

of ~250  $\mu\text{m}$ . In the case of 321 stainless steel, the Cr and Si concentrations were ~20-25 and ~0 wt.%, respectively, to a depth of 250  $\mu\text{m}$ . The Cr concentration in Alloy 292 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 (1652°F) to develop the oxide scales and were exposed to Gas 2 at 593°C (1100°F) for 142 h in Run 27. Figures 59-61 show SEM photomicrographs of the surfaces of annealed specimens after oxidation and oxidation/metal dusting treatments. Similar photomicrographs for the ChromeFlexed specimens are shown in Figs. 62-64. In general, the oxidized surface layers were intact after exposure to the metal dusting environment. There was some discoloration of the  $\alpha$ -oxidized specimens after exposure to the carbonaceous atmosphere but detailed Raman analysis of the specimen surfaces showed almost no carbon. Additional long-term experiments are planned with several of the surface-modified alloys.

#### PROJECT SUMMARY

The deposition of carbon from carbonaceous gaseous environments is prevalent in many chemical and petrochemical processes, such as reforming systems, syngas production systems, iron reduction plants, and others. One of the major consequences of carbon deposition is the degradation of structural materials by a phenomenon known as "metal dusting." 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

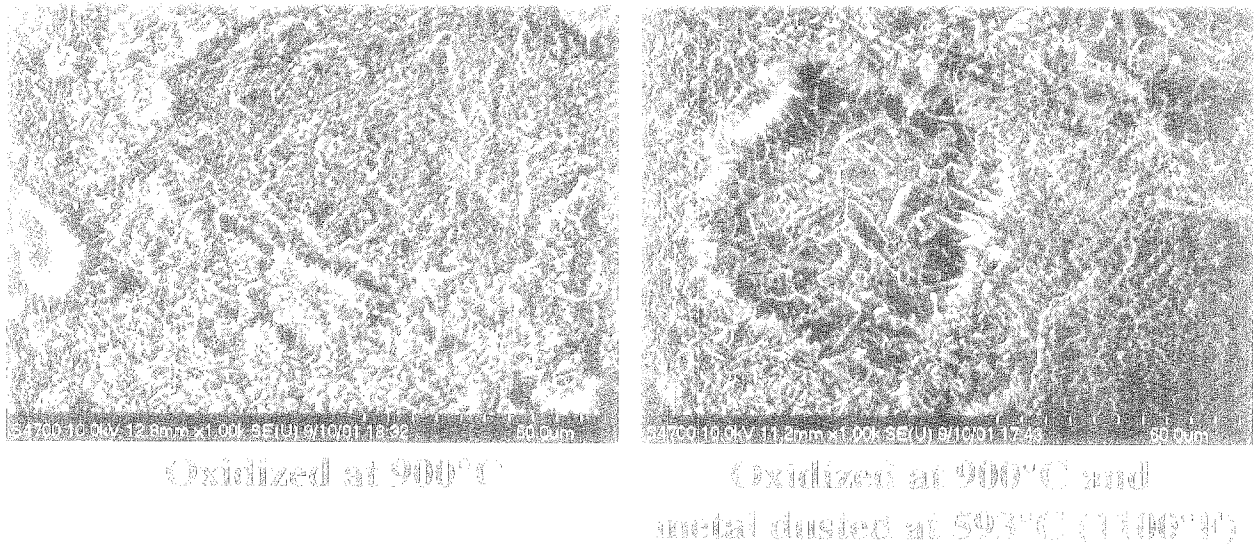


Fig. 59. SEM photomicrograph of surface of annealed 321 steel after (left) oxidation at 900°C in air and (right) oxidation at 900°C followed by metal dusting exposure for 142 h at 593°C.

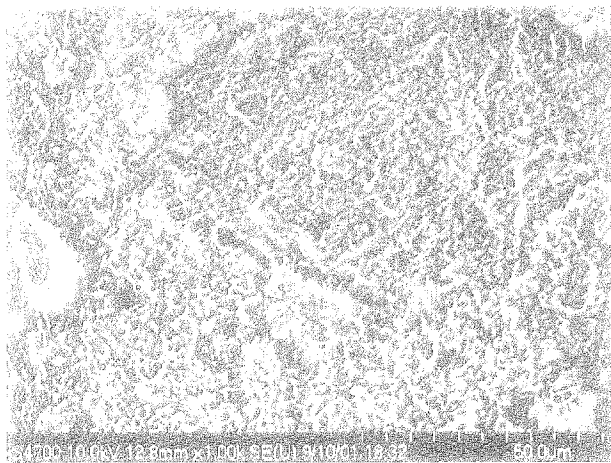


Oxidized at 900°C



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

Fig. 60. 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.

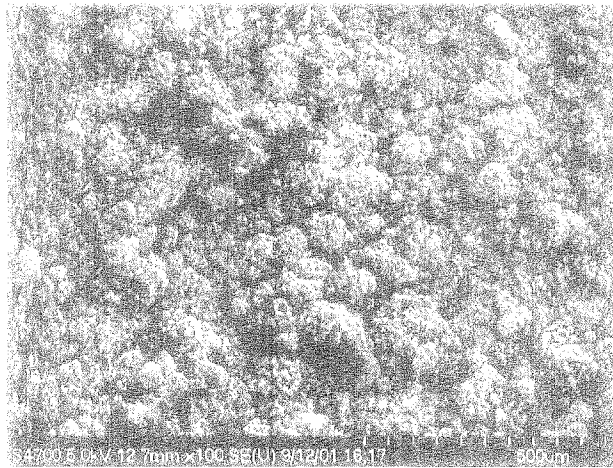


Oxidized at 900°C

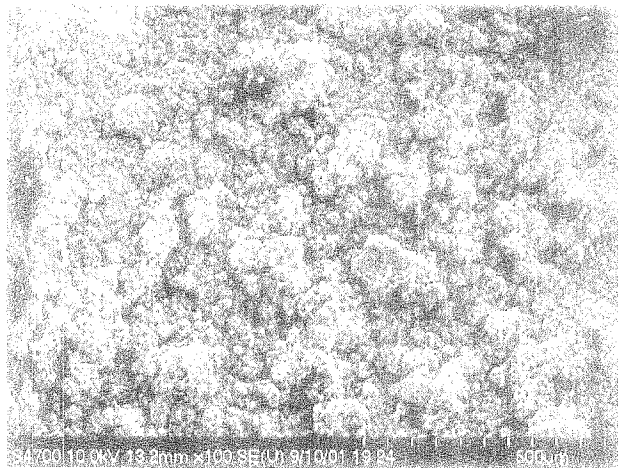


Oxidized at 900°C and metal dusted at 593°C (1100°F)

Fig. 61. 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.



Oxidized at 900°C



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

Fig. 62. SEM photomicrograph of surface of ChromePlaxed 322 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.

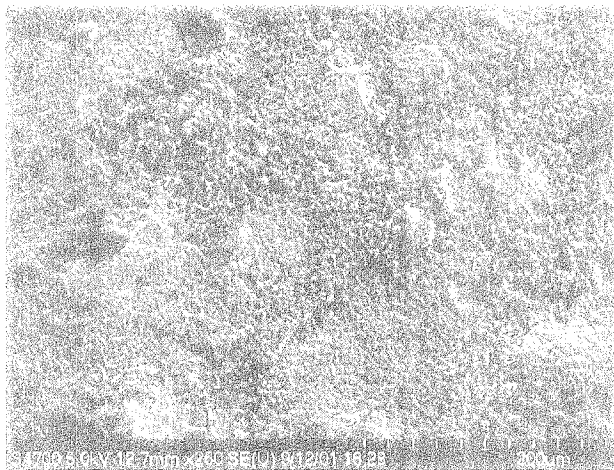


Oxidized at 900°C

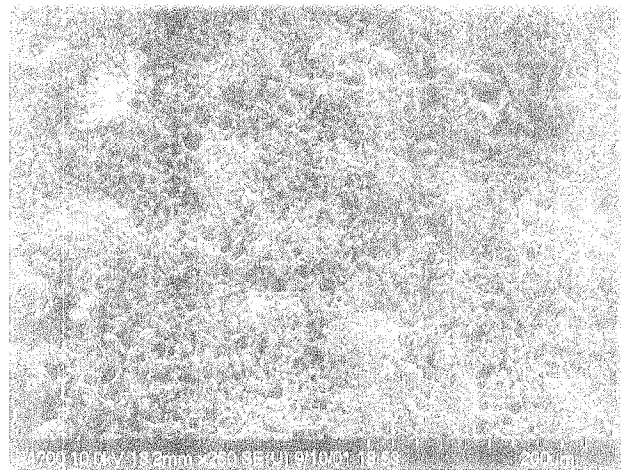


Oxidized at 900°C and  
metal dusted at 593°C (1100°F)

Fig. 63. SEM photomicrograph of surface of ChromePlaxed 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.



(left) oxidized at 900°C



(right) oxidized at 900°C and metal dusted at 593°C (1400h)

Fig. 84. SEM photomicrographs of surfaces of Chromia-Coated Alloy 800 after (left) oxidation at 900°C in air and (right) oxidation at 900°C, followed by metal dusting exposure for 1402 h at 593°C.

of metal dusting (regulation of the alloy). This first is influenced by  $ag$  in the gas mixture and availability of the catalytic surfaces for carbon-producing reactions to proceed. There may be a threshold in  $ag$  ( $\approx 1$ ) for carbon deposition. Metal dusting of the alloy in the reformer environment is determined by a competition between the oxide scale development and access of the virgin metal surface to the carbon deposits. The presence of an oxide scale may not prevent metal dusting, but can delay its initiation, thereby slowing the overall attack.

The local nature of dusting (initiated by pits on the alloy surface) on both Fe- and Ni-base alloys shows that defects in the oxide scales play a large role in initiation. Oxide scaling may not occur because of low  $ag$  or if the  $CO$  content in the environment is very low. Laboratory experiments have clearly monitored the effect of gas chemistry (in particular  $H_2O$  content) on the scaling, carbon deposition, and dusting initiation. It is evident that the environment in reformers is rich enough in  $CO$  that a Cr-rich alloy can develop a chromia scale (given enough exposure time) before carbon deposition.

Surface modification by preoxidation and/or coatings and alternative treatments are being examined at ARI to alleviate the metal dusting problem. Oxide coatings have the advantage in 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 observed in situ development of oxide scales, back diffusion of Al or Cr/Fe, 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.

The effort at ANL will emphasize the competitive nature of oxidation and carbon deposition and will assess the options for mitigating metal dusting in waste-heat boilers and eventually eliminating the boilers from the reformer systems, especially for H<sub>2</sub> production.

### ACKNOWLEDGMENTS

This work was sponsored by the U.S. Department of Energy, Office of Industrial Technologies, and Dr. Charles Sorrell was the Program Manager for the project. Specimens of various alloys were supplied by Haynes International, AvestaPolarit, Sandvik Steel, Special Metals, Allegheny Ludlum, and Krupp VDM. Alon Surface Technologies supplied the specimens with pack-diffusion layers.

### REFERENCES

1. P. A. Lefraicois and W. B. Hoyt, *Corrosion* **19** (10), 360, 1963.
2. R. F. Hochman, Proc. 4<sup>th</sup> Intl. Congress on Metal Corrosion, N. E. Hammer, ed., NACE, p. 258, 1972.
3. R. C. Scheler, *Hydrocarb. Process.* **51**, 73, 1972.
4. R. F. Hochman, Proc. Symp. on Properties of High-Temperature Alloys with Emphasis on Environmental Effects, Z. A. Foroulis and F. S. Pettit, eds., Electrochem. Soc., Pennington, NJ, p. 715, 1977.
5. H. J. Grabke, U. Gravenhorst, and W. Steinkusch, *Werkst. Korros.* **27**, 291, 1976.
6. H. J. Grabke, J. Hemptenmacher, and A. Munker, *Werkst. Korros.* **35**, 543, 1984.
7. H. J. Grabke and I. Wolf, *Mater. Sci. Eng.* **87**, 23, 1987.
8. R. A. Perkins, W. C. Coons, and F. J. Radd, *Properties of High-Temperature Alloys*, Electrochem. Soc., Pennington, NJ, 733, 1976.
9. H. J. Grabke, *Mat. Corr.* **49**, 303, 1998.
10. E. Q. Camp, C. Phillips, and L. Gross, *Corrosion*, **1**, 149, 1945; and **15**, 627, 1959.
11. R. E. Franklin, *Acta Cryst.* **4**, 253, 1951.
12. H. Krebs, *Fundamentals of Inorganic Crystal Chemistry*, McGraw-Hill, New York, p. 150, 1968.

13. R. O. Dillon and J. A. Woollam, Phys. Rev. B **29**, 3482, 1984.
14. F. Tuinstra and J. L. Koenig, J. Chem. Phys. **53**, 1126, 1970.
15. M. Nakamizo, H. Honda, M. Inagaki, and Y. Hishiyama, Carbon **15**, 295, 1977.
16. M. Nakamizo, H. Honda, and M. Inagaki, Carbon **16**, 281, 1978.
17. D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, P12-119 to P12-123, 1999.
18. H. E. Blayden, H. L. Riley, and A. Taylor, J. Am. Chem. Soc. **62**, 180-186, 1940.
19. W. D. Schaeffer, W. R. Smith, and M. H. Polley, Ind. Eng. Chem. **45**, 1721, 1953.
20. C. R. Kinney, Proc. Conf. on Carbon, U. of Buffalo, p. 83, 1956.
21. F. Tuinstra and J. L. Koenig, J. Chem. Phys. **53**, 1126-1130, 1970.
22. R. J. Nemanich and S. A. Solin, Solid State Comm. **23**, 417-419, 1977.
23. R. Al-Jishi, Phys. Rev. B **26** 4514-4522, 1982.
24. R. Vidano and D. B. Fischbach, J. Amer. Ceram. Soc. **61**, 13-17, 1978.
25. D. S. Knight and W. B. White, J. Mater. Res. **4**, 385-393, 1989.
26. R. J. Nemanich and S. A. Solin, Phys. Rev. B **20**, 392-401, 1979.
27. Y. Sato Y, M. Kamo, and N. Setaka, Carbon **16**, 279-280, 1978.
28. C. M. Chun, J. D. Mumford, and T. A. Ramanarayanan, Mat. Corr. **50**, 634-639, 1999.
29. M. Nakamizo, R. Kammereck, and P. L. Walker, Carbon **12**, 259-267, 1974.
30. R. Kammereck, M. Nakamizo, and P. L. Walker, Carbon **12**, 281-289, 1974.
31. T. P. Levi, N. Briggs, I. Minchington, and C. W. Thomas, NACE Corrosion 2001, Paper # 01375.
32. M. Maier, J. F. Norton, and P. D. Frampton, Mat. Corr. **49**, 330-335, 1998.
33. B. Baker and G. D. Smith, NACE Corrosion 2000, Paper # 257.

## DISTRIBUTION LIST FOR ANL-02/05

### Internal

|                 |               |           |
|-----------------|---------------|-----------|
| V. Maroni       | W. W. Schertz | Z. Zeng   |
| C. Marshall     | W. Shack      | TIS Files |
| K. Natesan (30) | W. K. Soppet  |           |
| R. Poeppel      | R.W. Weeks    |           |

### External

DOE/OSTI, for distribution (2)

ANL-E Library

ANL-W Library

L. Craig, Jr., Materials Technology Institute, St. Louis, MO 63141 (25 copies)

R. Jain, DOE Office of Industrial Technologies, Washington, DC 20585

D. Ozokwelu, DOE Office of Industrial Technologies, Washington, DC 20585

C. Russomanno, DOE Office of Industrial Technologies, Washington, DC 20585

D. Salem, DOE Office of Industrial Technologies, Washington, DC 20585

P. Scheihing, DOE Office of Industrial Technologies, Washington, DC 20585

C. Sorrell, DOE Office of Industrial Technologies, Washington, DC 20585

B. Valentine, DOE Office of Industrial Technologies, Washington, DC 20585