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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 reporting period, we conducted several exposure tests with coated and uncoated coupons including a “500-h” test. The first experiment was a 316-h test and was designed to look at the performance of Ti/Ta nitride coatings, which seemed to fare the best in earlier tests. The next experiment was a 112-h test with a range of pure metals and commercially available materials. Its purpose was to help identify those metals that best withstood gasifier environment, and hence should be good ingredients for coatings. Finally, we ran a “500-h” test, which was also our milestone, with coupons coated with Ti/Ta nitride or Cr/Al coatings.

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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 Conoco/ Phillips, 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 Conoco/Phillips' 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 reporting period, we conducted several exposure tests with coated and uncoated coupons including a “500-h” test. The first experiment was a 316-h test and was designed to look at the performance of Ti/Ta nitride coatings, which seemed to fare the best in earlier tests. The next experiment was a 112-h test with a range of pure metals and commercially available materials. Its purpose was to help identify those metals that best withstood gasifier environment, and hence should be good ingredients for sulfur-resistant coatings. Finally, we ran a “500-h” test, which was also our milestone, with coupons coated with Ti/Ta nitride or Cr/Al coatings. The tests showed that (1) Ni-containing alloys as well as high carbon steels cannot be coated effectively with Cr, and (2) that, in some cases, our coating procedure resulted in non-uniform coatings, and needs further refinement.

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 Conoco/Phillips, 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 Conoco/Phillips' 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

We conducted three tests with coated and uncoated coupons as well as tie rods that were received from WREL. The tests were designed to expose samples to a simulated gasifier environment at 900°C. The gas composition was set at 30.8% H_2, 46.7% CO, 20.8% CO_2, 1.7% H_2S and balance (20%) steam. The gas mixture was generated by blending steam with (1) a gas mixture of CO, CO_2, and H_2 and (2) a gas mixture of H_2S and H_2 in appropriate quantities. The total gas flow was set at 120 standard cm^3 per min (sccm).

Exposure to Simulated Coal Gas: Test 4

The samples used in Test 4 and the results of exposure are listed in Table 1. Several samples were coated with Ti/Ta nitride coatings in deposition Runs 51 and 52. We also included samples of conical ferrules (316 steel) used during the coating procedure as they too got coated. In both runs, several coupons were suspended in the fluidized bed simultaneously. Figure 1 shows the picture of the coated samples before they were exposed to simulated gasifier conditions at 900°C. The test was conducted for 316 h, after which the reactive gases were turned off and the furnace cooled to retrieve the samples for examination. Figure 2 is a photograph of the samples after exposure.

In each of the two coating runs used to prepare the samples, between four and six coupons were simultaneously suspended into the fluidized bed. We suspect that this procedure led to inhomogeneous coatings. The inhomogeneity was visible even before exposure to reactive gases. It is instructive to note that the areas that show a high degree of nitride coating (gold color) are also the areas most resistant to corrosion.

Table 1

Ti/Ta NITRIDE COATED SAMPLES TESTED AND THE RESULTS

TEST 4 (Jan 3, 2005)

Sample No.	Material	Coating Run	Appearance
1	HR160	51	No visible degradation
2	I800	51	Pools of molten product
3	SS410	51	Part of the surface is corroded; rest of the surface is normal
4	I625	51	No apparent degradation
5	I82	51	Badly corroded; beads of molten product
6	SS405	52	Part of the surface is corroded; rest of the surface is normal
7	SS316 (porous)	52	thick film of corroded product
8	HR160	52	No apparent degradation
9	Ferrules (SS316)	51	Corroded
10	Ferrules (SS316)	52	No visible degradation

These results indicate that the Ti/Ta nitride coatings are generally satisfactory on alloys such as HR160 and I625 (samples #1, #4, and #8). The results with steels containing Cr (samples #3 and #6) indicate that the coatings are not uniform. As indicated earlier, some of the areas in these samples may not have uniform coatings and these areas may be degraded, while the coated areas were protected. The Ni-containing steel samples (#2, #5, and #7) were badly corroded indicating that the presence of Ni in the alloy may hinder the diffusion of Ti into the sample. However, the results with sample #10 which appeared to have no visible degradation indicate that, under some conditions, the Ni-containing steels may be coated with a protective coating. We will investigate these conditions in the future.

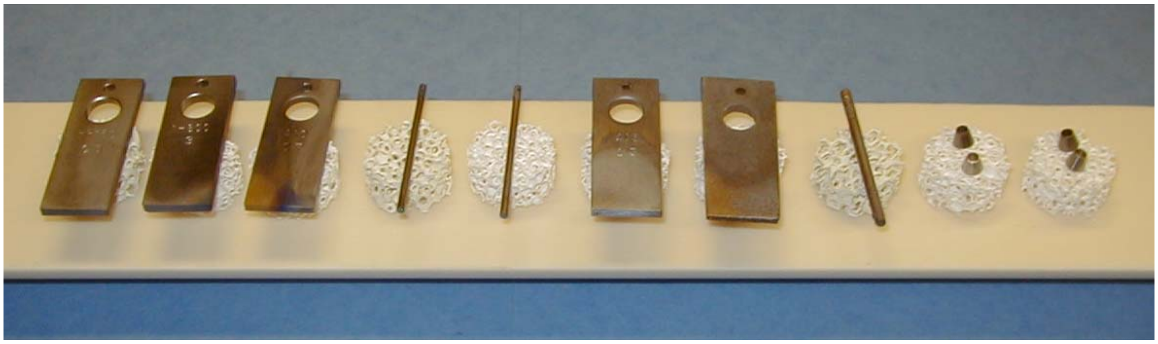

Figure 1. Samples used in Test 4 prior to exposure.

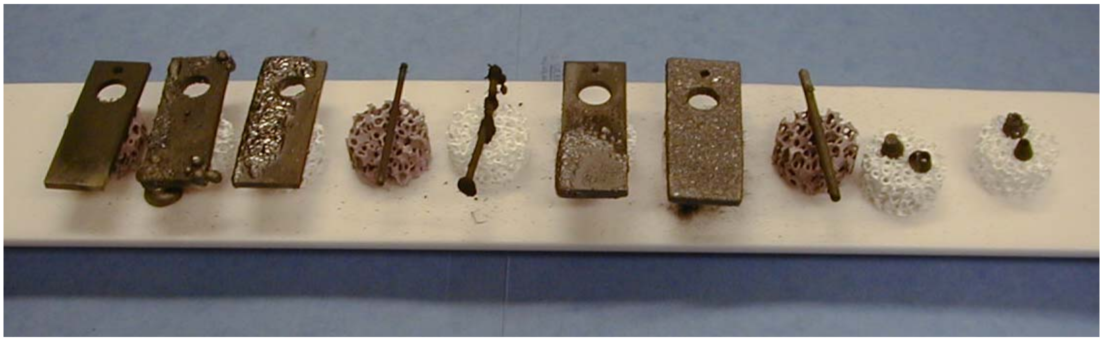

Figure 2. Test 4 samples after 316 h exposure.

Exposure to Simulated Coal Gas: Test 5

In this test, we exposed a range of pure metals and some common alloys to the reactive gases of a coal gasifier. These alloys included Kanthal (a Fe, Cr, Al alloy steel), Ti6Al4V, and commercial steel drill bits coated with TiN and ZrN. The purpose of this test was to identify those metals that were particularly resistant and hence would make good ingredients for the coatings. The samples were exposed to simulated gasifier environment for 112 h, after which they were retrieved for examination and analysis by using X-Ray Fluorescence (XRF). Table 2 lists the samples used in this test, as well as the levels of sulfur detected by XRF following exposure and the phases predicted by thermodynamics. Figures 3 and 4 are photographs showing the state of the samples before and after the exposure. Two observations that are immediately apparent are: (1) the Ta sample had completely disintegrated into flakes, and (2) the Co sample had apparently melted and flowed out through the pores of the alumina support.

Table 2

SAMPLES TESTED AND RESULTS OF TEST 5

Sample No.	Material	%Wt. Change	Weight Gain/SA (g/cm^2)[1]	Wt% S[2]	Predicted Phase[3]
1	Au	-7.06E-04	-3.08E-05	0	Au
2	Ti	6.64E-01	2.01E-02	0	TiO_2
3	Zr	3.51E-01		0	ZrO_2
4	Pt	-1.81E-03	-3.85E-02	0	Pt
5	Ta		Disintegrated into a powder	N.M.	Ta_2O_5
6	Nb	3.13E-01	7.29E-02	0.67	Nb_2O_5
7	Mo	2.37E-02	1.33E-03	12.6	MoS_2
8	W	-1.03E-04	-5.48E-06	0.66	WS_2
9	Cr	2.40E-03	2.99E-03	0.52	Cr_2O_3
10	V	2.75E-02	1.58E-02	0.04	V_2O_3
11	Ti6Al4V	-6.36E-01		N.M.	TiO_2, Al_2O_3
12	Co	1.27E-01	Melted	21.1	CoS
13	Fe	5.83E-01	2.09E-01	13.9	FeS
14	Ni	3.37E-01	1.08E-02	18.6	Ni_3S_2
15	Cu	2.52E-01	3.18E-02		CuS
16	Kanthal	-2.15E-03	-1.70E-02	0.27	Cr_2O_3, Al_2O_3
17	Ti /Steel	2.35E-01	7.04E-03	7.4	FeS
18	Zr /Steel	2.37E-01	-3.08E-05	13.5	FeS

Notes:

1. Based on measured surface area.
2. Measured by X-ray fluorescence analysis of the surface of the sample.
3. Predicted by thermodynamic equilibrium analysis at 900°C for the gas composition used. The equivalent partial pressures of O_2 and S_2 are 3.6 x 10^{-4} and 1.8 x 10^{-15} atm, respectively.

These results are in general agreement with the thermodynamic equilibrium analysis. The noble metals such as Au and Pt did not have a significant weight change as they remain in their metallic state. The highly reactive metals such as Ti, Zr, Cr, and V were converted mainly to their oxides. The small level of sulfur measured with Cr may indicate the formation of a chromium oxysulfide. Thermodynamic data for chromium oxysulfide are not readily available. Similarly, Ta and Nb are mainly converted to their oxides although a small amount of oxysulfides may have formed.

The surface of the base metals such as Co, Fe, Ni, and Mo have been converted mainly to their sulfides as indicated by a significant amount of sulfur measured on the surface. The 0.3 atomic fraction of S found on Co, Ni, and Mo surfaces indicate that the compounds are likely to be of Co_2S, Ni_2S, and Mo_2S, respectively. Again, thermodynamic data for these compounds are not available, so the calculations predicted higher sulfides than found experimentally. The phase diagrams of Co-S and Ni-S predict that a sulfur level of 25 wt% will melt at about 900°C. Although the weight gain observed with Fe sample is higher than those observed with Ni and Co, the measured S level on the surface was relatively low. This anomaly may be due to the formation of an iron oxide layer.

The alloy Kanthal containing Cr and Al had negligibly small weight change and very low sulfur levels indicating that Cr_2O_3 and Al_2O_3 form a protective layer. Similarly, the alloy Ti5Al4V also showed only a small weight change. Hence, our approach to apply coatings containing Cr, Al, and/or Ti is in agreement with the above results. Because the V sample showed very low levels of S, we may include coatings with V in our future experiments.

Exposure to Simulated Coal Gas: Test 6

The objective of this test was to determine the effect of long time (500 h) exposure to steel samples coated with either Ti/Ta nitride or Cr/Al coatings. The test was designed to examine coupons after exposure for about 100 h, and to then continue exposing those that showed good performance for additional 400 h.

The samples used are listed in Table 3. In Test 5, we had observed that the Co sample had melted and flowed down. We wanted to make sure that the sample had not simply fallen off the alumina support during the loading, and so we included it again in this run. This time we ensured that after the samples were loaded in the oven, the Co slug was still on its alumina perch.

Figure 5 shows photographs of these samples before exposure. The inhomogeneity of the coating on samples 5 (SS304, TiTa-N), 7 (SS409/CrAl-Al), 8 (SS409/CrAl-oxAl), and 10 (HR160/TiTa-N) can be seen in the photograph. Figure 6 shows the results after exposure for 122 h. As is evident, the Co sample (Sample #1) was again found to have melted and flowed through the support. The TiN-coated SS409 steel tube (Sample #2) showed evidence of corrosion at the cut ends, but not on the tube sides. The 409 steel coated with Cr-A (Sample #3) showed no signs of corrosion, but the similarly coated sample of 410 steel porous 316 steel, which was also coated with Cr-Al, was badly corroded. The sample of Co, TiN-coated 409 steel tube section and the porous

316 steel were removed, and the remaining samples were reloaded into the oven and exposed for additional 360 h, bringing the total exposure to 482 h.

The marked difference between samples 3 and 4 (SS409 and SS410), both of which were coated in the same run, is remarkable. Sample 3 showed only a few beads that may have resulted from pinhole imperfections in the coating, whereas sample 4 is completely corroded. This difference can be ascribed to the presence of carbon in SS410. Evidently, carbon binds to the Cr and interferes with the formation of a diffusion coating. Similarly, Ni (which is present in 300-series steels) also interferes with our coating procedures.

The HR160 and SS409 alloys coated with either a Cr/Al composition or Ti/Ta nitride suffered minimal degradation. However, only sample 8, which was coated with Cr/Al-oxAl composition showed no degradation after 482 h exposure. All these samples are being analyzed and the results will be reported in the next quarterly report.

The successful completion of this “500-h” test marks the achievement of one of our milestones.

CONCLUSIONS AND FUTURE WORK

Mixed coatings such as Ti/Ta-nitride and Cr/Al-Al(oxidized) seem to be the best. We have observed that in several instances the coating is not homogeneous, and we need to modify our procedure to rectify that problem. It also appears that presence of carbon and Ni in the steel interfere with our coating procedure and in the future we will focus on 409 steel.

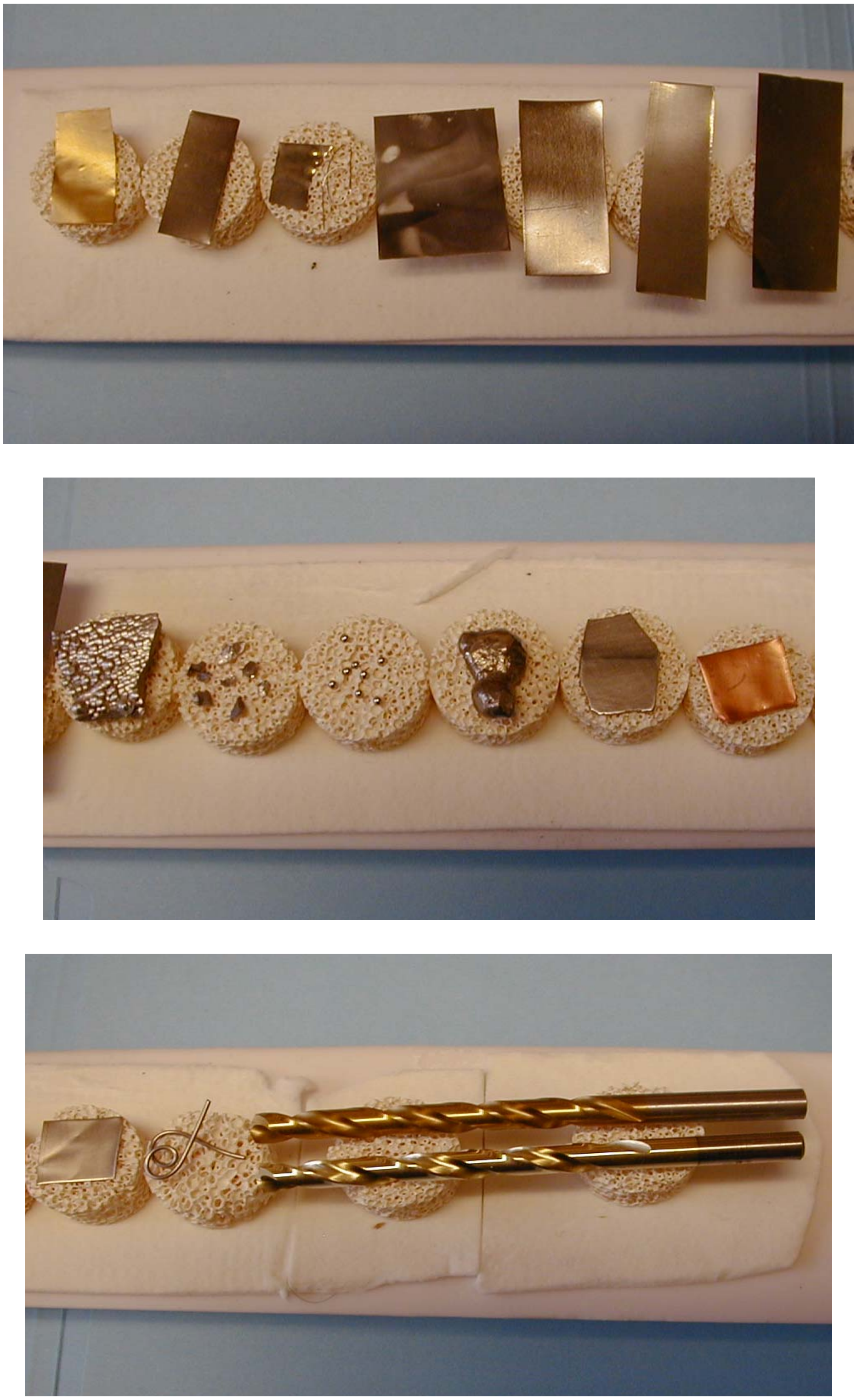

Figure 3. Samples before exposure to gasifier environment in Test 5. See Figure 4 for identification of the samples.

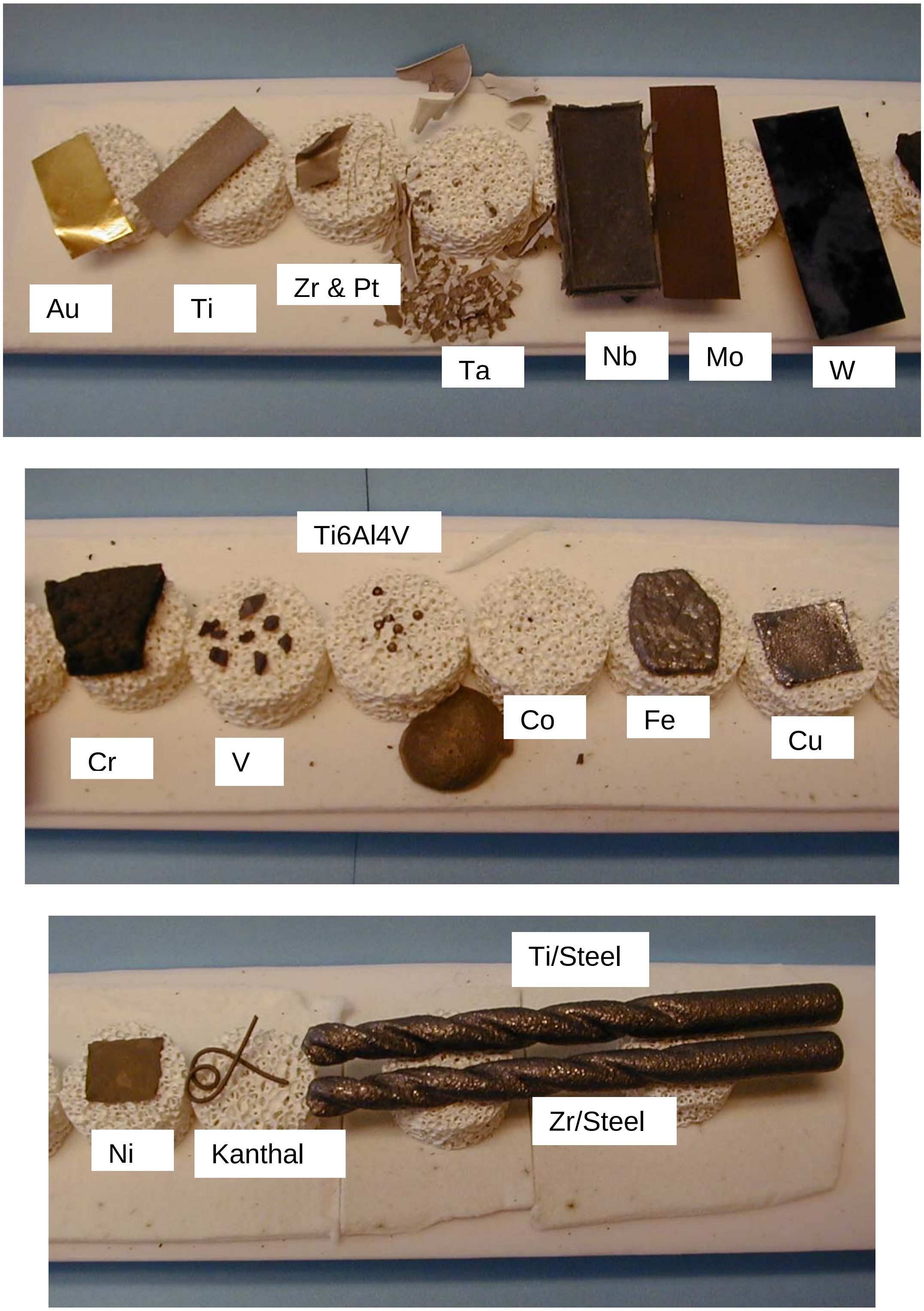
Au
Ti
Zr & Pt
Ta
Nb
Mo
W
Ti6Al4V
Cr
V
Co
Fe
Cu
Ti/Steel
Ni
Kanthal
Zr/Steel

Figure 4.

Table 3

SAMPLES USED IN TEST 6

Sample No.	Material	ID 1	Coating (Run)	Salient Observation
1	Cobalt	lump	none	Melted and flowed
2	SS409	tube	TiN (53)	Corrosion at tube edge
3	SS409	03	Cr-Al (54)	Some beads
4	SS410	03	Cr-Al (54)	Corroded
5	SS304	01	Ti/TaN (56)	In homogeneous coating; corrosion where coating was poor
6	SS409	04	Ti/TaN (56)	Same as #5
7	SS409	07	Cr-Al-Al (57)	Badly corroded
8	SS409	12	Ox. CrAl-Al (59)	No corrosion
9	SS316	Porous	Cr-Al-Al (61)	Badly corroded in 122 h
10	HR160	09	(Ti/Ta)N (60)	Some flakes, otherwise good

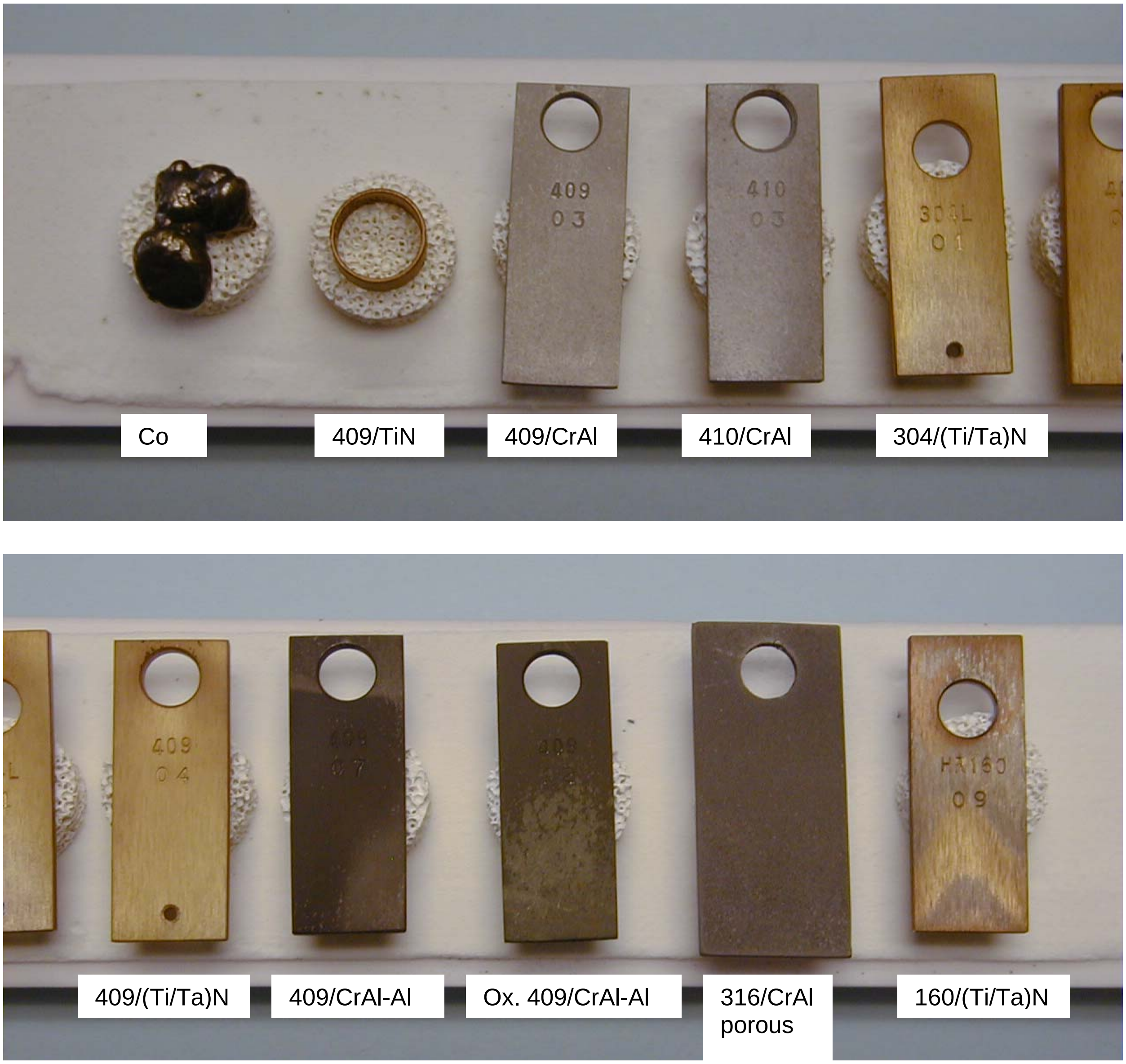

Figure 5. Samples used in Test 6 prior to exposure.

Figure 6. Samples in Test 6 after 100 h exposure. Note specs around the HR160 sample.

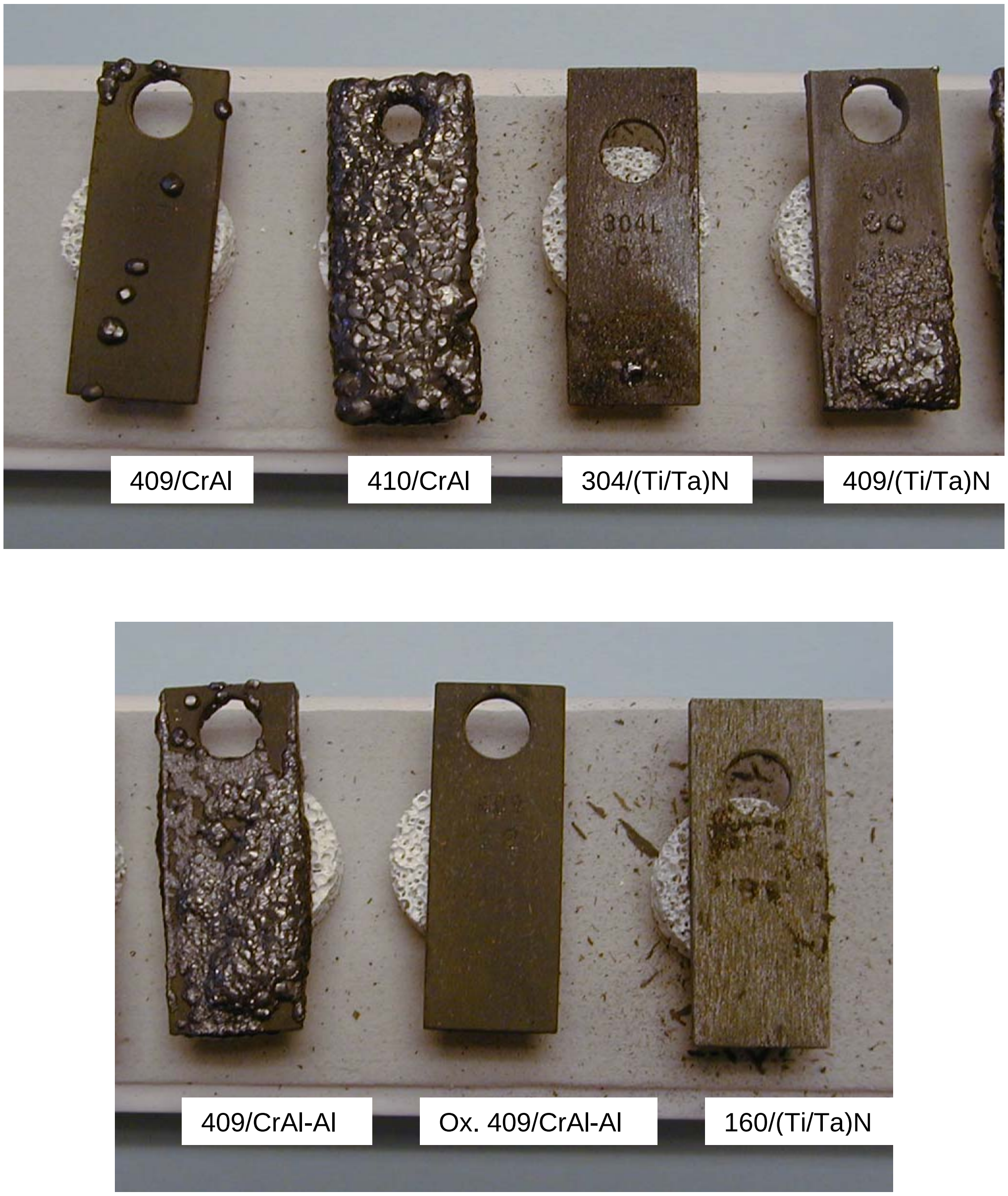

Figure 7. Samples after additional 300 h exposure. Note beads on SS409/CrAl; CrAl coating on SS410 did not survive; Note contrast of 409/CrAl-Al, and Ox.409/CrAl-Al.