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## **Diffusion Coatings for Corrosion-Resistant Components in Coal Gasification Systems**

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## 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), and report on the findings of four samples:

1. Analysis of two porous coupons after exposure to the porous metal particulate filter of the coal gasification power plant at 370°C for 2140 hours revealed that corrosion takes place in the bulk of the sample while the most external zone surface survived the test.
2. Coating and characterization of several porous 409 steel coupons after being coated with nitrides of Ti, Al and/or Si showed that adjusting experimental conditions results in thicker coatings in the bulk of the sample.
3. Analysis of coupons exposed to simulated coal gas at 370°C for 300 hours showed that a better corrosion resistance is achieved by improving the coatings in the bulk of the samples.

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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<sub>2</sub>S. 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. Analysis of two porous coupons after exposure to the porous metal particulate filter of the coal gasification power plant at 370°C for 2140 hours revealed that corrosion takes place in the bulk of the sample while the most external zone surface survived the test.
2. Coating and characterization of several porous 409 steel coupons after being coated with nitrides of Ti, Al and/or Si showed that adjusting experimental conditions results in thicker coatings in the bulk of the sample.
3. Analysis of coupons exposed to simulated coal gas at 370°C for 300 h showed that a better corrosion resistance is achieved by improving the coatings in the bulk of the samples.

## 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 situations 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 409 alloy steel plates showed significant resistance in a H<sub>2</sub>S (2%v/v) containing gas stream at 370°C while sulfidation attack occurred at 900°C. We showed that the challenge is to deposit these protective coatings on the surface and bulk of the porous metal filters. We adjusted our deposition process to achieve this goal. Table 1 summarizes coating and substrate composition of the tested specimens.

**Table 1. Coatings Description**

<b>Run</b>	<b>Material</b>	<b>Coatings / substrate</b>
62	SS316	(Ti,Ta)N
88	SS409	CrAl(ox)
93	SS409	(Ti,Si)N / (Ti,Al)N
102	SS409	(Ti,Al,Si)N
104	SS409	(Ti,Al)N / Nb

## ANALYSIS OF TWO POROUS COUPONS AFTER EXPOSURE TO THE GASIFIER GAS STREAM

Porous coupons from runs 62 and 88 were exposed at 370°C for 2140 h at the Wabash River Gasifier plant. After exposure, we could not observe internal porous structure of the sample from run 62, due to the growth of sulphide scales in the interior of the sample (Figure 1). Table 2 shows results of EDX measurements carried out at the marked points in the micrograph, which show high S contents in many areas, and we observed the presence of sulfide islands. The presence of neither Ti nor Ta was detected.

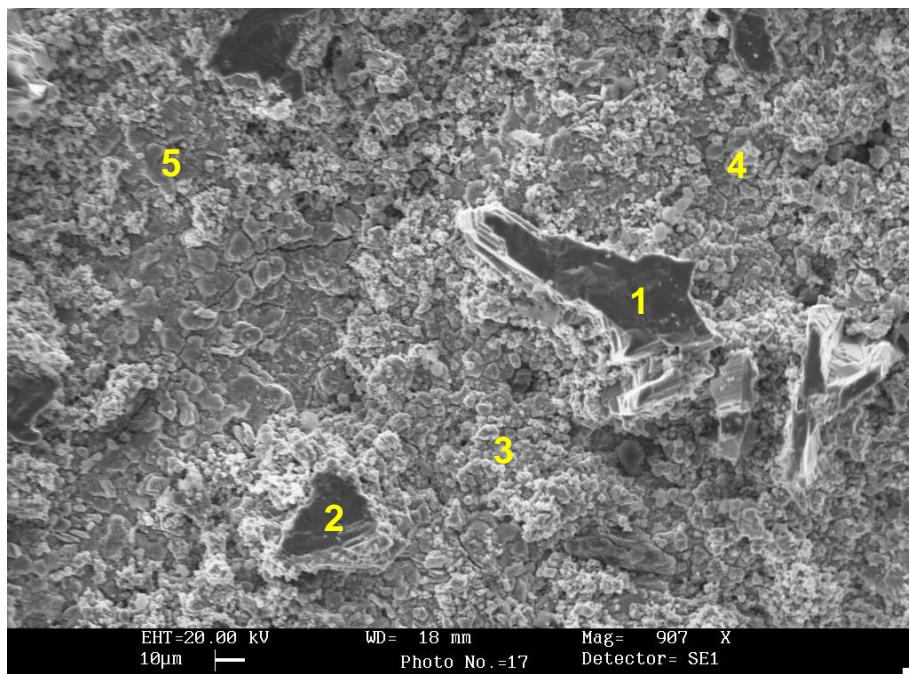


Figure 1. SEM of the top of sample from Run 62.

Table 2. EDX Analyses at Points Marked in Figure 2

Point	Atom% Si	Atom% S	Atom% Fe	Atom% Ni
1	-	45.5	14.6	39.5
2	-	45.8	23.2	30.7
3	-	31.3	37.1	30.8
4	-	22.9	38.7	37.3
5	6.47	33.2	34.0	26.4

A cross section of the sample, after cutting, mounting and polishing, is shown in Figure 2. The insets in the micrograph are EDX mapping for S, Cr, Fe, Ni. As can be seen, Cr and S maps are complementary, Fe is detected in all zones, and Ni is especially concentrated at the surface. This elemental distribution confirms that the scales formed after exposure are mainly Ni and Fe sulphides. This observation indicates that TiTaN-coated 316 alloy steel did not survive the corrosion test. Because Ni is attacked in sulphidizing atmospheres, 316 steel is not used for further tests.

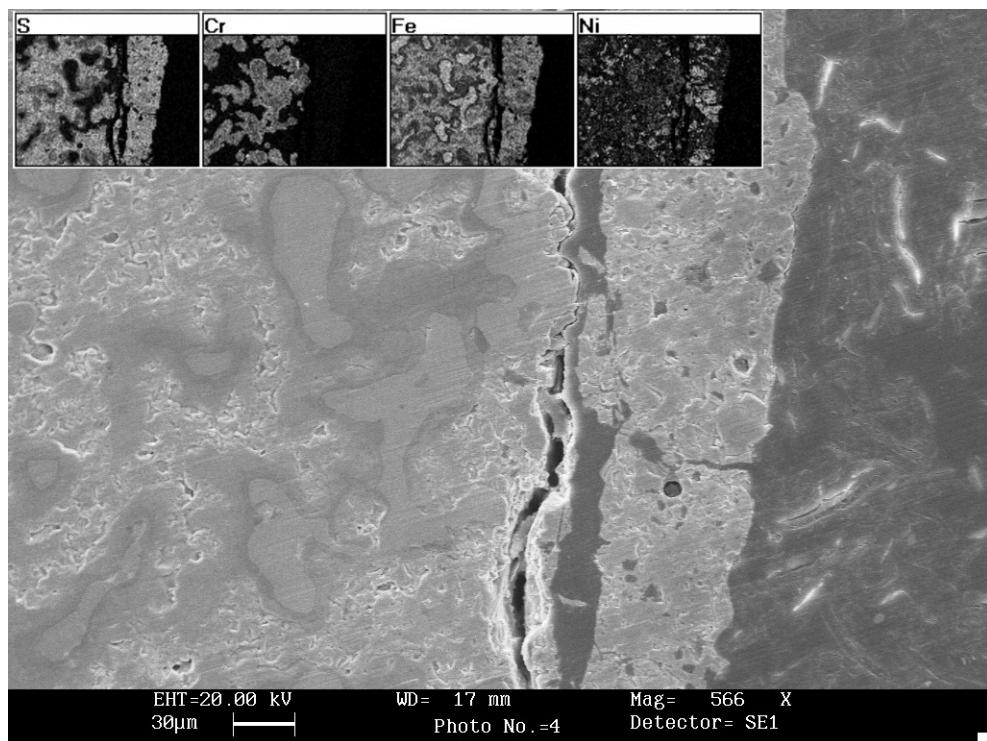


Figure 2. SEM cross-section view and map of EDX analyses for S, Cr, Fe and Ni.

The SEM photograph of the surface of a coupon from run 88 after being exposed to the gasifier plant environment can be seen in Figure 3. The morphology of the sample did not change after exposure; the porous structure generated by sintering alloy steel powder remains unchanged. Results regarding EDX surface analyses done in 3 different zones of the coupon are presented in Table 3. They show a high surface concentration of Al and a low concentration of S. According to these results, an alumina layer was formed that covered the steel and it prevented the formation of iron sulfide.

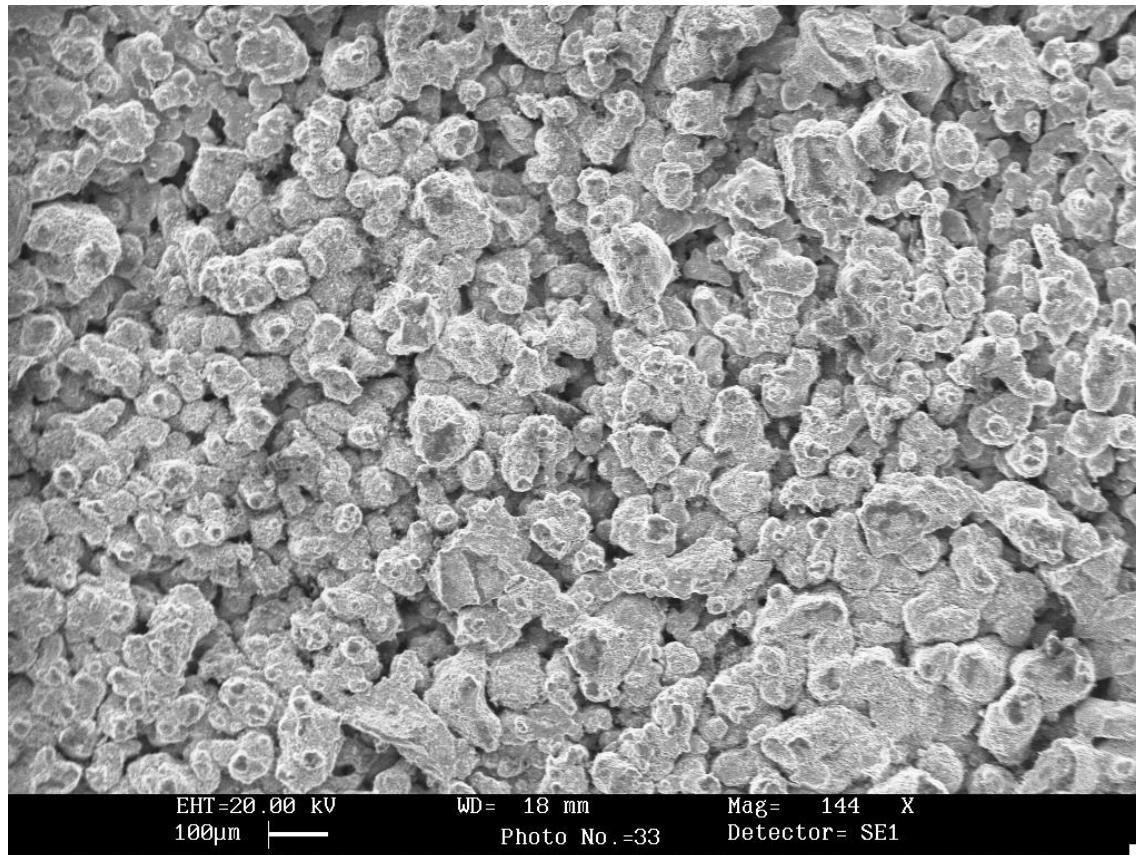


Figure 3. SEM of the surface of the porous coupon from run 88 after exposure in the gasifier.

**Table 3. EDX Results, Coupon from run 88 after Exposure in the Plant**

	Atom% Al	Atom % Si	Atom % S	Atom % Cr	Atom % Fe
zone 1	55.5	3.7	4.3	12.4	24.2
zone 2	58.7	3.5	2.6	4.7	30.7
zone 3	53.9	1.7	0.6	14.4	29.1

Figure 4 shows a cross-section view of the porous sample as observed in the SEM. We observed clearly that the external part of the coupon (approximately the first 100  $\mu\text{m}$ ) is different than in the bulk. To investigate the differences, insets in the same figure show EDX maps for Fe, Cr, Al, S and Ti, in this order. As observed, the external part is rich in Al. But beneath the external area, a solid was found inside the voids of the filter, composed of S and Fe. This observation suggests that an alumina layer was formed in the external portion that was protective against sulfidation, but such protection did not occur in the bulk of the sample. We believe that Al was not deposited in the interior portion of the sample. During coating deposition,  $\text{AlCl}_3(\text{g})$  reacts in contact with the coupon and it is depleted as the gas infiltrates into the bulk of the

sample. As a consequence, Al deposition is more efficient in the external parts of the coupon. In the outer zone, a protective alumina layer can be formed.

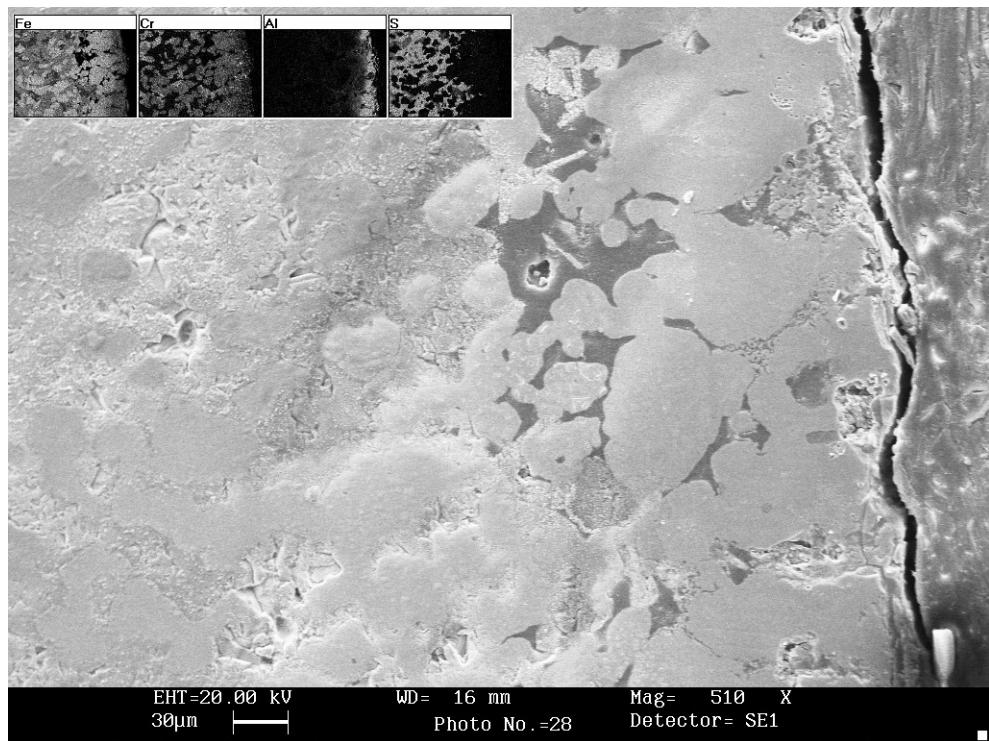


Figure 4. SEM cross section, porous coupon from run 88, and EDX map for Fe, Cr, Al and S.

#### **ANALYSIS OF SS 409 COUPONS COATED WITH NITRIDES OF TITANIUM, ALUMINUM AND/OR SILICON**

In runs 93, 102 and 104, we coated porous SS409 samples with several combinations of Ti-based nitrides and diffusion barrier layers. Figure 5 shows a typical cross-section of the coated samples after intentionally fracturing them. This process results in less overall modification of the coating morphology than cutting, mounting and polishing. The porous structure is clearly observed. An enlarged view of an area corresponding to the bulk of the sample is presented in Figure 6. As observed, the coating is conformal and is typical in a CVD deposition process. A continuous and conformal coating is needed to provide good protection against corrosion to a sample with an irregular shape such as a filter.

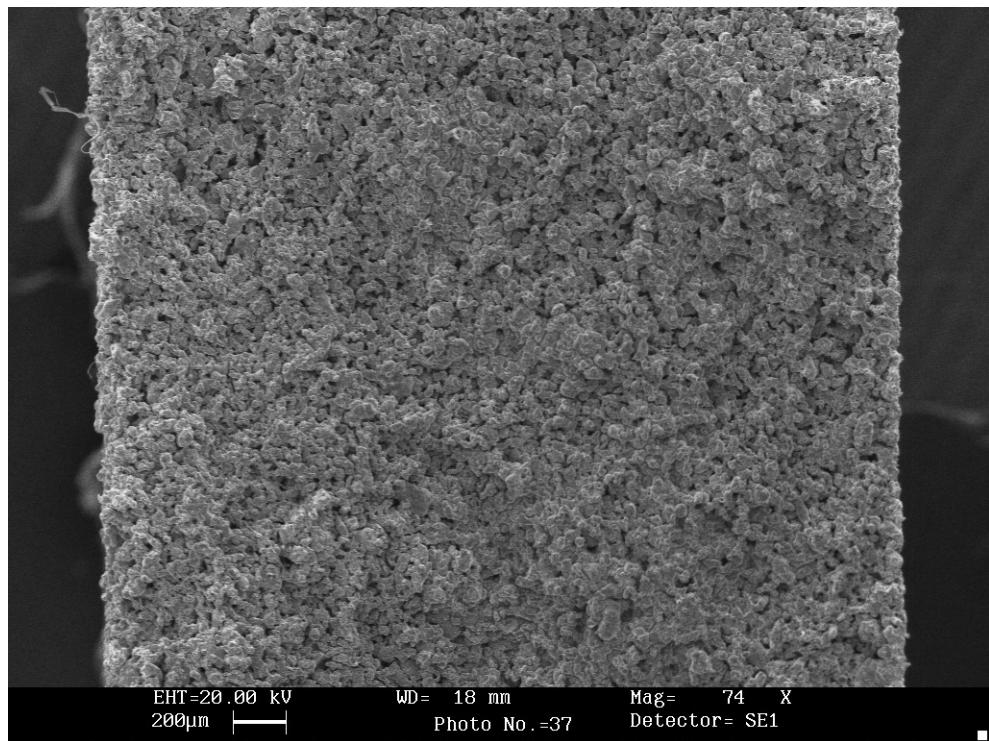


Figure 5. SEM cross-section view of a fractured sample (run 102).

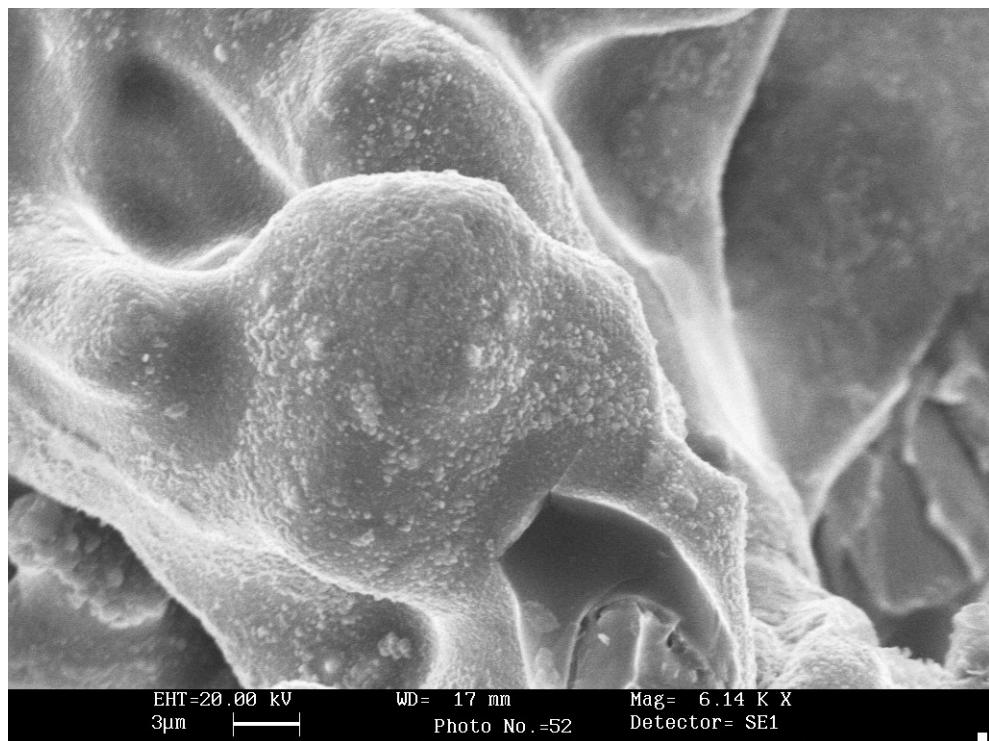


Figure 6. Enlarged view of a zone in Figure 5 (500 microns inside the bulk of the sample).

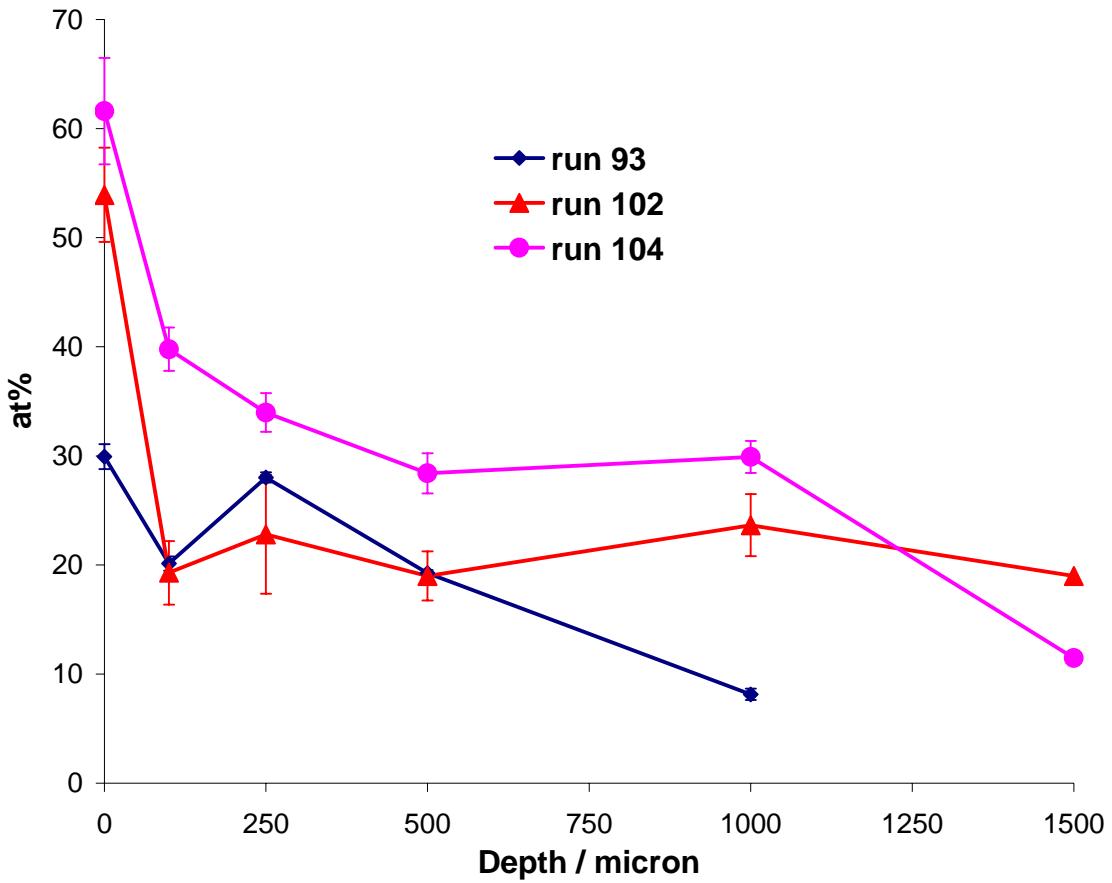


Figure 7. Evolution of Ti concentration with depth in the sample. EDX measurements were performed at different locations of the cross-section exposed after fracturing the sample.

Figure 7 depicts a comparison of Ti depth profile in coupons from runs 93, 102 and 104. In all cases, Ti concentration decreases progressively with depth, which means that the ceramic coating gets thinner as we get inside the coupon. This was an expected feature, because  $\text{TiCl}_4$  used for the deposition is consumed as the gas flows into the sample. The decrease in coating thickness with depth indicates that the bulk of the sample is prone to suffer a corrosive attack. As can be seen in the plot, coating in the bulk of the sample is thicker in runs 102 and 104 than in run 93. As a consequence, it is expected that they suffer a lower corrosion rate in the test.

Figure 8 shows two zones where, after fracturing the sample, a cross-section of the coating in run 104 was exposed. In this area, a clean fracture took place and thus the thin Nb interlayer is clearly observed between the substrate and the TiAlN coating.

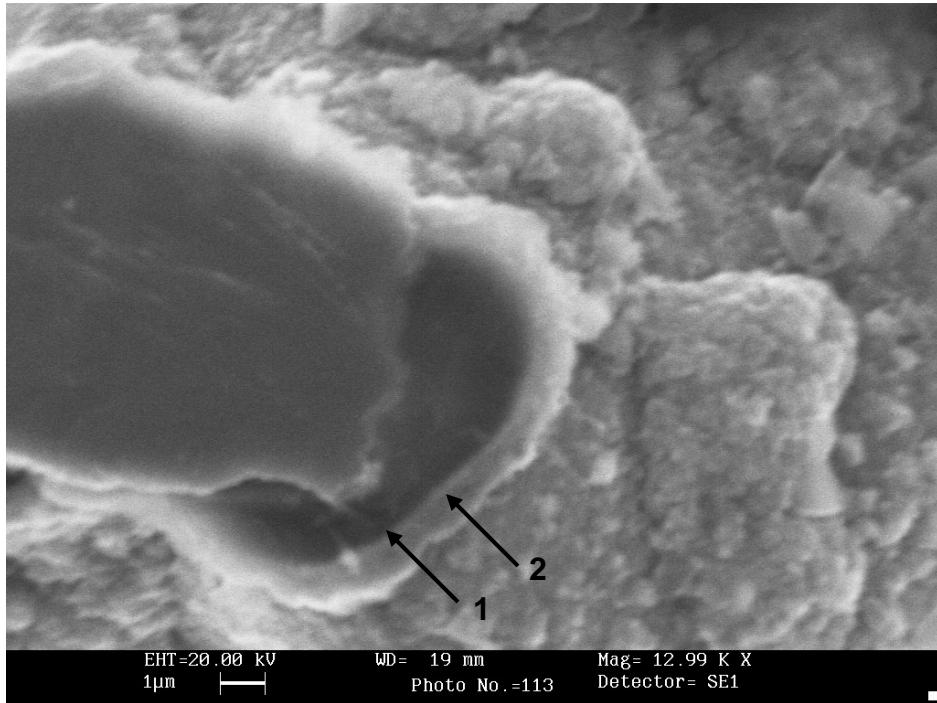


Figure 8. SEM view of a fractured zone (run 104, depth in the sample: 500  $\mu\text{m}$ ). The Nb layer (1) and the ceramic coating (2) are clearly observed.

## ANALYSIS OF COUPONS EXPOSED TO SIMULATED COAL GAS

In previous reports, we described the setup for exposure of coupons to simulated coal gas. Some porous coupons were exposed at 370°C for 300 h. As discussed in a previous report, the sample from run 93 was attacked in the corrosion test. We observed that iron sulfide scales that plugged the pores were formed in its bulk, but in the most external part of the coupon (close to the surface) the coating was protective and the porous structure was intact. As mentioned above, runs 102 and 104 aimed for better corrosion resistance through improvement of the coatings at the bulk of the coupons. Figure 9 shows a picture of samples from runs 102 and 104 before (left) and after (right) the corrosion test. The appearance of the samples suffered only minor changes during the test, but both suffered a weight gain: 5.1 % (run 102) and 7.9 % (run 104), slightly lower than what we found in run 93 (10.3 %). However, a better estimation of the corrosion resistance requires observation of the bulk of the coupons, as will be next discussed.

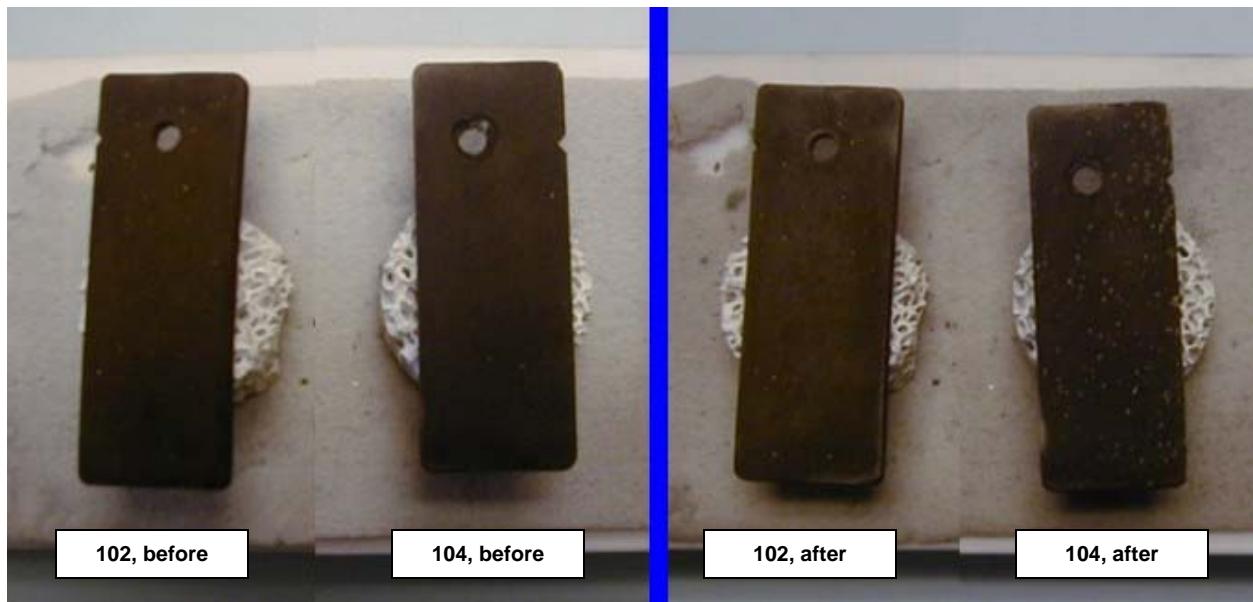


Figure 9. Samples before and after exposure for 300 h at 937°C in simulated gasifier test.

Figures 10, 11 and 12 show cross-section views of fractured coupons from runs 93, 102 and 104 after exposure for 300 h to our low-temperature corrosion test. As can be seen in run 102, we could extend the zone where the coatings provide enough protection versus sulfidation. It seems therefore that protection of the full sample bulk could be achieved with even longer deposition times. We observed that the sample containing a Nb-based interlayer has even higher corrosion resistance in the tested atmosphere. As shown in Figure 12, most of the sample survived the test and sulfide scales were only found in the most internal part of the coupon.

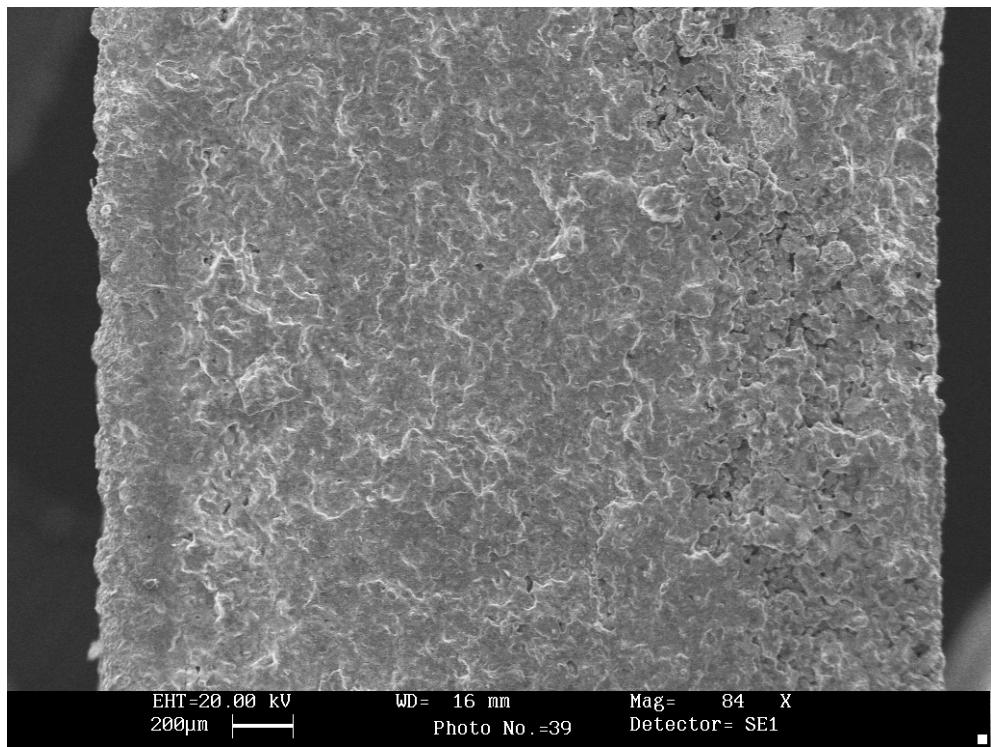


Figure 10. Cross-section of a fractured coupon from run 93 after exposure for 300 h to the low-temperature corrosion test.

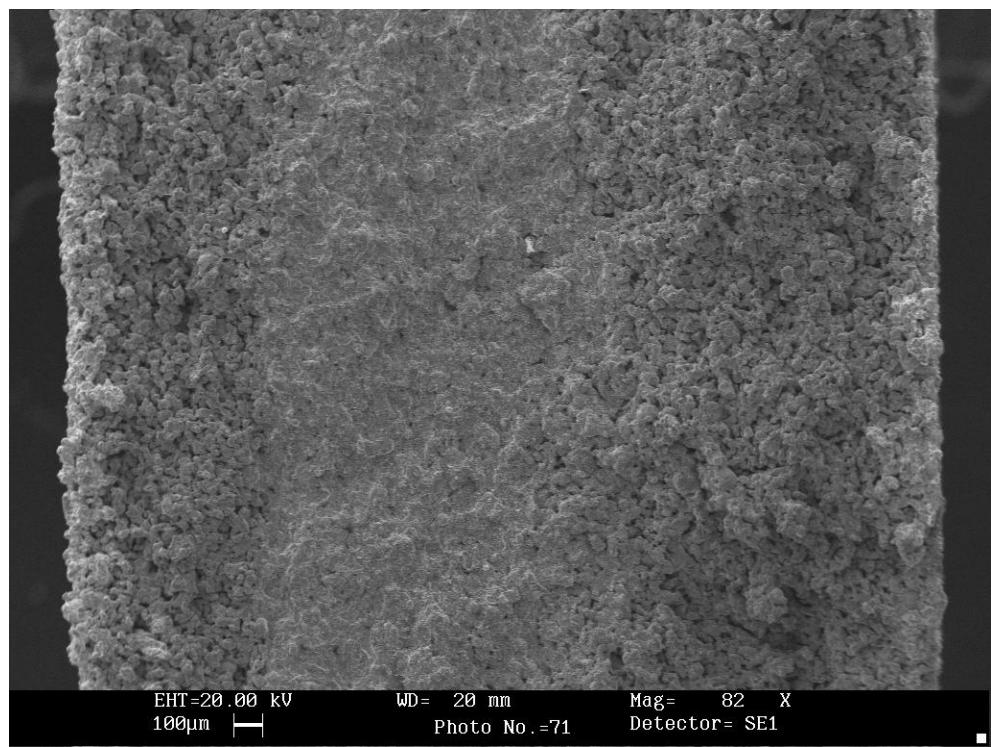


Figure 11. Cross-section of a fractured coupon from run 102 after exposure for 300 h to the low-temperature corrosion test.

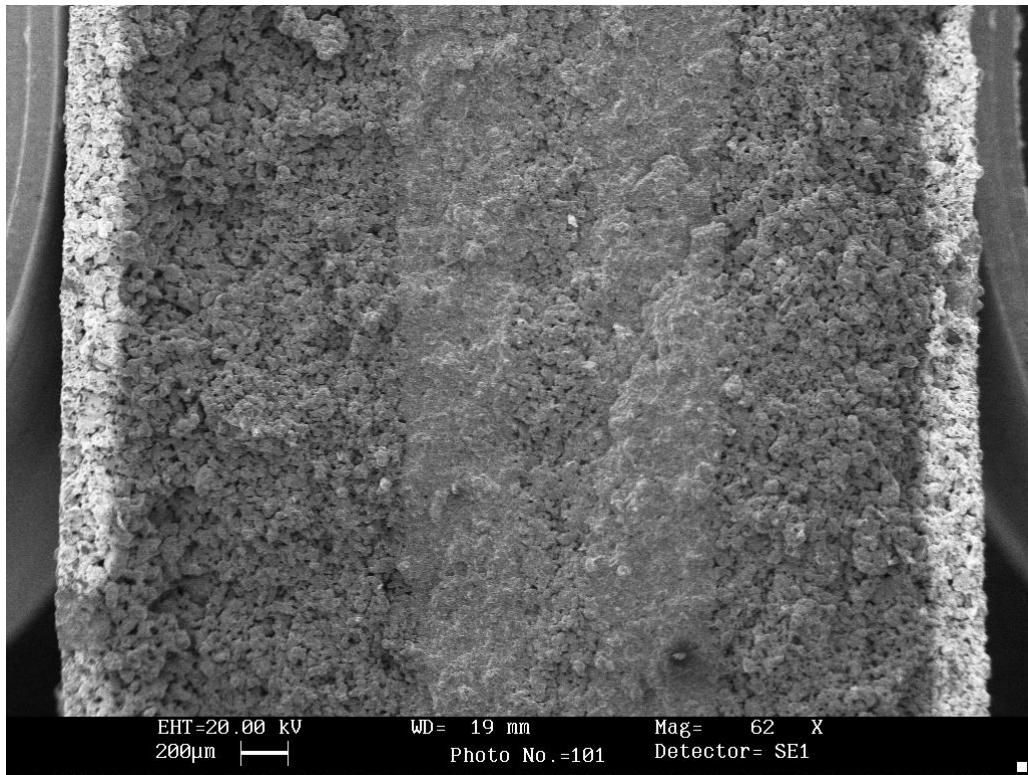


Figure 12. Cross-section of a fractured coupon from run 104 after exposure for 300 h to the low-temperature corrosion test.

## CONCLUSIONS AND FUTURE WORK

- Titanium-based nitride coatings were found to provide protection to 409 alloy steel porous coupons in the simulated corrosion test.
- A diffusion barrier layer made of Nb increases the corrosion resistance of the coatings.
- We have identified the corrosion at the bulk of the porous samples to be the limiting factor for the filter performance.

After these promising results, in the next quarter, future runs are planned in which further improvement will be made in our deposition process in order to extend protection to the whole bulk of the coupons.