

METAL DUSTING BEHAVIOR OF COATINGS

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ABSTRACT

Surface modification by preoxidation and/or by coatings and alternative materials are being examined at ANL to alleviate the metal dusting problem. Oxide coatings have the advantage that they can minimize carbon-producing reactions (by reducing the availability of catalytic surface) and can also act as a barrier to minimize carbon ingress and pitting of the substrate alloy. We have selected in-situ development of oxide scales, pack diffusion of Al or Cr/Si, and thermal spray of FeAl as avenues for further study. Preliminary tests showed virtually no carbon in pre-oxidized layers of Al-, Cr-, and Si-enriched layers that were subjected to metal dusting environments.

INTRODUCTION

Metal dusting is a catastrophic corrosion phenomenon that leads to the disintegration of structural metals and alloys into dust composed of fine particles of the metal/alloy, carbides, and carbon (Natesan et al. 2002). Metal dusting occurs at intermediate temperatures of 400-800°C, but this type of corrosion is possible at any temperature at which the carbon activity (a_C) in the gas phase is $\gg 1$. There are two major issues of importance in metal dusting. First is formation of carbon and subsequent deposition of carbon on metallic materials. Second is the initiation of metal dusting degradation of the alloy. The first is influenced by a_C in the gas mixture and the availability of the catalytic surface for carbon-producing reactions to proceed. There may be a threshold in a_C ($\gg 1$) for carbon deposition. Metal dusting of the alloy in the reformer environments is determined by a competition between the oxide scale development and access of the virgin metal surface to the carbon deposit. The presence of an oxide scale may not prevent metal dusting but can delay its initiation, thereby slowing the overall attack.

Coatings can minimize gas phase reactions by lack of availability of metal surfaces for catalysis. This, in turn, can minimize or eliminate coking and carbon deposition. Furthermore, coatings can act as barriers to carbon ingress into the substrate alloy since carbon diffusion through oxide scales is generally orders of magnitude lower than through the alloys. Among the oxides as coatings, the potential candidates are chromia, alumina, and silica. Iron oxide may not be a viable candidate unless the Fe-oxide to Fe-carbide reaction is slow enough that oxide can be maintained for the desired service life. The present paper discusses the application of oxide scales developed in-situ on metallic surfaces or oxide coatings applied by external methods to mitigate metal dusting degradation.

EXPERIMENTAL PROGRAM

Three approaches are being examined for the development of oxide surface layers for evaluation in metal dusting environments. The first approach is to develop the oxide layer on the structural alloys by a preoxidation treatment. In this case, the specimens are exposed to either

air or a low- pO_2 (established by H_2/H_2O or CO/CO_2 gas mixtures) environment at temperatures between 750 and 900°C. Generally, depending on the Cr content of the alloy and pO_2 in the exposure environment, the alloys develop (Fe,Cr) or (Ni,Cr) spinels or “pure” Cr oxide on the surface. Regulating the exposure time and temperature can control the thickness of the oxide layer.

The second approach involves a pack diffusion process in which the alloy surface is enriched in oxide-forming elements such as Al, Cr, and/or Si. Subsequently, the surface-enriched alloy is oxidized in air to develop the oxide scale of choice. Pack diffusion is widely used to confer oxidation resistance on ferrous alloys. Pack diffusion processes include aluminizing, chromizing, and siliconizing. Specimens/components are packed in metal powders in sealed heat-resistant retorts and heated inside a furnace to precisely controlled temperature-time profiles. In the aluminizing process, a source of Al reacts with a chemical activator on heating to form a gaseous compound (e.g., pure Al with NaF to form AlF). This gas is the transfer medium that carries aluminum to the component surface. The gas decomposes at the substrate surface, depositing Al and releasing the halogen activator. The halogen activator returns to the pack and reacts with the Al again. Thus, the transfer process continues until all of the aluminum in the pack is used or until the process is stopped. The coating forms at temperatures ranging from 700 to 1100°C over a period of several hours.

The third is thermal spray approach in which the surface treatment involves energizing the surface of the workpiece in order for adhesion to take place. Conventional surface finishing methods involve heating an entire component, but the thermal spray technique usually adds energy and material into the surface, keeping the bulk of the object relatively cool and unchanged. This allows surface properties to be modified with minimal effect on the structure and properties of the underlying material. Coatings can be sprayed from rod or wire stock or from powdered materials. The material (e.g., wire) is fed into a flame where it is melted. The molten stock is then stripped from the end of the wire and atomized by a high velocity stream of compressed air or other gas, which propels the material onto a prepared substrate or workpiece. The basic steps involved in any thermal coating process are substrate preparation, masking and fixturing, coating, finishing, inspection, and stripping (if necessary). Roughening is also necessary for most of the thermal spray processes to ensure adequate bonding of the coating to the substrate. Specimens with a thermal spray coating of FeAl are included for evaluation in metal dusting environments.

Materials for In-situ Scale Development

The test materials for in-situ scale development include a number of Fe- and Ni-base alloys, predominantly those commercially available. In the present paper discussions pertain only to Fe-base alloys whose nominal compositions are listed in Table 1. The specimens were preoxidized by exposing them in an H_2 -2 vol.% H_2O gas mixture at 900°C for 200 h. The gas mixture established a pO_2 of 2.1×10^{-20} atm at 900°C.

Pack-Diffusion Coatings

Specimens with Al (termed “aluminizing”) and Cr,Si (termed “ChromePlexing”) enrichment were obtained from Alon Surfaces for evaluation in metal dusting environments. Substrates selected for Al enrichment included three Fe-base alloys (T22, 800, and 321 stainless steel) and three Ni-base alloys (601, 625, and HR160). Substrates selected for ChromePlexing included only the three Fe-base alloys since it was not feasible to enrich Cr/Si on Ni-base alloys.

Table 1 Nominal chemical compositions (in wt.%) of alloys selected for the experimental program.

Material	C	Cr	Ni	Mn	Si	Mo	Al	Fe	Other
T22	0.20	2.3	–	0.6	0.5	1.0	-	Bal	–
T91	0.08	8.6	0.1	0.5	0.4	1.0	-	Bal	N 0.05, Nb 0.07, V 0.2
153MA	0.05	18.4	9.5	0.6	1.4	0.2	-	Bal	N 0.15, Ce 0.04
253MA	0.09	20.9	10.9	0.6	1.6	0.3	-	Bal	N 0.19, Ce 0.04
353MA	0.05	24.4	34.7	1.4	1.3	0.1	-	Bal	N 0.18, V 0.06
321L	0.02	17.4	9.3	1.8	0.5	-	-	Bal	N 0.02, Ti 0.3
310	0.03	25.5	19.5	1.7	0.7	-	-	Bal	-
800	0.08	20.1	31.7	1.0	0.2	0.3	0.4	Bal	Ti 0.31
803	0.08	25.6	36.6	0.9	0.7	0.2	0.5	34.6	Ti 0.6
38815	0.01	13.9	15.3	0.6	5.8	1.0	0.13	Bal	-
MA956	-	20.0	-	-	-	-	4.5	Bal	Ti 0.5, Y ₂ O ₃ 0.6
321	0.04	17.3	10.3	1.2	0.4	-	-	Bal	Ti 0.4, N 0.01
APMT	0.04	21.7	-	0.1	0.6	2.8	4.9	Bal	-
4C54	0.17	26.7	0.3	0.7	0.5	-	-	Bal	N 0.19

Figures 1-3 show scanning electron microscopy (SEM) micrographs of cross sections of alonized Fe-base alloys (T22, 321 stainless steel, and Alloy 800) along with elemental profiles as a function of coating thickness obtained by energy dispersive X-ray spectroscopy (EDX). Aluminum concentration at the surface of all three alloys in the as-coated condition was in a range of 35-45 wt.%. The depth profile in T22 shows a gradual decrease in Al concentration to a depth of $\approx 300 \mu\text{m}$. The aluminum concentration profile for 321 stainless steel (which contains $\approx 10.3 \text{ wt}\% \text{ Ni}$) is less gradual, but the depth of the Al-enriched layer is $\approx 200 \mu\text{m}$. In Alloy 800 (which contains $31.7 \text{ wt}\% \text{ Ni}$) a layer of Ni_3Al intermetallic forms on the interface between the Al enriched layer and the alloy substrate. This layer seems to slow the diffusion of Al into the substrate. As a result, the Al concentration profile is much flatter (28-36 wt.% Al) over a distance of $140 \mu\text{m}$, after which there is a sharp drop in Al concentration.

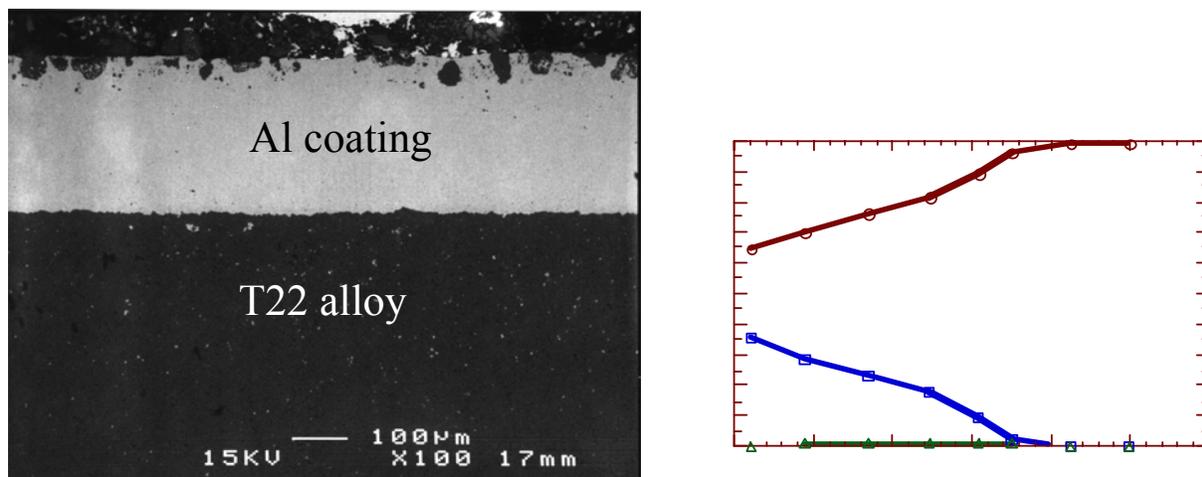


Figure 1 SEM photomicrograph of cross section of alonized T22 steel and EDX elemental depth profiles of Al and Fe for the specimen in the as-coated condition.

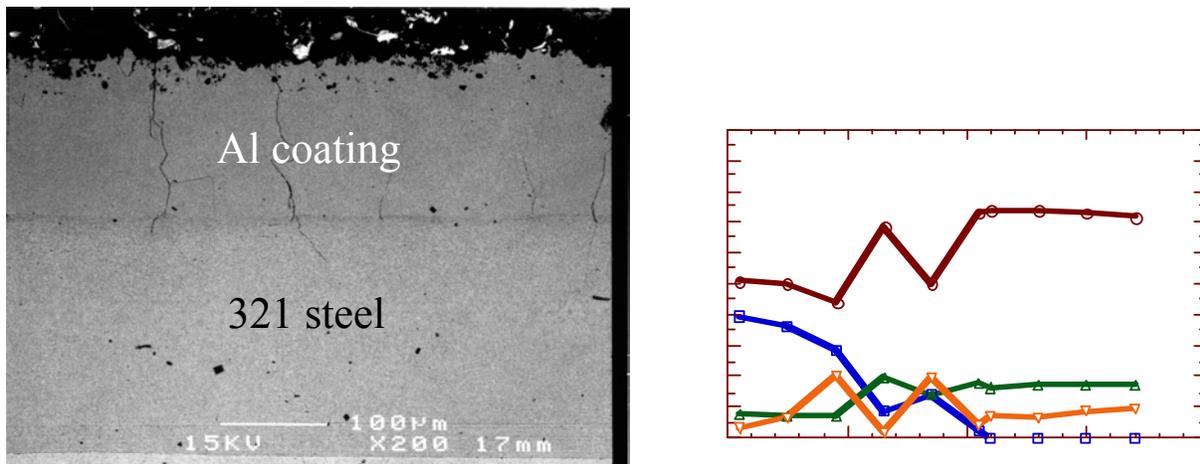


Figure 2 SEM photomicrograph of cross section of alonized 321 stainless steel and EDX elemental depth profiles of Al, Fe, Cr, and Ni for the specimen in the as-coated condition.

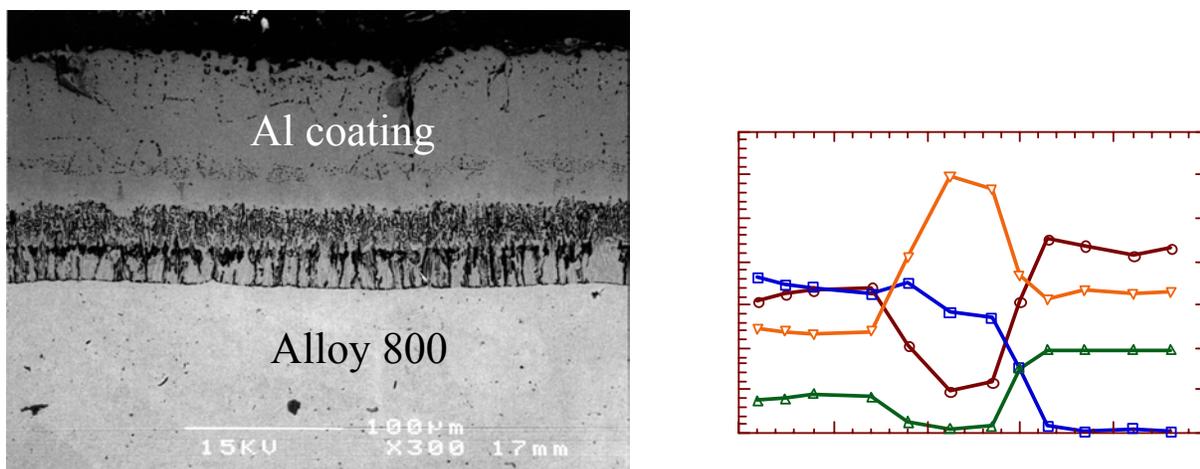


Figure 3 SEM photomicrograph of cross section of alonized Alloy 800 and EDX elemental depth profiles of Al, Fe, Cr, and Ni for the specimen in the as-coated condition.

Figures 4-6 show SEM photomicrographs of cross sections of ChromePlexed Fe-base alloys (T22, 321 stainless steel, and Alloy 800) along with elemental profiles as a function of coating thickness obtained by EDX analysis. Chromium and silicon concentrations at the surface of T22 steel were 12 and 2.5 wt.%, respectively. The elemental profiles shows that these concentrations remain fairly constant up to a depth of $\approx 250 \mu\text{m}$. In the case of 321 stainless steel the Cr and Si concentrations were $\approx 20-25$ and ≈ 5 wt.%, respectively, to a depth of $250 \mu\text{m}$. The Cr concentration in Alloy 800 was in the range of 20-30 wt.%, while the Si content was similar to that of 321 stainless steel.

Specimens with pack-diffusion coatings were oxidized in air for 200 h at 900°C to develop the oxide scales.

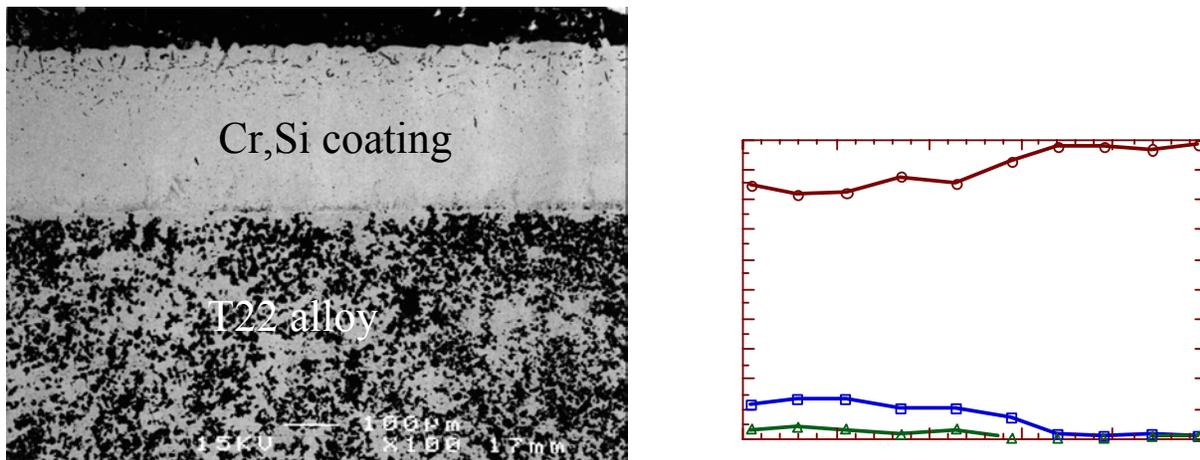


Figure 4 SEM photomicrograph of cross section of ChromePlexed T22 steel and EDX elemental depth profiles of Si, Fe, and Cr for the specimen in the as-coated condition.

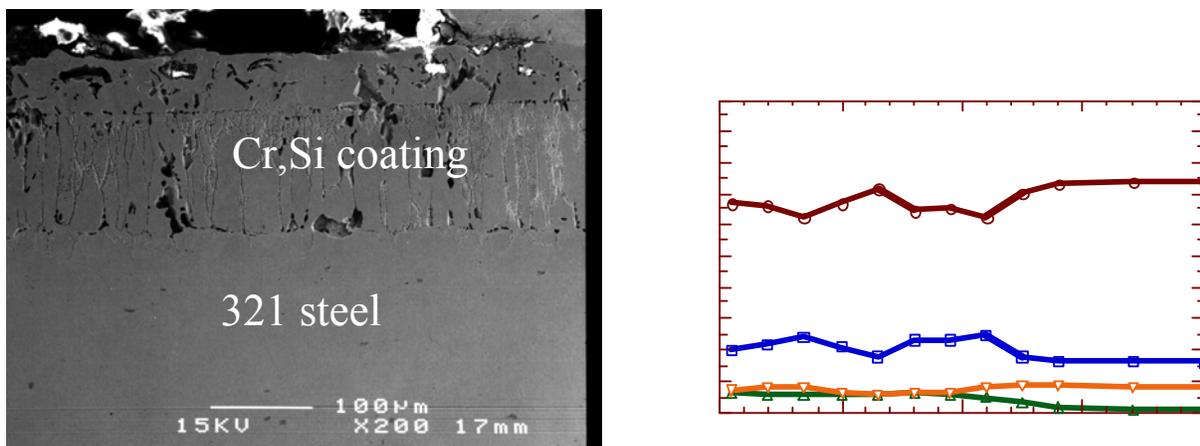


Figure 5 SEM photomicrograph of cross section of ChromePlexed 321 stainless steel and EDX elemental depth profiles of Si, Fe, Cr, and Ni for the specimen in the as-coated condition.

Metal Dusting Exposures

The metal dusting exposures of preoxidized Fe-base alloy specimens and oxidized pack-diffusion coated specimens were conducted in test systems that were described in another paper in this proceedings. The preoxidized Fe-base alloy specimens were exposed for 311 h at 593°C in a gas mixture with a composition (in vol.%): 66.2 H₂, 23 CO, 7.1 CO₂, 1.4 CH₄, and 2.3 H₂O. The carbon activity established by the gas mixture [based on the reaction: CO(g) + H₂(g) = C + H₂O(g)] at 593°C is 33. The oxidized pack-diffusion coatings were exposed for 142 h at 593°C to a gas mixture of composition (in vol.%): 52 H₂, 18 CO, 5.6 CO₂, 1.1 CH₄, and 23 H₂O. This gas mixture simulates the effluent of a H₂ reformer, and the carbon activity (based on the same reaction as above) established by this gas mixture at 593°C is 2.0.

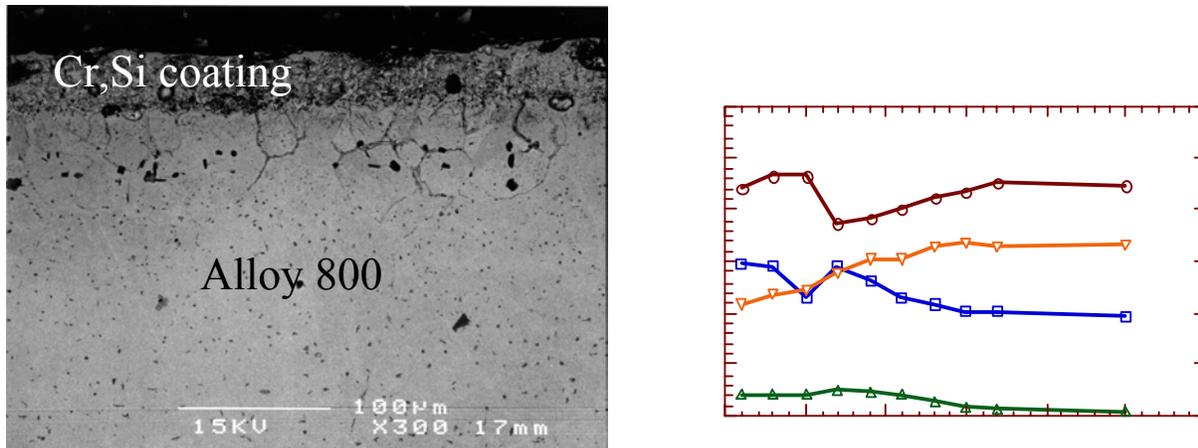


Figure 6 SEM photomicrograph of cross section of ChromePlexed Alloy 800 and EDX elemental depth profiles of Si, Fe, Cr, and Ni for the specimen in the as-coated condition.

TEST RESULTS AND DISCUSSION

Specimens with In-situ Oxide Scales

Weight changes were determined for the preoxidized Fe-base alloy specimens after exposure in the metal dusting environment for 311 h at 593°C. The microstructure of each specimen was examined with a JOEL-6400 scanning electron microscope. The samples were electrolytically etched in 10% acetic acid solution at 10 V for 30 s. Raman spectra were obtained with 60 mW of 476-nm radiation from a Kr-ion laser. The incident beam impinged on the specimen at a $\approx 45^\circ$ angle from the normal. Scattered light was collected with a $f/1.4$ lens and analyzed with a triple Jobin-Yvon grating spectrometer and a CCD detector. All of our spectra were acquired for 300 s at room temperature.

Table 2 shows the weight change data for specimens tested in the metal dusting environment. A comparison of the data on these specimens with earlier-developed information on specimens without preoxidation showed that preoxidation in the H_2 - H_2O environment had no significant benefit from the standpoint of either carbon deposition (indicating no reduction in catalytic activity) or pitting/metal dusting attack.

The raman spectroscopy is an excellent tool to study the phases in thin oxide layers. Possible phases such as Cr_2O_3 , $FeCr_2O_4$, and Fe_3O_4 spinels in the oxide scales have been studied by Raman scattering (Thibeau et al. 1978; Farrow et al. 1980; Thierry et al. 1988; Rensch et al. 1996;). Major Raman bands for Cr_2O_3 and Fe_3O_4 spinel are at 550 cm^{-1} and 670 cm^{-1} , respectively. In this work, we used Raman spectroscopy to study the phase composition of oxide scales and the relationship between phase composition and metal dusting.

For example, the Raman spectra showed that the ratios of the intensity of the 550 cm^{-1} band (Cr_2O_3) over the 684 cm^{-1} band (Fe,Cr spinel) for pre-oxidized specimens are less than those without the pre-treatment (see Fig. 7). High spinel content in oxide scales is not good to resist metal dusting corrosion. The oxygen pressure in our preoxidation step may be too high to

oxidize

Table 2 Weight loss data for preoxidized* alloys after exposure at 593°C for 311 h in a gas mixture of composition (in vol.%) 66.2% H₂-7.1% CO₂-23% CO-1.4% CH₄-2.3% H₂O.

Alloys	Mass loss (mg/cm ² ·h)	Visual examination
T22	0.7	Heavy carbon deposition
T91	0.032	Pits, carbon deposition
153MA	5.3x10 ⁻³	Pits
253MA	4.3x10 ⁻³	Dark spots
321L	~0	Pits
310	~0	Light carbon deposition
800	~0	Pits
803	~0	Light carbon deposition
38815	~0	Clean surface
MA956	~0	Dark surface
321	9.3x10 ⁻⁴	Pits
APMT	~0	Dark surface
4C54	~0	Dark surface

* Specimens were pre-oxidized in a H₂O/H₂ atmosphere at 900°C for 200 h.

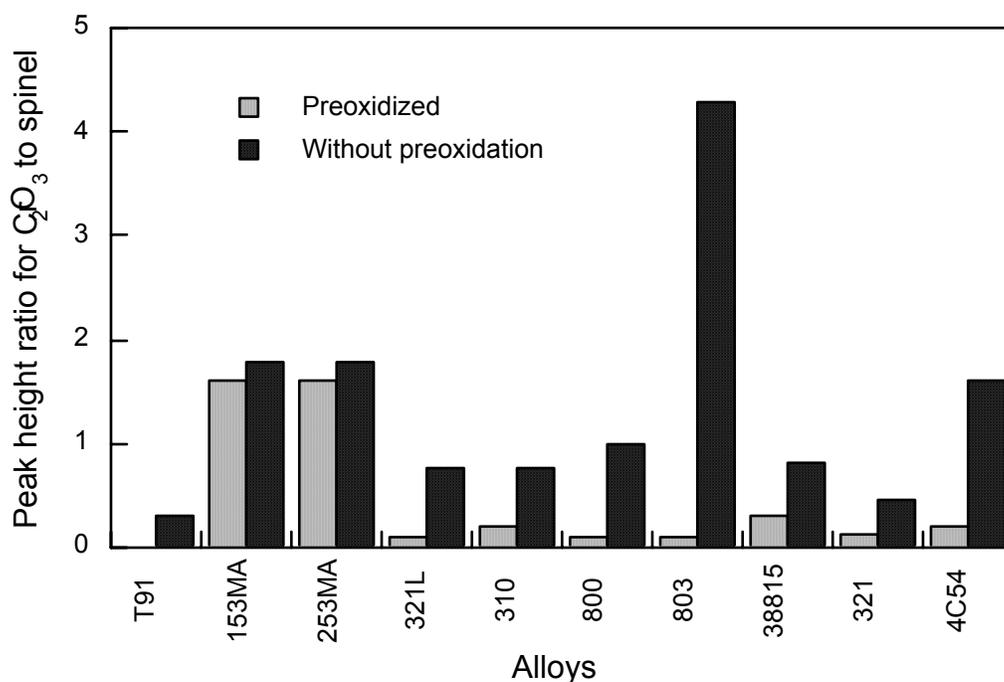


Figure 7 The intensity ratio of band 550 cm^{-1} (Cr_2O_3) over band 684 cm^{-1} (spinel) after exposure in a metal dusting environment for specimens with and without preoxidation in 2.3 vol.% H_2O - H_2 gas mixture for 200 h at 900°C .

iron and to form a spinel phase. If the oxidation condition results in only Cr_2O_3 phase in the scale, the scale will be resistant to coking and to subsequent metal dusting of the underlying alloy. Additional long-term tests with and without preoxidation treatments are in progress to establish the optimum oxide composition/phase to obtain adequate resistance to metal dusting.

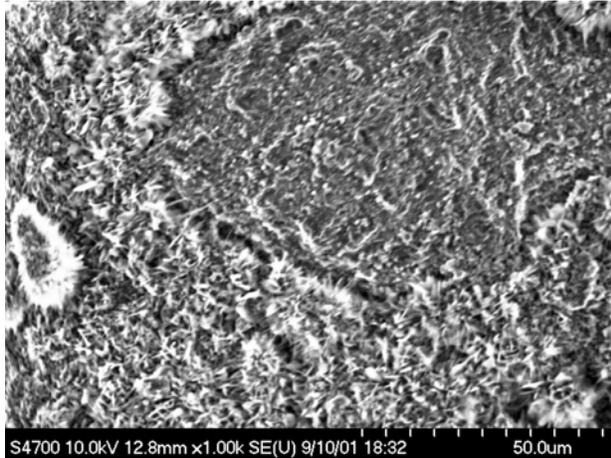
Pack-Diffusion Coatings

Specimens with pack-diffusion coatings were oxidized in air for 200 h at 900°C to develop the oxide scales and, subsequently, were exposed to the gas with 23 vol.% H_2O at 593°C for 142 h. Figures 8-10 show SEM photomicrographs of surfaces of alonized specimens after oxidation and oxidation/metal dusting treatments. Similar photomicrographs for the ChromePlexed specimens are shown in Figs. 11-13. In general, the oxidized surface layers were intact after exposure in the metal dusting environment. There was some discoloration of the air-oxidized specimens after exposure to the carbonaceous atmosphere, but detailed Raman analysis of the specimen surfaces showed almost no carbon. The preliminary results clearly showed that the oxide layers developed on pack-diffusion coated specimens minimize the catalytic reactions that can lead to carbon generation and deposition. Additional long-term experiments are in progress with several of the surface-modified alloys to establish the integrity of these preformed oxide layers in resisting metal dusting degradation.

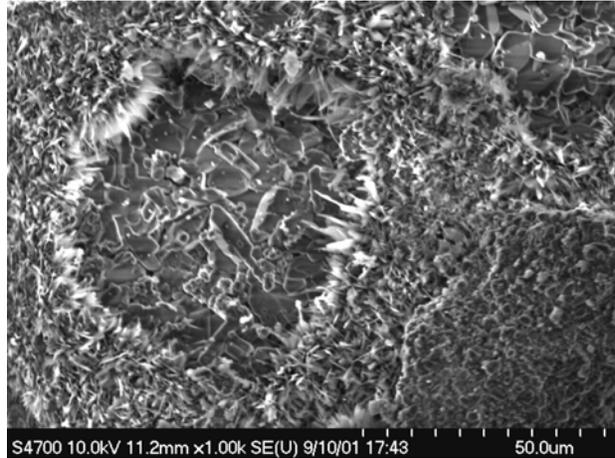
SUMMARY

Effort is underway at Argonne National Laboratory to mitigate metal dusting degradation of alloys by forming oxide scales either in-situ or by the pack-diffusion technique. Experiments

were conducted to examine the viability of oxide scales preformed in a low oxygen environment established by a H₂-H₂O gas mixture. A detailed analysis of the Raman spectra on various specimens with and without preoxidation showed that the relative amounts of (Fe,Cr) spinel and chromia in the oxide scale determine the susceptibility of the scale to metal dusting. The higher the

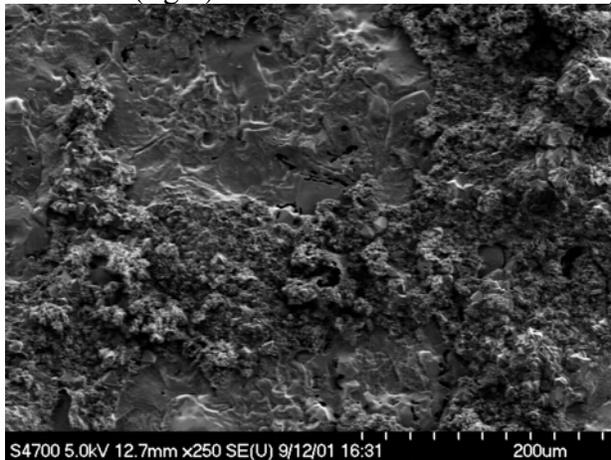


Oxidized at 900°C

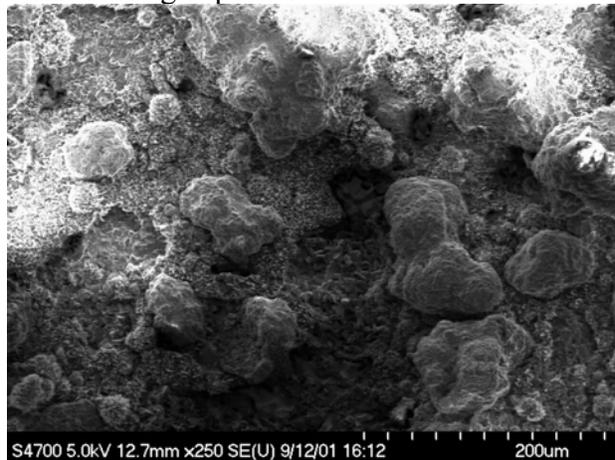


**Oxidized at 900°C and
metal dusted at 593°C (1100°F)**

Figure 8 SEM photomicrograph of surface of alonized T22 steel after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.

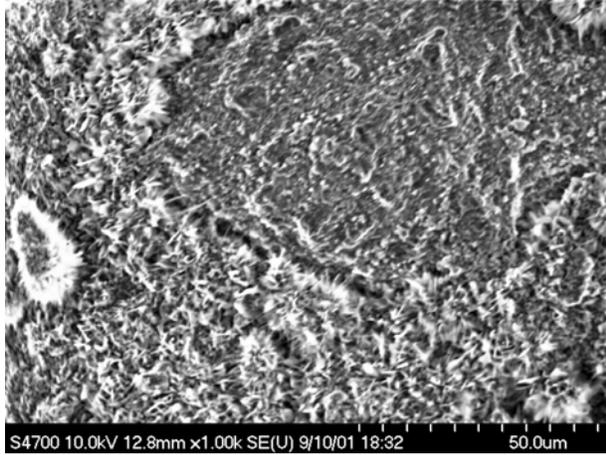


Oxidized at 900°C

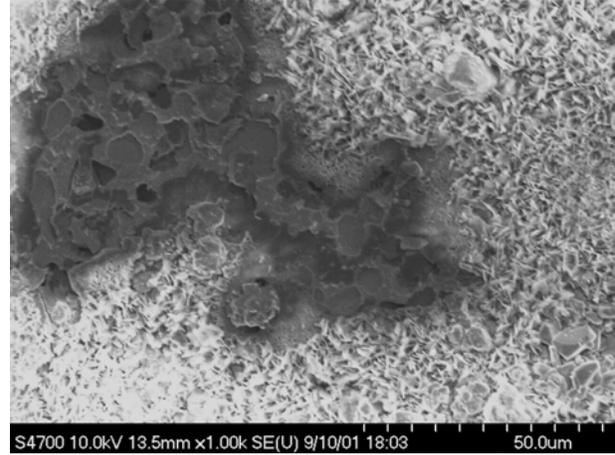


**Oxidized at 900°C and
metal dusted at 593°C (1100°F)**

Figure 9 SEM photomicrograph of surface of alonized 321 stainless steel after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.



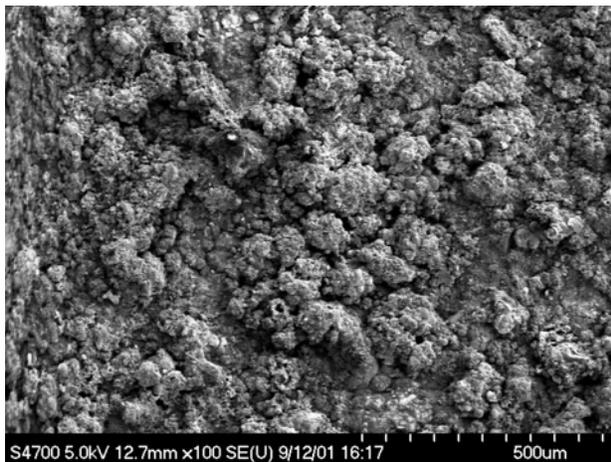
Oxidized at 900°C



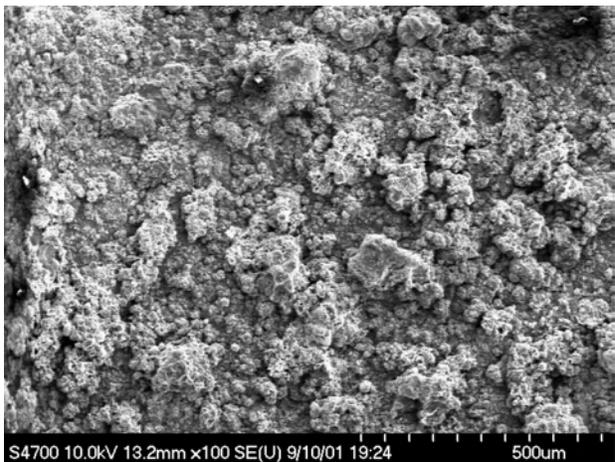
**Oxidized at 900°C and
metal dusted at 593°C (1100°F)**

Figure 10 SEM photomicrograph of surface of alonized Alloy 800 after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.

amount of spinel, the greater the chance that it will be reduced in the metal dusting environment, with the resultant Fe leading to carbon-forming reactions and subsequent metal dusting attack. A “pure” chromia can enhance the resistance to metal dusting since this oxide will be stable in the low pO_2 atmosphere prevalent in process environments. Preliminary results showed that the oxide coatings formed by the pack-diffusion approach can definitely retard the catalytic reactions that can lead to carbon formation and deposition. Additional experiments are in progress to assess the role of oxide scale composition and microstructure in the mitigation of metal dusting degradation.

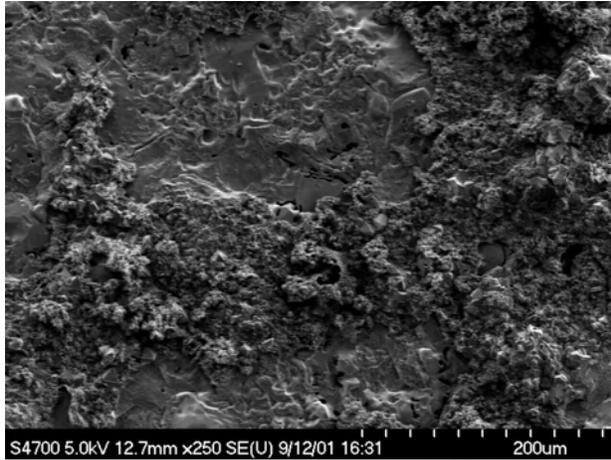


Oxidized at 900°C

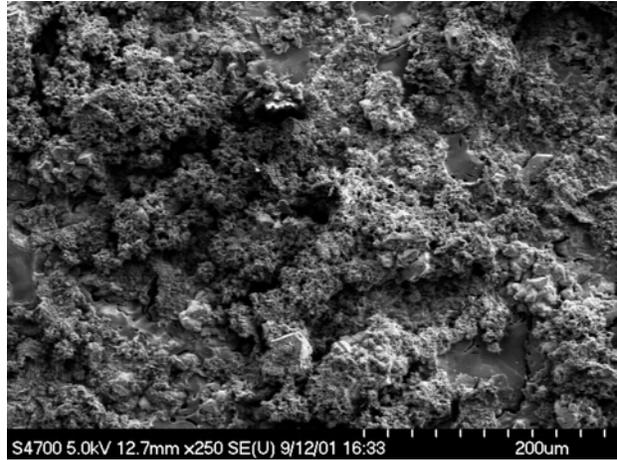


**Oxidized at 900°C and
metal dusted at 593°C (1100°F)**

Figure 11 SEM photomicrograph of surface of ChromePlexed T22 steel after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.



Oxidized at 900°C

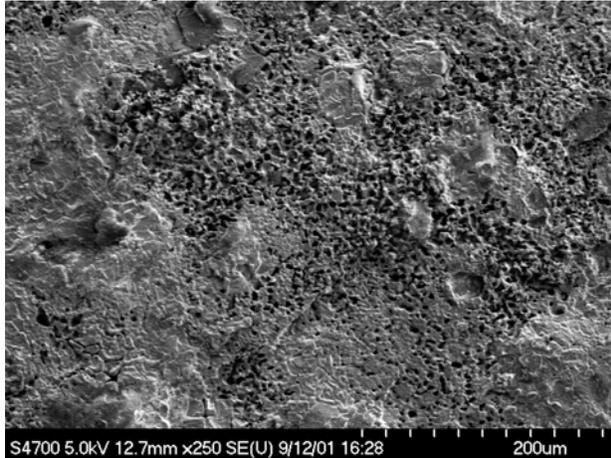


**Oxidized at 900°C and
metal dusted at 593°C (1100°F)**

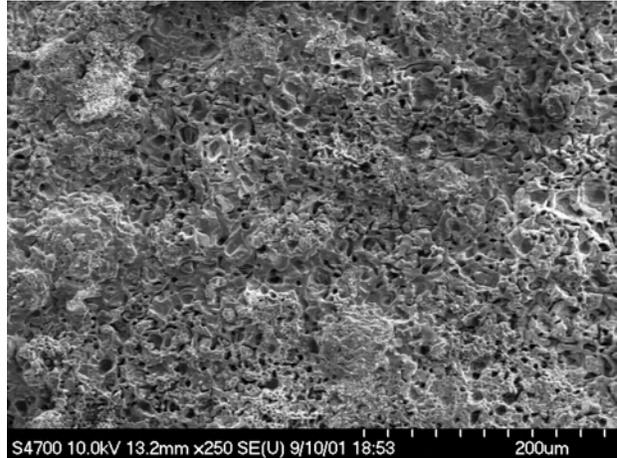
Figure 12 SEM photomicrograph of surface of ChromePlexed 321 stainless steel after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.

ACKNOWLEDGMENTS

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Oxidized at 900°C



**Oxidized at 900°C and
metal dusted at 593°C (1100°F)**

Figure 13 SEM photomicrograph of surface of ChromePlexed Alloy 800 after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.

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