SRI International

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Diffusion Coatings for Corrosion-Resistant Components in Coal Gasification Systems

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DISCLAIMER

ABSTRACT

Heat-exchangers, particle filters, turbines, and other components in integrated coal gasification combined cycle system must withstand the highly sulfiding conditions of the high-temperature coal gas over an extended period of time. The performance of components degrades significantly with time unless expensive high alloy materials are used. Deposition of a suitable coating on a low-cost alloy may improve its resistance to such sulfidation attack, and decrease capital and operating costs. The alloys used in the gasifier service include austenitic and ferritic stainless steels, nickel-chromium-iron alloys, and expensive nickel-cobalt alloys.

During this period, we analyzed several coated and exposed samples of 409 steel by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX). We report here on findings of this analysis:

1. A SS409 coupon that was coated with multilayered combined nitrides of Ti, Al, and Si showed adherent coatings on the surface;
2. A similarly coated coupon, after exposure to simulated coal gas at 900°C for 300 h, revealed that the coating has cracked during the exposure;
3. An SS409 coupon that was coated with nitrides of Ti and Si with a barrier layer of tungsten in between to improve the adhesion of the coating and to prevent outward diffusion of iron to the surface.
4. A porous coupon was coated with nitrides of Ti and Al and examination of the coupon revealed deposition of Ti at the interior surfaces. A similarly prepared coupon was exposed to simulated coal gas at 370°C for 300 h, and it showed no corrosion.

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EXECUTIVE SUMMARY

Advanced coal gasification systems such as integrated coal gasification combined cycle (IGCC) processes offer many advantages over conventional pulverized coal combustors. Heat-exchangers, filters, turbines, and other components in IGCC plants often must withstand the highly sulfiding conditions at high temperatures. In collaboration with U.S. Department of Energy and ConocoPhillips, we are developing corrosion-resistant coatings for high-temperature components in IGCC systems.

SG Solution's coal gasification power plant in Terre Haute, IN, uses ConocoPhillips' E-Gas technology. The need for corrosion-resistant coatings exists in two areas: (1) the tube sheet of a heat exchanger at ~1000°C that is immediately downstream of the gasifier, and (2) porous metal particulate filter at 370°C, which is downstream of the heat exchanger. These components operate at gas streams containing as much as 2% H_2S. A protective metal or ceramic coating that can resist sulfidation corrosion will extend the life-time of these components and reduce maintenance.

During this period, we analyzed several coated and exposed samples of 409 steel by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) and report on findings of four samples:

1. An SS409 coupon that was coated with nitrides of Ti, Al, and Si showed adherent coatings on the surface;
2. A similarly coated coupon, after exposure to simulated coal gas at 900°C for 300 h, revealed that the coating has cracked during the exposure;
3. An SS409 coupon that was coated with nitrides of Ti and Si with a barrier layer of tungsten in between to improve the adhesion of the coating and to prevent outward diffusion of iron to the surface.
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INTRODUCTION

Heat-exchangers, filters, turbines, and other components in coal-fired power plants must withstand demanding conditions of high temperatures and pressure differentials. Further, the components are exposed to corrosive gases and particulates that can erode the material and degrade their performance. In collaboration with U.S. Department of Energy and ConocoPhillips, SRI International recently embarked on a project to develop corrosion-resistant coatings for coal-fired power plant applications. Specifically, we are seeking to develop coatings that would prevent the corrosion in the tube-sheet of the high-temperature heat recovery unit of a coal gasification power plant of SG Solution's plant in Terre Haute, IN, which uses ConocoPhillips' E-Gas technology. This corrosion is the leading cause of the unscheduled downtime at the plant and hence success in this project will directly impact the plant availability and its operating costs. Coatings that are successfully developed for this application will find use in similar situation in other coal-fired power plants.

WORK PERFORMED

Previously, we showed that the coatings of nitrides of Ti, Al, and Si can provide alloy steels significant resistance to sulfidation attack in simulated coal gas streams. In the bench scale tests, the coated coupons showed significant resistance in a H_2S (2%v/v) containing gas stream at 370°C while sulfidation attack occurred at 900°C. To understand the cause of sulfidation attack, we analyzed the coated coupons using scanning electron microscopy and energy dispersive X-ray analysis.

ANALYSIS OF SS 409 COUPON COATED WITH NITRIDES OF TITANIUM AND SILICON

Figure 1 is a scanning electron microscopy picture of the cross-section of a SS 409 steel coated with titanium, silicon, and aluminum nitrides. As can be seen from the figure, the coating was uniform, adherent, and had a thickness around 7-8 μm. Figure 2 shows a EDX analysis of a line scan and Figure 3 shows an elemental depth profile for Al, Si, Ti, Cr, Fe (values are normalized to 100% considering only these elements). Different zones are clearly distinguished: an external TiSiN layer followed by a TiAlN layer and a TiAl diffusion zone. The Si peak at the interface between the coating and the substrate is related to an intentionally added Si layer for a short time at the end of the TiAl diffusion step. The purpose of this addition is to provide interdiffusion to increase adhesion and provide a thermodynamic sink to slow down the diffusion of Fe to the surface which is known to cause sulfidation under the operating conditions.

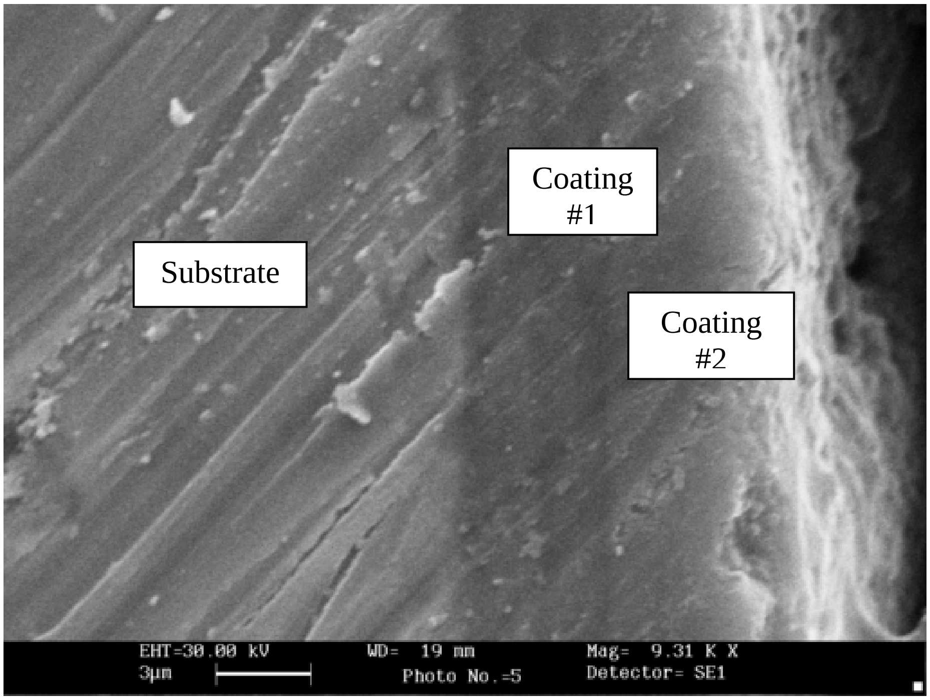

Figure 1. Cross section of a (Ti, Al, Si) nitride coating on SS 409 alloy steel.

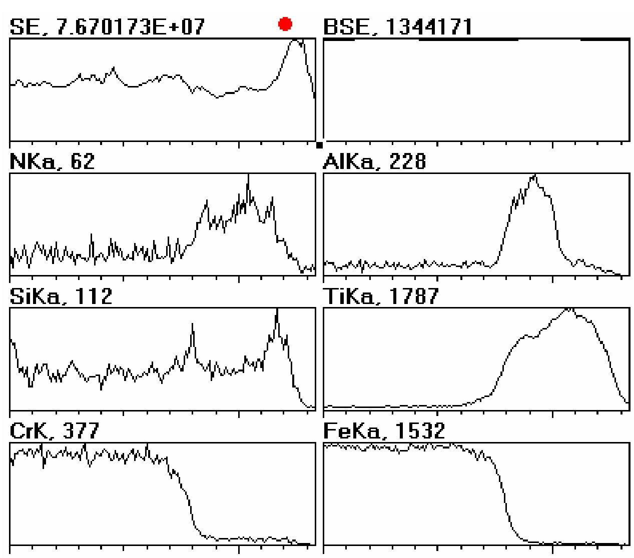

Figure 2. Elemental profile of the coating shown in Figure 1.

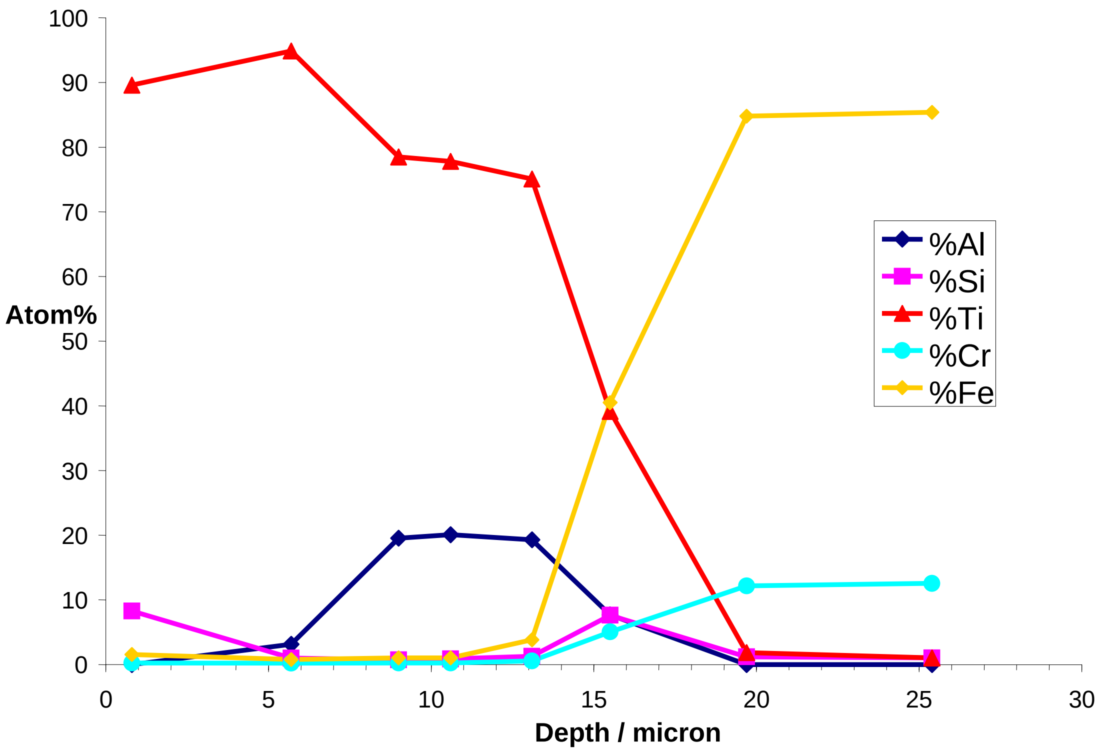

Figure 3. Depth profile of the elements in the coated specimen shown in Figure 1.

ANALYSIS OF SS 409 COUPON COATED WITH NITRIDES OF TITANIUM AND SILICON, AND EXPOSED TO SIMULATED COAL GAS AT 900°C

A sample of the coated alloy was exposed to a simulated coal gas stream containing H_2S at 900°C for 300 h. At the end of the exposure period, the coated sample showed significant sulfidation attack as evidenced by the formation of a scale and a weight gain of ~12%. The cross section of the coupon is shown in Figure 4. In the SEM photograph, the top section is the specimen, the middle section is the coated layer, and the bottom of the photograph shows the polymeric mounting. Figure 4 shows that, after exposure to the sufiding gas stream, the coating layer has cracked allowing H_2S to penetrate the coating and react with the substrate. The EDX analysis showed that the coating still contained Ti, as expected (Figure 5). However, it also shows the presence of Cr, which was not in the original coating. We believe that the Cr may have diffused along the pore surfaces to the outer boundary. The presence of Cr near the surface also indicates that the coating was adherent for some period of time allowing the Cr to migrate through the coating layer. Alternatively, Cr may have diffused as an oxyhydroxide vapor species under the high temperature, high steam concentration environment. Additional studies are needed to clarify these issues.

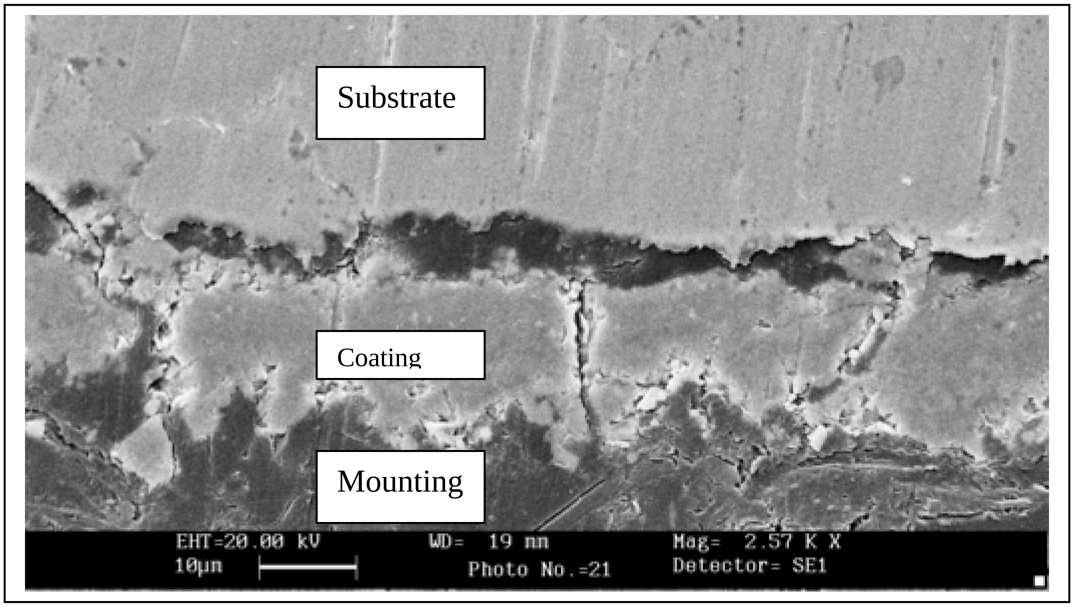

Figure 4. The cross section of a (Ti,Al,Si) nitride coated sample after exposure to a simulated coal gas at 900°C for 300 h.

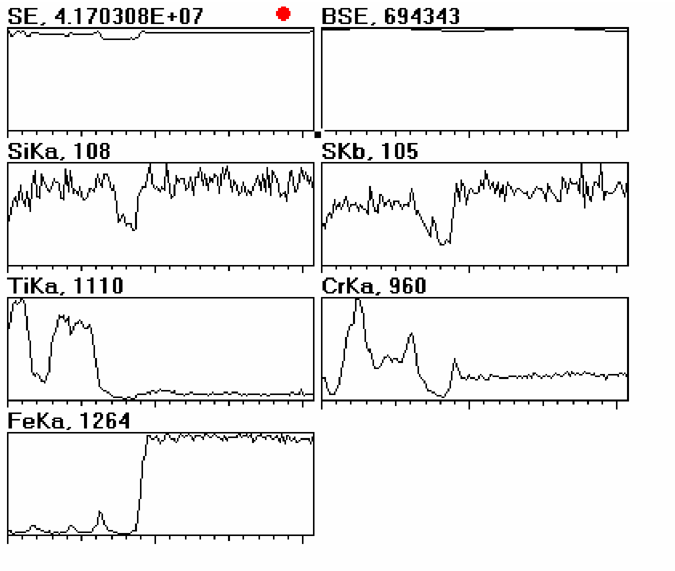

Figure 5. EDX analysis of the cross section of the sample area shown in Figure 4.

ANALYSIS OF SS 409 COUPON COATED WITH NITRIDES OF TITANIUM AND SILICON WITH TUNGSTEN BARRIER LAYER

To eliminate the cracking of the coating and to prevent migration of the substrate elements to the outer surface of the coating, we deposited a layer of tungsten (W) on the substrate before the deposition of (Ti,Al) nitride layer. Such layers are often used in the semiconductor fabrication as diffusion barriers. Note that we did not include silicon nitride in this coating because Si can react with W to form tungsten silicide, which may not be adherent with the substrate.

Figure 6 illustrates the SEM photograph of the nitride coating with W diffusion barrier. In this picture, the top is the substrate, the middle is the coating and the bottom is the specimen mount. The light thin layer between the substrate and the coating is the W diffusion barrier. The (TiAl) nitride coating is homogeneous and free of cracks. The layered structure is clearly seen in the EDX analysis and the EDX elemental depth profile: the steel substrate, a diffusion layer (Ti,Al), a W layer and a TiAlN film on top. In the next quarter, we will test coupons with similar coating to simulated coal gas stream.

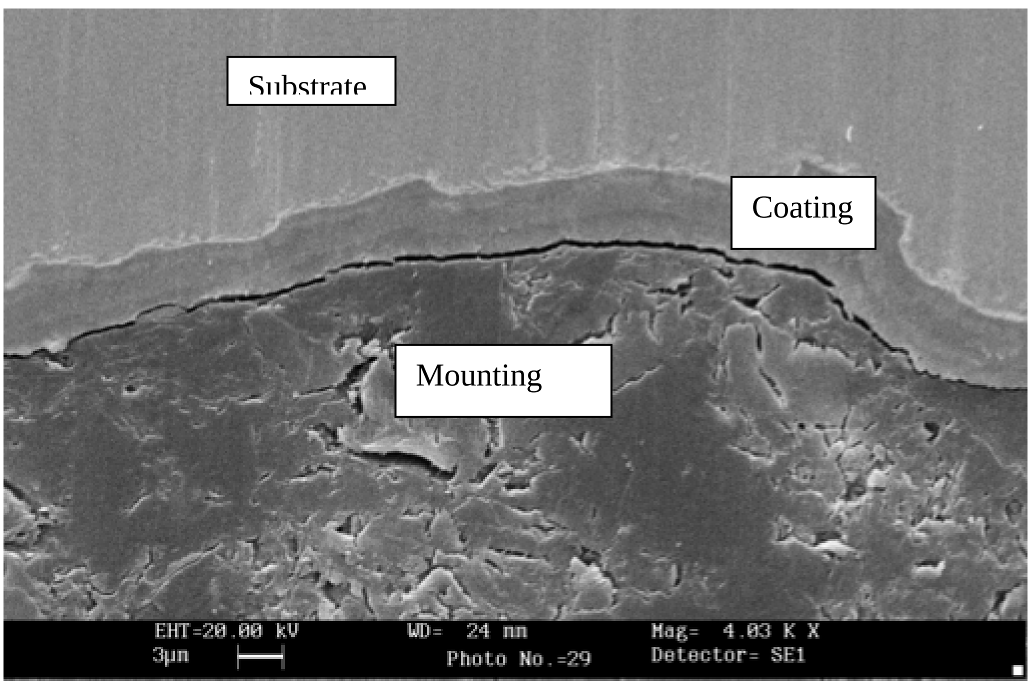

Figure 6. SEM photograph of a nitride coating on SS409 alloy with W diffusion barrier.

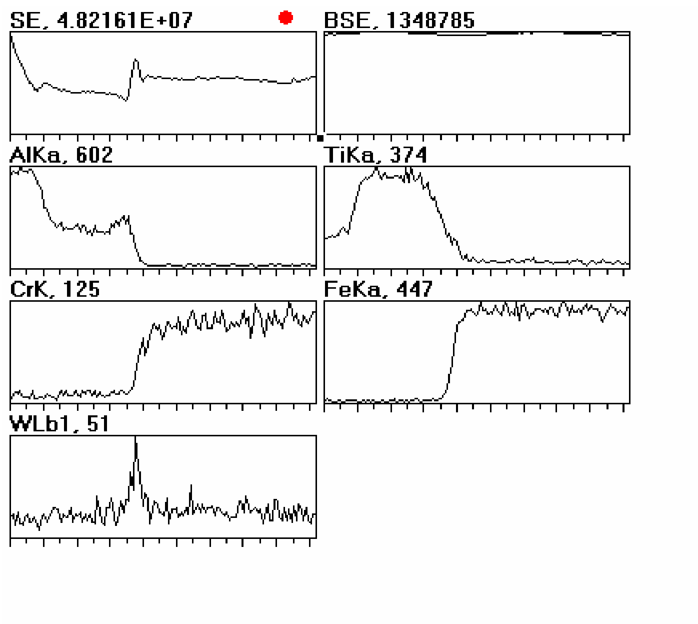

Figure 7. Elemental profile of the coating shown in Figure 6.

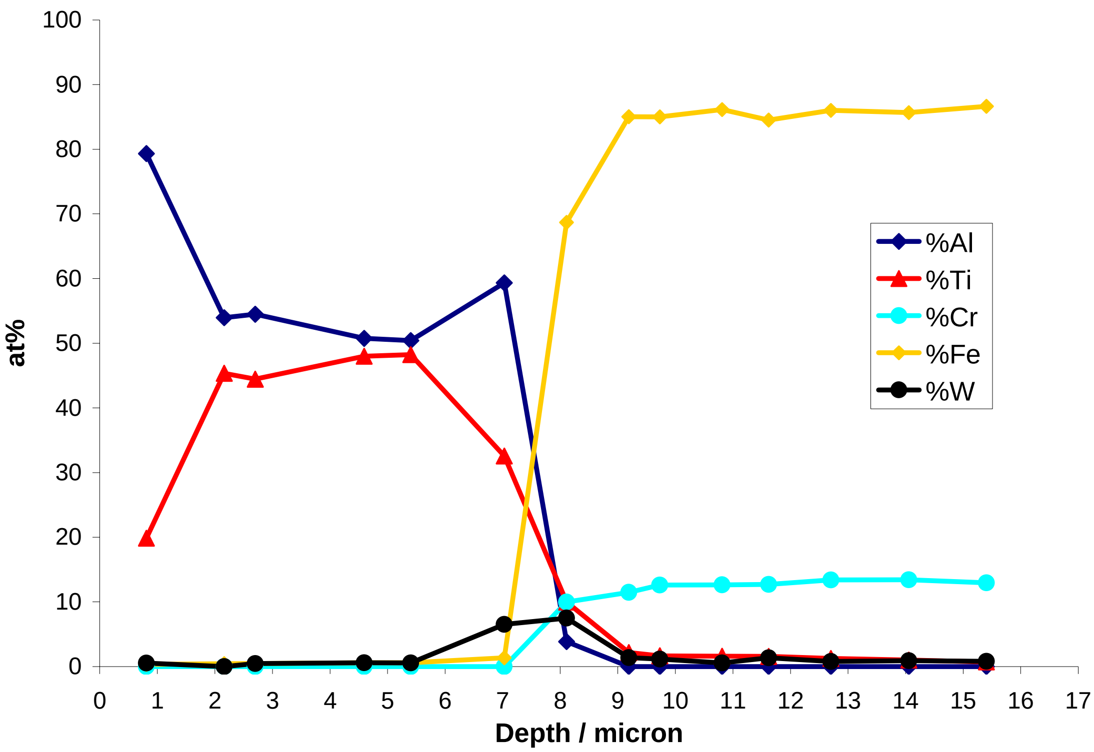

Figure 8. Profile of the elements in the coated specimen shown in Figure 6.

ANALYSIS OF A POROUS COUPON FABRICATED WITH SS 409 POWDER AND COATED WITH NITRIDES OF TITANIUM AND ALUMINUM

The uniformity of the coating inside a porous sample, similar to that of a stainless steel barrier filter was also examined. We reported previously the fabrication of porous coupons of SS409 alloy steel and their performance in a simulated coal gas environment at 370°C, similar to that expected in a barrier filter condition.

A photograph of the cross section image, as observed by SEM is shown in Figure 9. The photograph shows that the external part of the sample is more porous than the interior, an artifact from the sintering procedure. Figure 10 shows the SEM image of an enlarged area of the specimen (mounting polymer is the dark zone in the right). As can be seen from the Figure 10, a homogeneous coating with a thickness around 2 to 3 μm was deposited. Figure 10 also depicts the result of an EDX analysis of a line-scan in that zone (analysis performed across the marked yellow line). As observed, Ti was deposited both in the external part of the sample (directly exposed to the fluidized bed) and in the internal part (exposed to one of the internal voids of the porous material). This is a good indication that infiltration of reactants to coat the internal surfaces of a filter is possible. Al signal is remarkably higher in the external zone. This could either be explained by a lower $AlCl_3$ partial pressure in the gas phase or by a faster depletion of this reactant. As can be seen, Ti is again detected in all internal surfaces, but Al only found in the most external surface.

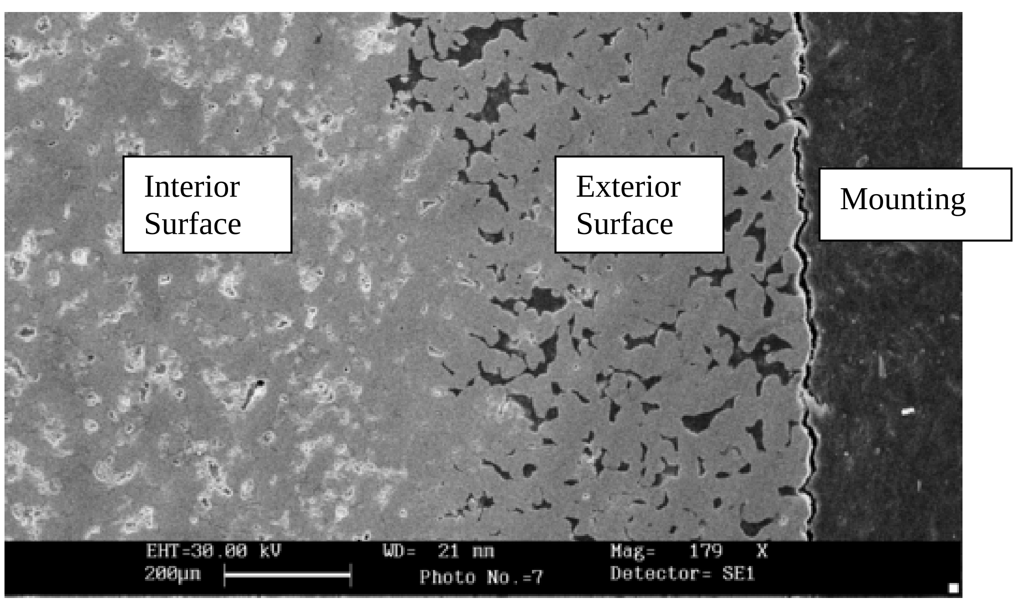

Figure 9. SEM photograph of a nitride coating on a porous SS409 alloy.

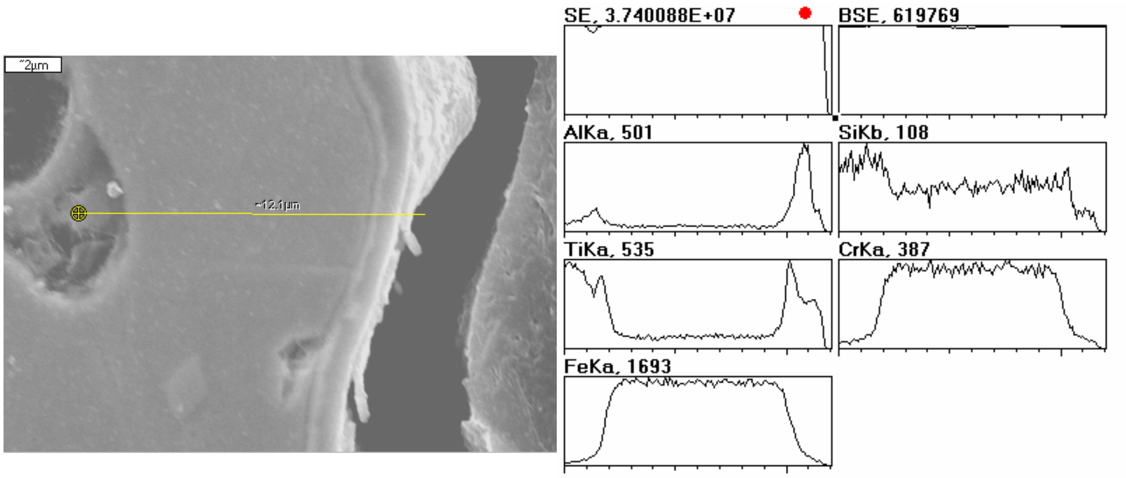

Figure 10. Magnified image of the exterior of the porous specimen and corresponding element profile.

CONCLUSIONS AND FUTURE WORK

1. An SS409 coupon that was coated with nitrides of Ti, Al, and Si showed adherent coatings on the surface;
2. A similarly coated coupon, after exposure to simulated coal gas at 900°C for 300 h, revealed that the coating has cracked during the exposure;
3. An SS409 coupon that was coated with nitrides of Ti and Si with a barrier layer of tungsten in between to improve the adhesion of the coating and to prevent outward diffusion of iron to the surface.
4. A porous coupon was coated with nitrides of Ti and Al and examination of the coupon revealed deposition of Ti at the interior surfaces. A similarly prepared coupon was exposed to simulated coal gas at 370°C for 300 h, and it showed no corrosion.

In the next quarter, we will expose the nitrided alloy steel coupons to simulated coal gas containing H_2S to determine their long term performance.