

ENGINEERED OXIDE NANOFILMS PREPARED FROM SOLUTIONS AT RELATIVELY LOW TEMPERATURES

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ABSTRACT

Engineered oxide nanofilms, prepared from solutions and heat-treated at up to about 450°C, are described. Films consist of layers of ca. 50-100 nm thickness, built up from oxide nanoparticles of 3 – 8 nm dimension. Most cations can be deposited, from a solution liquid which is tailored to this cation. The liquid attaches itself to a solid surface, and reacts with the native oxide on this surface. Upon heating, the solution molecules decompose and are eliminated, leaving the cation on the surface as an oxide. Heating also promotes an interaction of the cation, the oxygen atoms, and the elements in the substrate, resulting in an interdiffusion zone between the nanofilm and the substrate. Mixtures of solutions, or single solutions containing a mixture of cations, can be used, to form multi-cation oxides, such as yttria-stabilized zirconia, indium-titanium oxide, Gd-doped ceria, and so on.

These nanofilms offer numerous interesting properties, including coking resistance, carburization protection, corrosion- and erosion-resistance as “passive” behaviors, and are being developed for more “active” areas such as fuel cell electrodes and electrolytes, and solar photovoltaic receivers.

The process for depositing these nanofilms is simple, involving minimum substrate surface preparation; application of the liquid via any of a number of means (spraying, spinning, dipping, swabbing, etc.); and heat-treatment via simple furnacing, and/or induction, infrared, laser, or microwave heating.

THE C3 COATING TECHNOLOGY

C3 International, LLC (“C3”) is the developer and owner of the patented Metal Infused Surface Treatment (“MIST”) technology, which allows for in situ creation of metal oxides on metal and ceramic surfaces from nearly all metals of the periodic table. The MIST technology also allows for nearly any combination of any or all of those elements to create novel surface nanofilms that can resist fouling, erosion, corrosion, and many other types of damage mechanisms. Recent efforts by C3 staff have developed nanofilms for “active”, rather than simply “passive” films, for use in solar photovoltaic cells, solid oxide fuel cells, and other electronic or ionic conducting applications.

Nanofilms developed by C3 have included stabilized zirconia (using various types of stabilizer cation), cerium oxide, aluminum oxide, combined alumina-silica, and others.

C3’s technology has recently been recognized by the materials community in America as being extremely important. C3 was awarded an “R&D-100” award in 2006 as one of America’s most important new technologies, and in 2007, the technology was further recognized by being awarded a “Nano-25” award as one of the 25 most significant nano-materials innovations of the year. C3 is the first nongovernmental agency to open office space in a U. S. Department of Energy (“DOE”) sponsored lab, Oak Ridge National Laboratory (“ORNL”). As such, we have been working very closely with the scientists there to characterize our novel materials and understand their functional mechanisms.

Scanning Auger nanoprobe studies (Figure 1), along with transmission electron microscopic analyses (performed at ORNL) of C3's nanofilms (Figures 2 and 3), show an interdiffusion region where the coating layer material has diffused into the substrate, significantly increasing the bond strength and reducing the risk of its spalling off the surface.

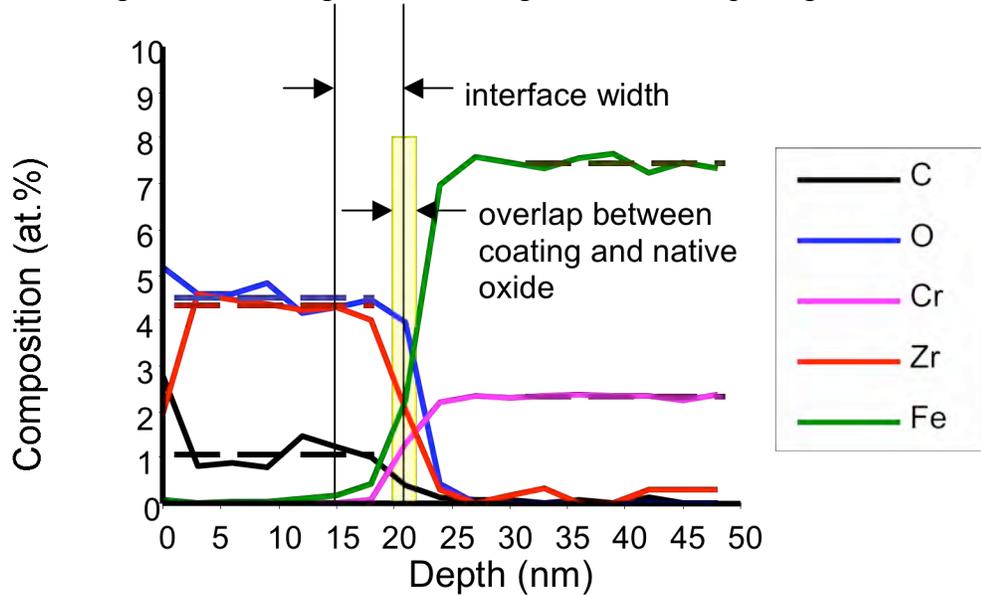


Figure 1. Scanning Auger nanoprobe results on a C3 zirconia film deposited on steel.

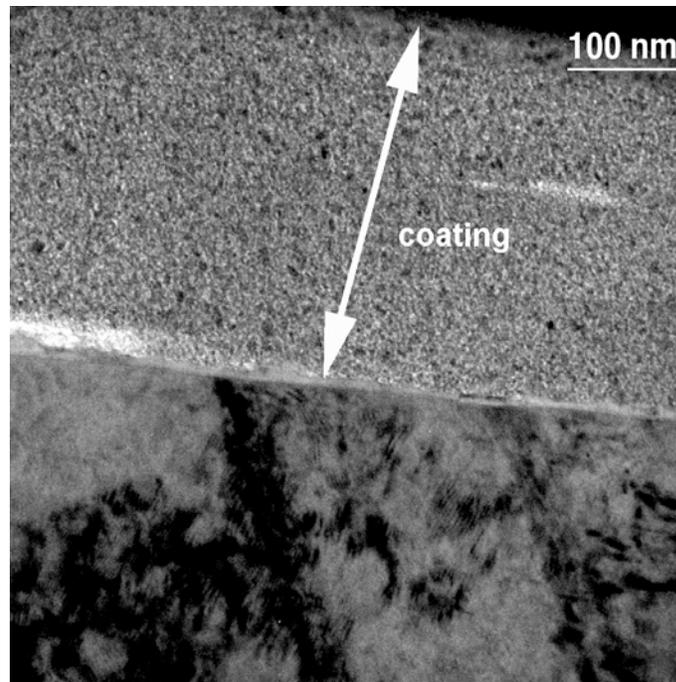


Figure 2. Transmission electron micrograph of a C3 zirconia film deposited on steel. Careful observation will show that there are three layers, resulting from three applications.

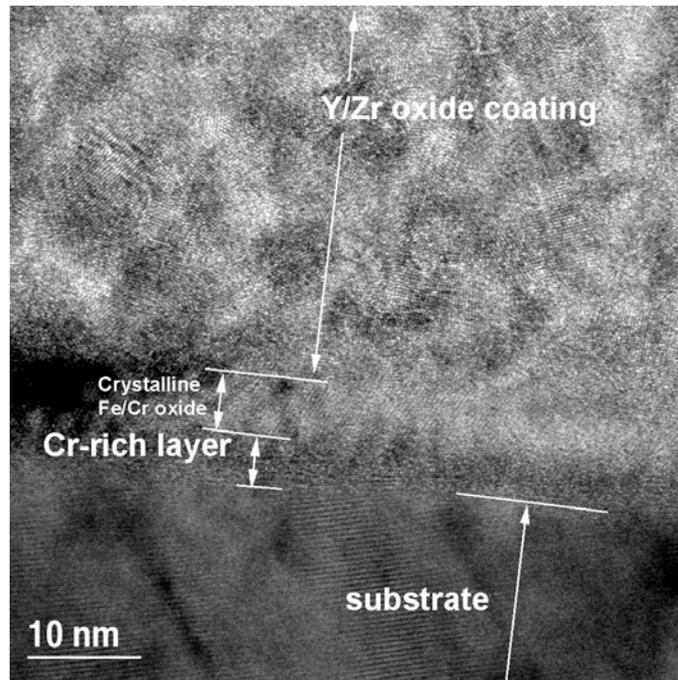


Figure 3. Transmission electron micrograph of a C3 zirconia film deposited on steel. Note the reaction and interdiffusion layer under the film.

Scientists at ORNL noted the crystallites created by our process were 3 to 8 nanometers in dimension. This finding was verified by synchrotron x-ray diffraction analysis performed through the High Temperature Materials Laboratory's (HTML) User Program, with diffraction being performed at the National Synchrotron Light Source at Brookhaven National Laboratory (Figure 4). We believe this small particle size results in extremely strong and dense films, while the interdiffusion region allows for inter-mixing of alloy and film constituents, and subsequently increases the bond strength between the alloy and the engineered nanofilm.

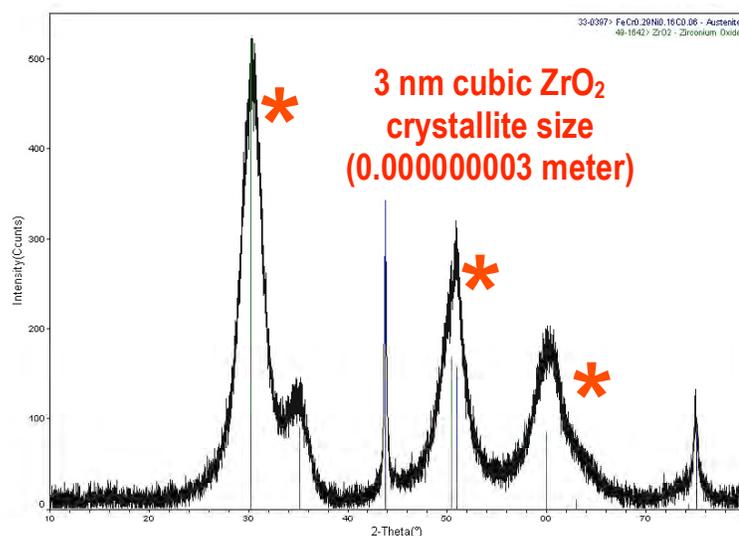


Figure 4. Synchrotron x-ray diffraction pattern of C3 zirconia nanofilm.

Nanofilms have been developed to resist corrosion in several industrial applications. One particular film has been developed which is extremely resistant to aqueous-based corrosion, including aqua regia. (See Figures 5 and 6 below) This same film has been proven to be resistant to elevated temperature salt-spray corrosion.



MIST Die Casting Coating



MIST Corrosion Coating

Figure 5. Aqua Regia Test. Sample exposed to specific volume of 3 parts HCl to 1 part HNO₃ for 1 hour. Dark region on left specimen is coating; light region is corrosion area, where film has been eaten through.



MIST Die Casting Coating



MIST Corrosion Coating

Figure 6. High Temperature Salt Spray Test. Samples heated to 1652°F in air, then periodically sprayed with 10% salt water solution for 1 hour. Circular region on left specimen is corrosion through the film.

These films are deposited in a very simple fashion: the metallic surface is prepared by simple cleaning and/or surface finishing techniques; a low-viscosity liquid precursor containing the cation(s) of interest is applied to the metal surface, by spraying, dipping, spinning, swabbing, or any other technique for applying a liquid to a surface; the metal part or component so coated is

heated in air or inert gas atmosphere to about 450°C to remove the hydrocarbon backbone of the precursor and leave behind the cation as an oxide film.

The technology is also unique in its ability to lay down nanofilms in-situ, onto very large systems, including those where line-of-sight access is not available. Many other coating technologies require vacuum, or at least controlled atmosphere, equipment, which greatly limits the size of component that can be coated. These expensive processes also, of course, increase cost of the coating. C3's lack of need for line-of-sight access, as required for processes like physical vapor deposition or sputtering, is another plus for C3's technology. The low viscosity liquid can be applied in various ways to any size or complexity of shape component. For example, in February of 2009 a carbon-fouling-resistant C3 coating was applied to the INSIDE of 3200 (continuous) feet of 3+ inch diameter tubing, in-situ, at a petroleum refinery in Wyoming. In June 2009, another refinery was a test site, which required the coating of the interior of over 10,000 ft of tubing (see following section).

One of the potential problems of preparing these nanofilms on metallic surfaces arises from the temperature currently required to produce the oxide nanofilm (450°C). This temperature may be too high for some metals, or for alloys which have been heat-treated to develop specific structures or stress states, e.g., levels of martensite in steels, or tempering schedules applied. C3 is working to evaluate newer potential precursor molecules and heating techniques, which will either allow lower temperature final heat-treatment steps, or allow use of rapid surface heating of the substrate-chemical deposit combination in such a manner as to not alter the structure/stress state of the underlying alloy. It is already known that these engineered nanofilms can be heat-treat cured by use of rapid infra-red heating techniques, wherein the surface of the alloy is barely changed while the coating matures. Similarly, surface heating of the alloy by e.g., induction may allow the bulk temperature of the component to remain unchanged while the coating cures. Laser heat-treatment curing can also be utilized, as could microwave heating of the film precursor.

COKING AND CARBURIZATION RESISTANCE EXAMPLES

The major application for C3's zirconia nanofilm is in the petroleum refinery operation called "coking".

Petroleum Refining Industry Overview

Oil refineries in the United States are operating at increased production capacity in order to keep up with consumer demand for gasoline and diesel fuels, which continues to increase in spite of recent economic and environmental developments. Worldwide consumer demand is being fueled by a number of factors, including the dramatic economic expansion and development that is ongoing in China and India, which have increased both drivers and transportation of goods.

As demand grows, the supply of easy to refine "light sweet" crude oil is declining, forcing the oil industry to utilize larger percentages of "heavy" and "sour" crude oil. The cost to retrieve and process this lower-grade ("heavy sour") crude oil is significantly higher than that of the higher quality ("light sweet") crude oil that the industry has relied on for the past century. Increasing quantities of crude oil must be processed by a "delayed coker" in the refining process, upgrading it into fuel. While this "coking" process has existed for over 70 years, declining crude oil quality and increasing end product demand is resulting in increased usage for this delayed coking process.

Fundamentally, all process heaters suffer from some level of fouling accumulation, which results in decreased heat transfer rates. To achieve the same throughput and conversion at

decreased heat transfer rates, the corresponding result is for the process heaters to burn more fuel, which represents in a major inefficiency. Fouling mitigation, which is the core of the Coker Coaters, LLC (a subsidiary of C3 International, LLC) technology, can have a significant effect in reducing the emissions in these largest emitters.

Fouling occurs at varying rates for different types of process heaters. Typically the larger the molecules being processed or the higher the severity (or temperature) of the process, the higher the fouling rate. For this reason, C2 has chosen its initial focus to be on the highest fouling processes in the sector to achieve the largest benefits. These are the delayed coker furnaces. As the technology matures, other process heaters including ethylene cracker furnaces and heat exchangers will be considered to further improve the benefits.

Delayed Coking Process

Delayed coking is a thermal conversion process which is heavily dependent on heat input from hydrocarbon fired furnaces. Coker heaters are directly affected by the heavier crudes that they are now having to process. Heavy crudes contain long hydrocarbon chains that must be heated to high temperature in order to be turned into more useful products. Heating the oil until it separates at a molecular level is called thermal cracking. This is done by running the heavy oil, called “resid” through approximately 3,600’ of metal tubes in a very large heater, which heats the oil to about 900-950 degrees F.

The problem of fouling within delayed coker heaters is that coke attaches to the inside walls of the heating tubes rather than traveling downstream to be removed in the coke drum. Coke 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.

The petroleum refining industry and its equipment and materials suppliers have been grappling with the coking problem for decades. Papers have been published in numerous venues describing the phenomenon,^{1,7} chemical additives to the resid, new techniques for pigging, and, of course, numerous coating techniques^{2,3} and new tubing or piping materials.⁴⁻⁶

The coke must be cleaned out. One method is a process called mechanical pigging. Pigging involves shooting a semisolid cylinder with tungsten carbide teeth through the tubes, where these teeth tear off and clean out the coke. On average, this cleaning process typically takes four days per shutdown, and is required every three to 12 months, depending upon the type of oil used at the refinery and the process conditions. There are about 200 delayed coker heaters in North America and over 375 worldwide.

Through mitigation of the fouling via application of C2’s patented MIST technology, coker heater fuel consumption at constant throughput can be reduced by as much as 2-3%.

The fouling issues with delayed cokers are well understood. Industry has been searching for mitigation techniques for these services for decades. C2 has passed a critical test for the process in an independent laboratory (see following) and is working towards field application and commercialization with a number of industry majors. This test is a modified Alcor test for residual oil fouling which is used to characterize novel materials and additives in an accelerated ninety minute fouling test at 1000 °F. This test has been used in the petrochemical industry for more than twenty years. The results have been compared to prior materials and chemistry and have shown remarkable results.

The test, performed at F.A.C.T. in Houston, by Dr. Ghaz Dickakian, involves circulating residual oil over tubes of standard petroleum refinery alloy, which contain internal heaters held

at constant power level. The temperature of the oil is measured versus time, and, as coke build up on the alloy heater tubes, the temperature of the oil decreases. Several compositions of C3 nanofilms were tested in this apparatus (results below).

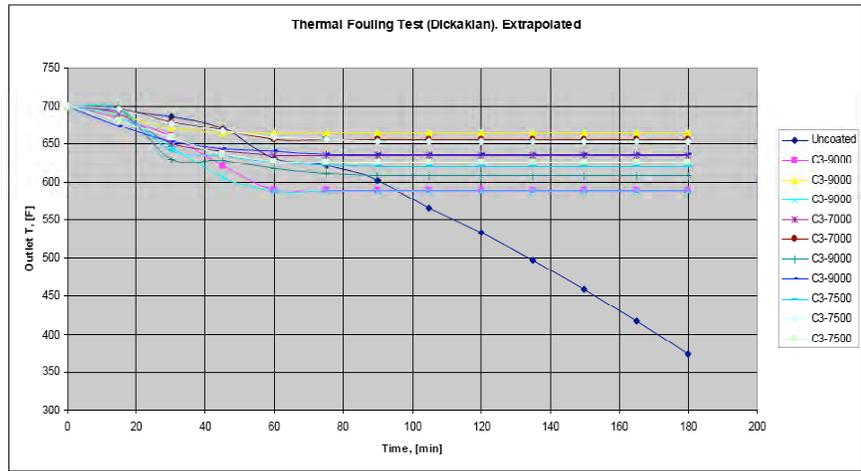


Figure 7. Temperature versus time for residual oil flowing over heater tubes being maintained at a constant internal temperature. Note that the uncoated tube becomes coated with coke and heat transfer is reduced, while all of the C3 coating compositions reach a plateau at which further temperature decay is prevented (e.g., heat transfer is maintained because of lack of fouling by coke).



Figure 8. Uncoated (top) and C3 nanofilm coated (bottom) alloy tube exposed to residual oil on the outside, while being heated by heaters inside the tubes. Note that the C3 coated tube has much less, and more uniform, coke buildup.



Figure 9. The Frontier Oil Company's (left) and a larger Houston-area refiner's (right) cokers, into whose coker heater tubing C3 has successfully emplaced engineered nanofilms, via in-the-field installation.

A second (potential) major application operation called “ethylene cracking”. 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.

An experiment was performed in the Corrosion Science and Technology Group of the Materials Science and Technology Division of ORNL, to simulate ethylene cracking conditions. Alloy samples, with and without a C3 rare-earth element (REE)- stabilized zirconia nanofilm, were exposed to a slowly flowing 99% H₂/1% CH₄ atmosphere at 900°C for times up to 1000 hours. Complete test details and results are being prepared for a future paper, so only a summary of the coking and carburization results will be presented here.

Figure 10, below, shows the measured weight gains for the typical petroleum refinery tubing alloy, I803, with and without the C3 nanofilm. Here the weight pickup of the coated steel sample is seen to vary from about 80% less at 200 hours to about 50% less at 1000 hours.

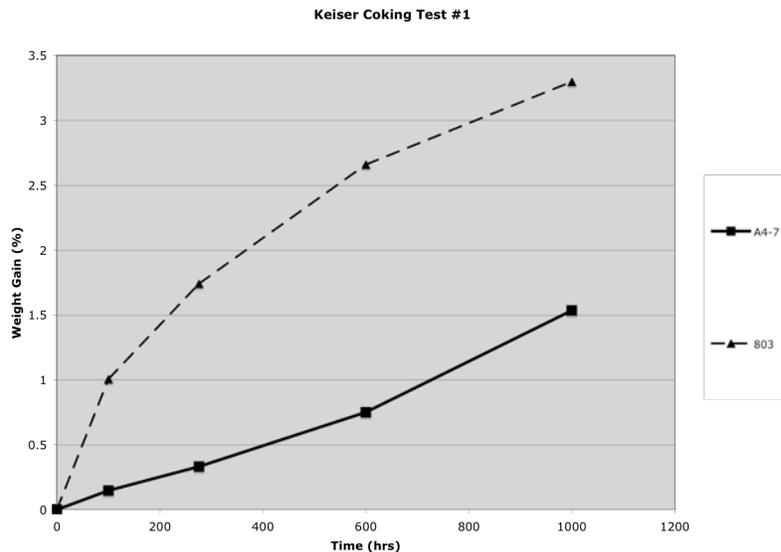


Figure 10. Coking and carburization test results. Weight gain for the uncoated I 803 steel coupon is significantly greater than for the coated coupon.

Most of this weight gain is from carburization, as will be shown later, but some coke deposition is also evident. SEM examination of the tested coupon surfaces showed copious carbon deposits.

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 in Figure 11, along with corresponding wavelength-dispersive x-ray analytical elemental 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.

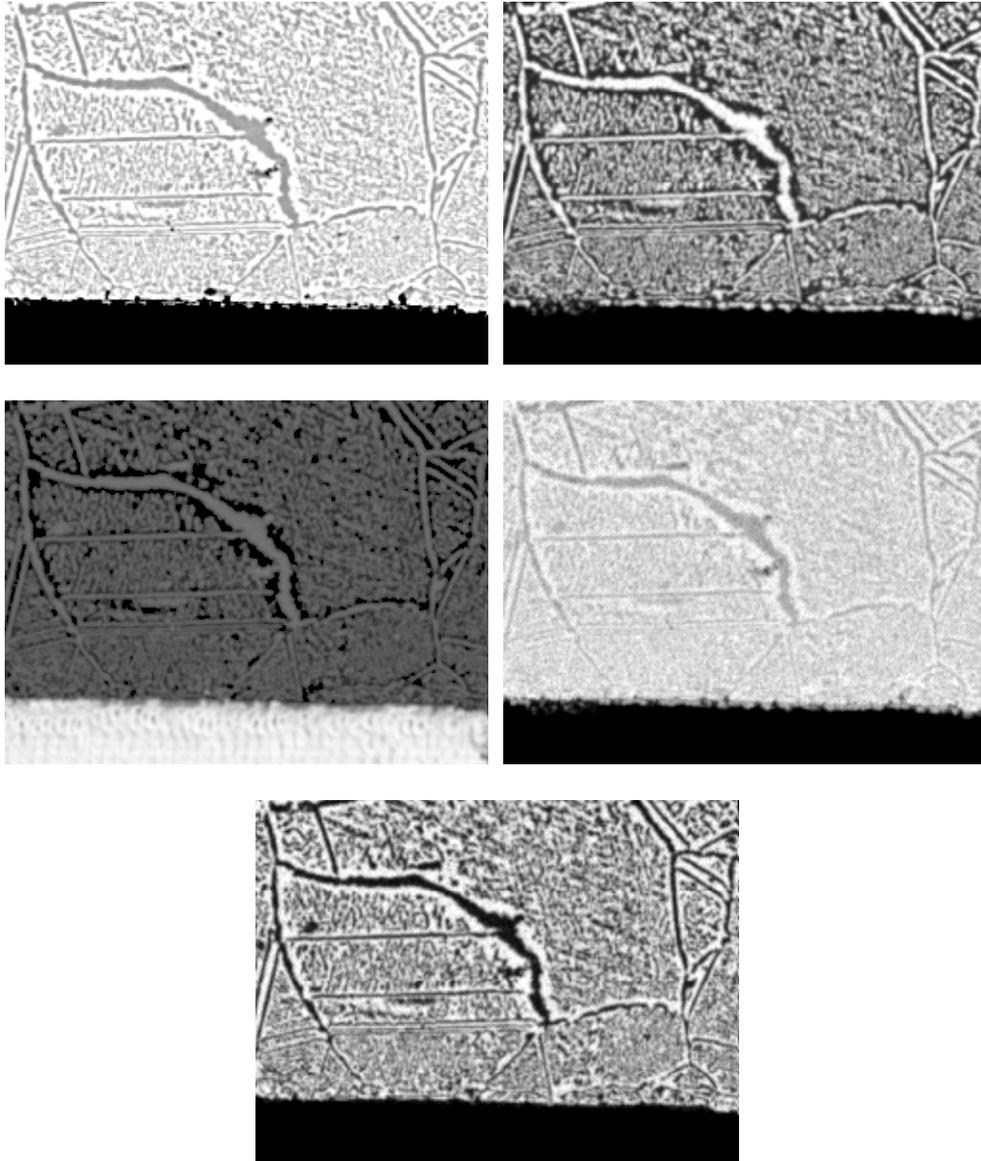


Figure 11. Electron microprobe results for uncoated alloy I803 specimen. Top left: BSE image. Top right: Cr image. Middle left: C image. Middle right: Fe image. Bottom: Ni image.

Electron microprobe analyses of the stabilized zirconia-coated specimen yield similar results: chromium carbides are found throughout the alloy internal structure (Figure 12), and chromium is found at the specimen surface along with Zr, REE, and O.

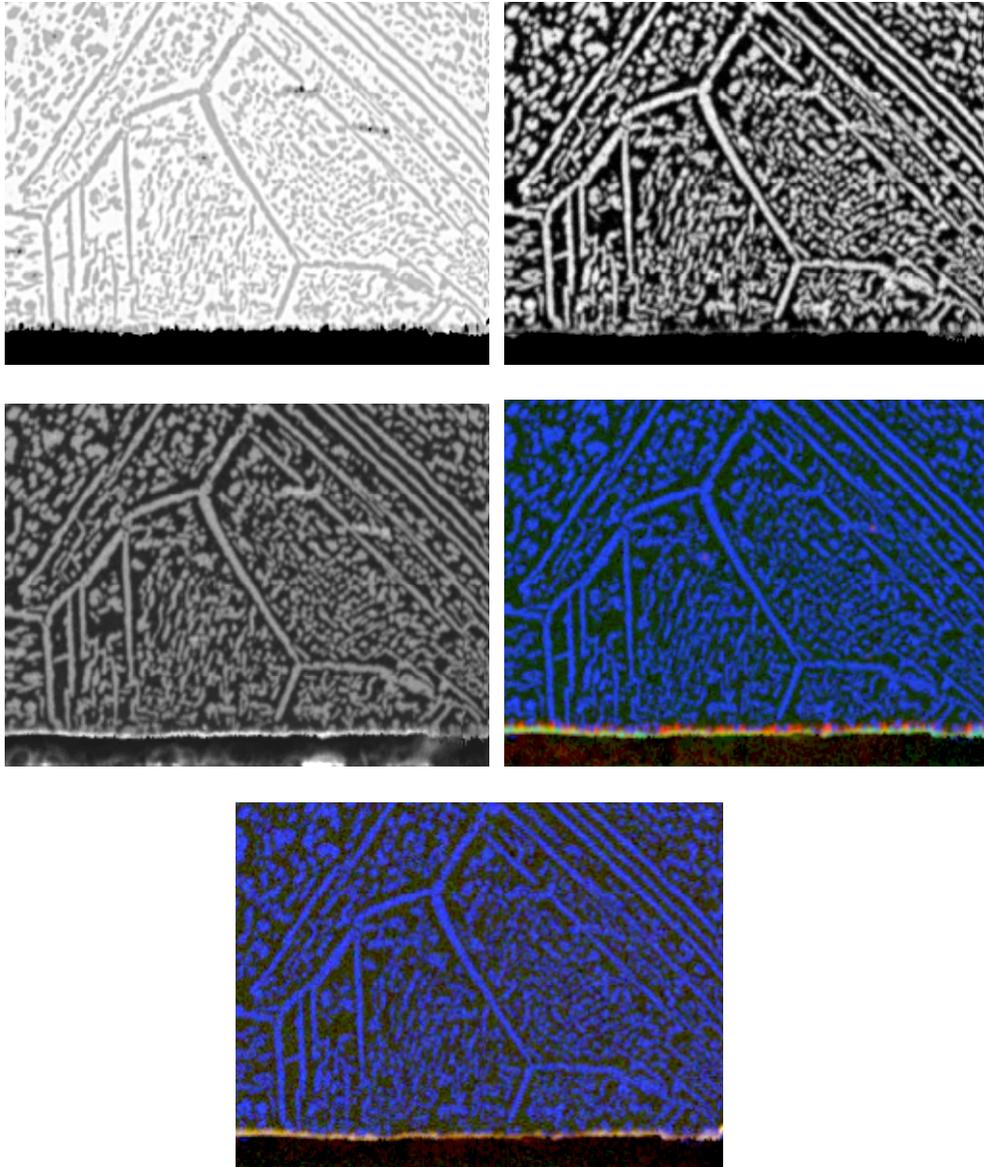


Figure 12. Electron microprobe results for stabilized zirconia-coated alloy I803 specimen. Top left: BSE image. Top right: Cr image. Middle left: C image. Middle right: O-Zr-Cr image. Bottom: Zr-REE-Cr image.

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 two 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 (Figure 13) and a coated specimen (Figure 14).

The uncoated alloy specimen shows high carbon levels throughout the specimen, while the coated specimen shows a much lower carbon level and more uniform levels of Cr, Ni, and Fe through the center of the specimen than the uncoated specimen.

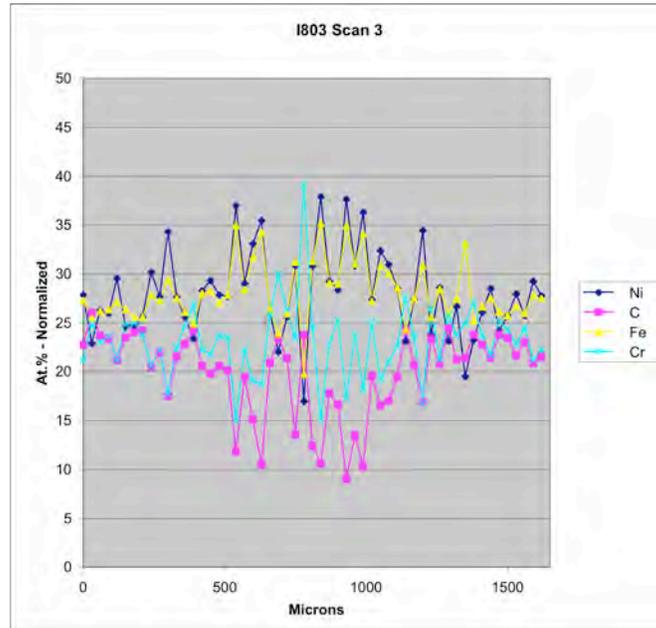


Figure 13. Microprobe results on an uncoated I803 alloy specimen exposed to 99% H₂/1 % CH₄ at 900°C for 1000 hours. Significant carbon pickup is noted, with nearly one atom in five in the structure being replaced by carbon.

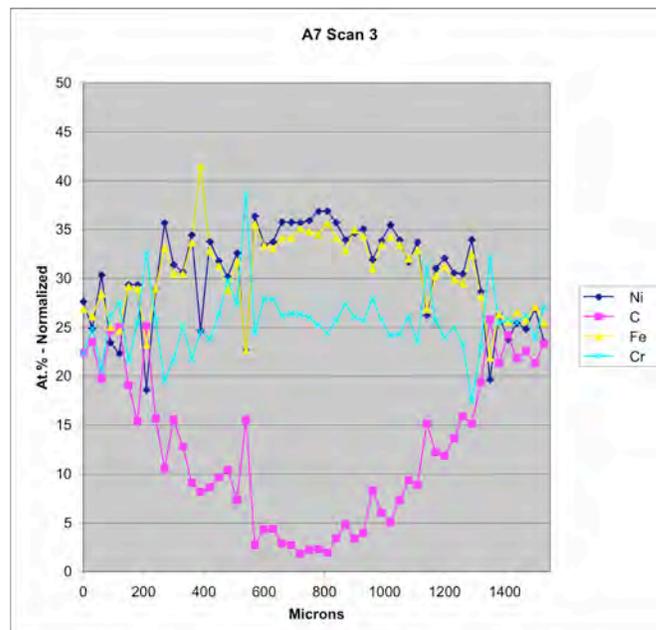


Figure 14. Microprobe results on a stabilized zirconia-coated I803 alloy specimen exposed to 99% H₂/1 % CH₄ at 900°C for 1000 hours. Carbon pickup is much reduced from the previous specimen.

Table 1 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.

Table 1. Electron Microprobe Data for Uncoated and C3-Coated Coupons

SPECIMEN	X-Section #	Normalized Atomic Percent (Avg. of 52 Point Counts)				
		Ni	C	Si	Fe	Cr
I803 Uncoated	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
I803 Coated	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

Table 2 illustrates the average carbon content (column 2) of the two specimens, then presents the percentage difference between uncoated I803 and the coated specimen (column 3). The nanofilm has reduced the carbon uptake by 50%.

The fourth and fifth columns present the average weight changes of the two materials, and the difference between the coated material 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.

Table 2. Carbon Pickup of Uncoated and C3-Coated Coupons

Specimen	At % Carbon	Difference (%)	% Wt. Change After 1000 hr	Difference (%)
I803	20.4		3.3	
A7	10.3	50	1.54	53

CONCLUSIONS

Results of weight gain measurements, electron microscopy, and electron microprobe analyses of materials exposed at 900°C for 1000 hours in a flowing atmosphere of 99% H₂ and 1% CH₄ have shown that an engineered nanofilm of 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. 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.

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