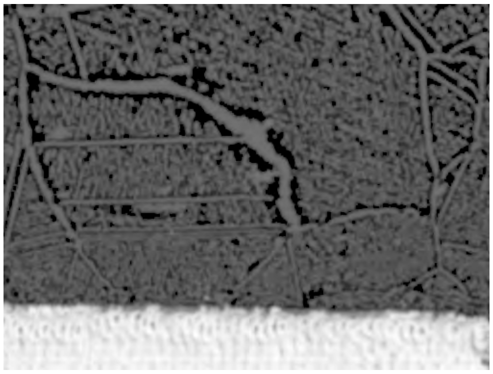
BSE mage of same area as above

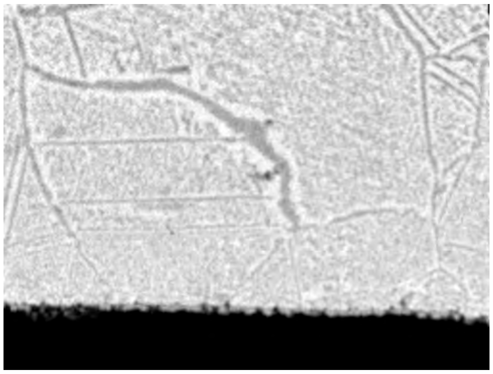
Specimens were mounted in epoxy, cut into two portions across their diameters, and polished for electron microprobe analysis. Several analyses were performed as described earlier. A BSE image of the uncoated alloy I803 specimen is presented below, along with corresponding wavelength-dispersive x-ray analytical photographs.

The microstructure of the alloy has been radically altered by the exposure to the methane/hydrogen mixture, with large amounts of carbon having been absorbed and converted into chromium carbides both in the grains and grain boundaries.

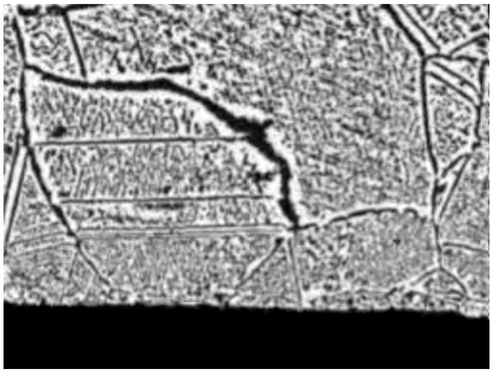

BSE image


Cr


C



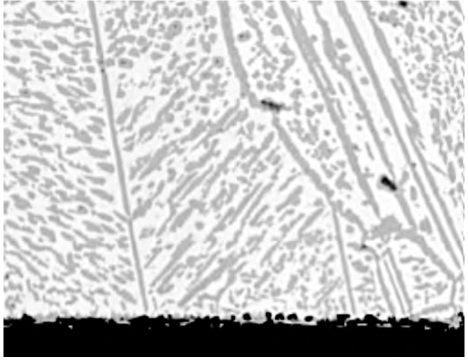
Fe



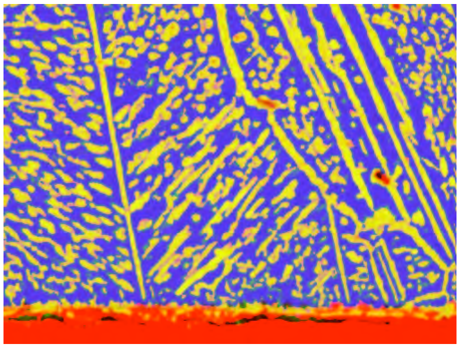
Ni

A specimen of the aluminosilicate/CeZr composite-coated material (C5) was similarly examined. Again, the results indicate large amounts of carbon have been absorbed and chromium carbides have formed throughout the specimen. Analyses for oxygen and zirconium (second colored image) indicate that the CeZr coating remains relatively intact at the surface, although Cr appears to exist above the coating.

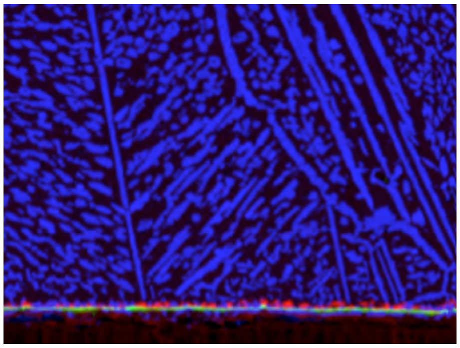
Microprobe of C5



Secondary



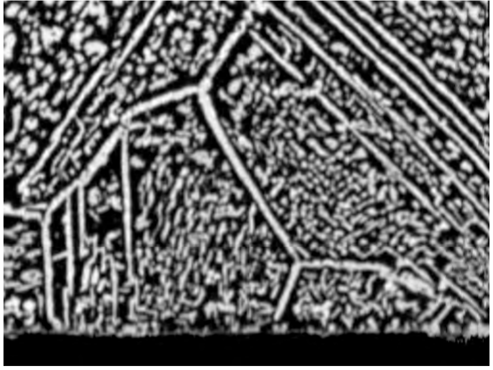
C-Cr-Ni



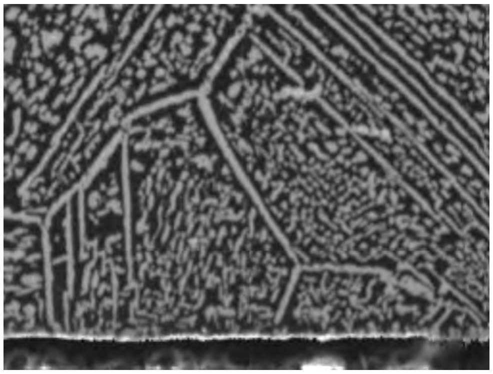
O-Zr-Cr

Electron microprobe analyses of specimen A7 (CeZr) yield similar results: chromium carbides are found throughout the alloy internal structure (three figures below), and chromium is found at the specimen surface along with Zr, Ce, and O (next two figures).

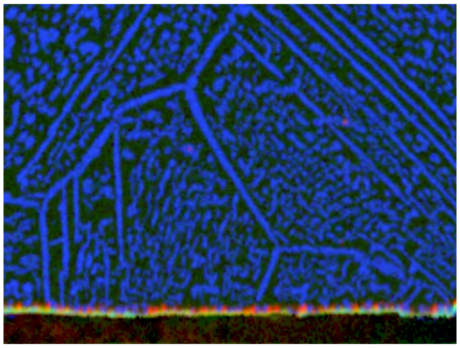
Secondary



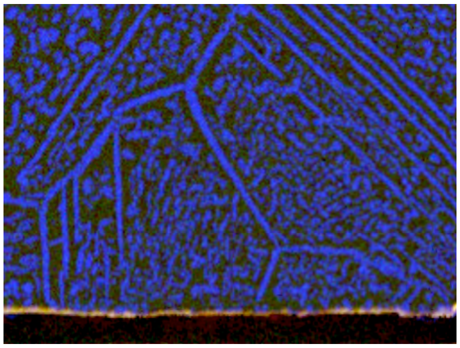
Cr



C



O-Zr-Cr



Zr-Ce-Cr

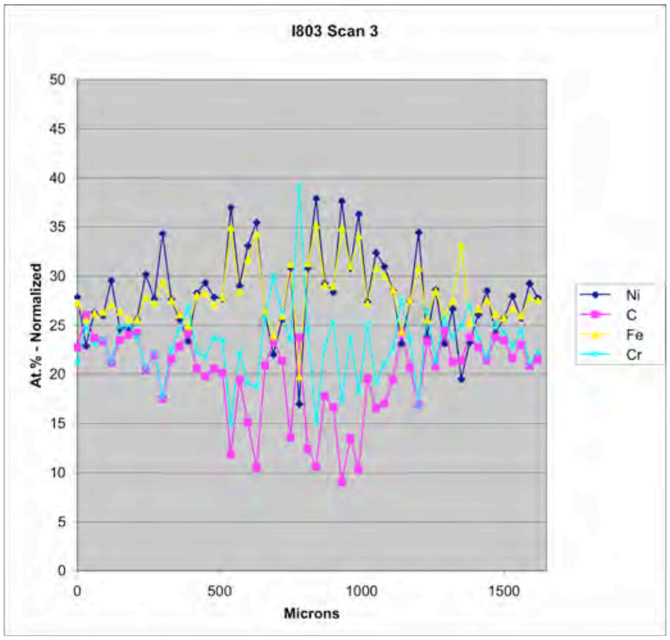
In an attempt to determine the extent of carbon penetration into the specimens, four scans completely across each specimen, at locations roughly one-quarter of the distance from each end, were set up. The probe stopped at 52 locations and measured Cr, Fe, Ni, Si, and C. The entire data set is not presented here, but the following three figures and the table provide summaries.

First is illustrated one of the scans (the third of each set of four) from each of the uncoated alloy, an aluminosilicate/CeZr coated specimen: C5), and a CeZr coated specmen (A5).

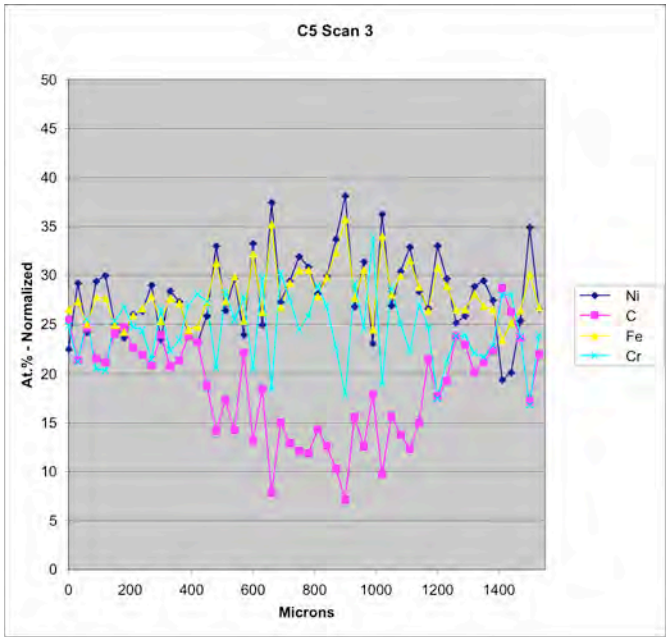
The uncoated alloy specimen (first figure) shows high carbon levels throughout the specimen, while the C5 specimen (second figure) shows slightly lower carbon levels with more of a trough (less carbon in the specimen center).

The CeZr specimen (third figure) shows much lower carbon levels than either of the other two and more uniform levels of Cr, Ni, and Fe through the center of the specimen than the others.

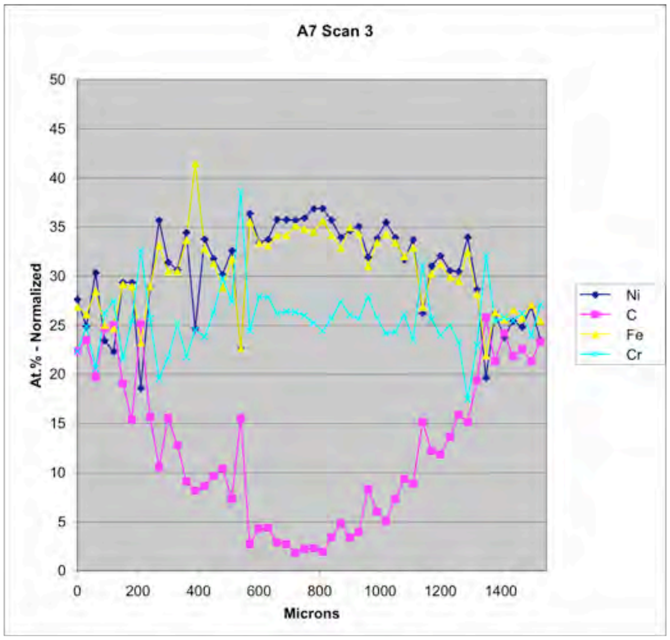
I803



C5



A7



The following table summarizes the probe data from these specimens, presenting the normalized atomic percent of the five elements averaged over the 52 counting locations along each of the four scans across the specimen.

| | | Normalized Atomic Percent (Avg. of 52 Point Counts) | | | | |
|---|---|---|---|---|---|---|
| SPECIMEN # | X-Section # | Ni | C | Si | Fe | Cr |
| I803 | 1 | 26.9 | 21.1 | 0.8 | 27.2 | 24.1 |
| | 2 | 28.4 | 19.8 | 0.8 | 28.1 | 23.0 |
| | 3 | 28.0 | 19.9 | 0.8 | 28.1 | 23.1 |
| | 4 | 27.1 | 20.7 | 0.8 | 27.5 | 23.8 |
| | Average | 27.6 | 20.4 | 0.8 | 27.7 | 23.5 |
| C5 | 1 | 28.7 | 17.0 | 0.9 | 28.9 | 24.5 |
| | 2 | 27.8 | 18.3 | 0.8 | 28.3 | 24.8 |
| | 3 | 28.2 | 18.5 | 0.8 | 28.0 | 24.5 |
| | 4 | 28.1 | 18.9 | 0.8 | 28.2 | 24.0 |
| | Average | 28.2 | 18.2 | 0.8 | 28.4 | 24.5 |
| A7 | 1 | 32.5 | 8.8 | 1.0 | 31.7 | 26.1 |
| | 2 | 31.6 | 10.4 | 0.9 | 31.1 | 26.0 |
| | 3 | 30.5 | 12.4 | 0.9 | 30.5 | 25.6 |
| | 4 | 32.1 | 9.5 | 0.9 | 31.5 | 26.1 |
| | Average | 31.7 | 10.3 | 0.9 | 31.2 | 26.0 |

The following table illustrates the average carbon content (column 2) of the three specimens, then presents the percentage difference between I803 and specimens C5 and A7(column 3). The aluminosilicate/CeZr film (C5) has reduced the carbon uptake of the alloy by about 11 percent. The CeZr film alone (A7), however, has reduced the carbon uptake by 50%.

The fourth and fifth columns present the average weight changes of the three types of material, and the difference between the two coated materials versus the uncoated, respectively. The similarity in reduction in carbon uptake inside the specimens and the differences in total measured weight change indicate that the films were actually effective at preventing carburization of the alloy. The amount of coke buildup on the surface is likely a small contributor to the weight changes observed.

| Specimen | At % Carbon | Difference (%) | % Wt. Change After 1000 hr | Difference (%) |
|---|---|---|---|---|
| I803 | 20.4 | | 3.3 | |
| | | 11 | | 9 |
| C5 | 18.2 | | 3 | |
| | | 50 | | 53 |
| A7 | 10.3 | | 1.54 | |

## DISCUSSION

Results of weight gain measurements, optical and electron microscopy, and electron microprobe analyses of materials exposed at 900°C for 1000 hours in a flowing atmosphere of 99% $H_2$ and 1% $CH_4$ have shown that an engineered nanofilm of ceria-stabilized zirconia is effective at reducing carburization of an underlying alloy substrate. The film remains relatively intact, although it appears that chromium from the alloy has migrated outward through it, and carbon has migrated inward through it. Utilization of an aluminosilicate underlayer for the CeZr is not as effective as utilization of the CeZr alone. It is not known at this point how the reduction in carburization of the alloy has affected its properties, such as strength and ductility. Further experimentation, perhaps using small tensile specimens, is warranted.

## ACKNOWLEDGEMENTS

Our special thanks go to Mr. Larry Walker for electron microprobe measurements, Ms. Tracie NNNNNN for SEM analysis, and Mr. Hu Longmire for metallographic preparation and analysis. They are all staff at the Oak Ridge National Laboratory, in Oak Ridge, TN.