Conf-9205123--7

# OXIDATION/SULFIDATION BEHAVIOR OF Fe–Cr ALLOYS: A REACTIVE-ELEMENT EFFECT*

by

K. Natesan and J.-H. Park
Materials and Components Technology Division
Argonne National Laboratory
Argonne, IL 60439

ANL/CP--75787

DE92 016172

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

April 1992

JUN 24 1992

Invited paper to be presented at the 6th Annual Conference on Fossil Energy Materials, Oak Ridge, TN, May 12–14, 1992.

*Work supported by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program, Work Breakdown Structure Element ANL-3, under Contract W-31-109-Eng-38.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

# OXIDATION/SULFIDATION BEHAVIOR OF Fe–Cr ALLOYS: A REACTIVE ELEMENT EFFECT

K. Natesan and J.-H. Park
Argonne National Laboratory
Materials and Components Technology Division
Argonne, IL 60439

## ABSTRACT

Corrosion resistance of a number of structural alloys in high–temperature environments is achieved by the formation of a continuous chromium oxide scale. Research on high–temperature corrosion of structural alloys has been in progress to reduce the rate of oxidation, improve the adhesion of oxide scale to the substrate alloy, and stabilize the oxide scale against other corrosive agents such as sulfur, chlorine, alkalies, and ash/sorbent deposits. Extensive research is being conducted at Argonne National Laboratory to (1) evaluate mechanisms of oxidation, sulfidation, and breakaway corrosion of chromia– and alumina–forming alloys exposed to mixed–gas atmospheres that span a wide range of oxygen, sulfur, and chlorine activities typical of combustion and gasification systems; (2) develop an understanding of the role of several microalloy constituents (e.g., Zr, Nb, Y, Ce, V) in oxidation/sulfidation processes and scale breakdown; (3) characterize the physical, chemical, and mechanical properties of surface scales that are resistant to sulfidation attack; and (4) evaluate the role of deposits, such as alkali sulfates, alkali chlorides, ash, and sulfur sorbents, in the corrosion behavior of metallic alloys, selected coatings, and ceramic materials.

In this paper, experimental data are presented on the oxidation behavior of Fe–25Cr, Fe–25Cr–0.3 and 1.0Y, and Fe–25Cr–1Ce alloys at temperatures from 700 to 1000°C for time periods of 24 to 120 h in oxygen partial pressures in a range of $10^{-4}$ to 1 atm. The test results showed total spallation of oxide scale from Fe–25Cr alloy, whereas no spallation was observed with Y– and Ce–doped alloys. Based on additional test results, it was concluded that the primary cause of scale spallation is grain growth in the alloy substrate during the oxidation process. Additions of reactive elements such as Y and Ce seem to pin the grain boundaries in the substrate alloy, thereby minimizing grain growth. As a result, Y– and Ce–doped alloys developed superior oxidation resistance even under thermal quenching conditions. Alloy grain growth studies showed a tenfold increase in grain size in Fe–25Cr alloy, whereas the increase in Y– and Ce–doped alloys was <1% of the original size. Lack of grain growth in doped alloys improved adhesion of oxide scales.

## INTRODUCTION

Corrosion resistance of a number of structural alloys in high-temperature environments is achieved by the formation of a continuous chromium oxide ($Cr_2O_3$) scale.[1,2] The scale can be treated principally as a rate-determining solid-state diffusion barrier between the environment and alloy substrates. Research on high–temperature oxidation of structural alloys has two basic objectives: determining alloying additions to reduce the rate of oxidation, and improving the adhesion of oxide scales to substrate alloys.[3] It is generally recognized that, when alloys contain so–called reactive elements (sometimes known as oxygen (O)–active elements), i.e, yttrium (Y), lanthanum (La), cerium (Ce), etc., they exhibit a lower oxide growth rate and an enhanced adhesion of the oxide layer to the base alloy.[4] Research on reactive–element additions has two main objectives: slowing the ionic transport rate through the scale, and increasing the degree of scale adhesion to the base alloy.

The objective of the study described here is to evaluate the oxidation behavior of chromia-forming alloys of Fe-25Cr base composition with and without additions of reactive elements. Alloys with Y and Ce additions in a range of 0.1-1.0 wt.% were used to determine the nature of the reactive–element effect on high–temperature oxidation. Thermogravimetric analysis (TGA) and postexposure microscopic examinations were conducted on samples prepared by thermal oxidation of chromium (Cr) and Fe-25Cr alloys with and without additions of reactive elements The evaluation of oxidation kinetics included detailed analyses of scale–spalling characteristics and substrate alloy grain growth that occurs during oxidation. Detailed information on the oxidation behavior of these alloys is presented elsewhere[5] and a brief description of results is presented in this paper.

## EXPERIMENTAL PROCEDURE

### Thermogravimetric Measurements

Oxidation experiments were performed with an electrobalance at temperatures from 700 to 1000°C in O, air, 1 vol% $CO\text{-}CO_2$, and 18 vol.% $CO\text{-}CO_2$ environments. Most of the tests were conducted with Fe-25Cr and Fe-25Cr-0.3Y alloys. However, some tests were conducted in $O_2\text{-}N_2$ gas mixtures (with an oxygen partial pressure [$pO_2$] of $10^{-4}$ atm) at 1000°C on Fe-25Cr alloys containing 1.0 wt.% Y or Ce.

### Alloy Grain–Growth Tests

Specimens of Fe-25Cr, Fe-25Cr-1Y, and Fe-25Cr-1Ce alloys were used in tests to evaluate the effect of alloy grain growth on the adhesion of thermally formed scales to substrate alloys. The specimens were tested at 1000°C for <1 to 24 h. The specimens were wrapped in tantalum (Ta) foil (which served as an O getter) and enclosed in quartz capsules under vacuum. The microstructures of annealed specimens were examined by optical microscopy and scanning electron microscopy (SEM). In addition, large–grain specimens of Fe-25Cr (annealed at 1000°C for ≈25 h) were oxidized in TGA tests similar to those described earlier.

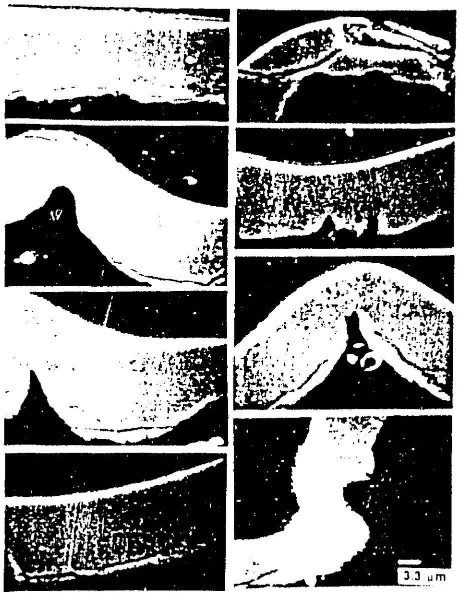

Fig. 1. Cross-sectional views of totally spalled scale from an Fe–25Cr alloy specimen that was oxidized for 24 h.

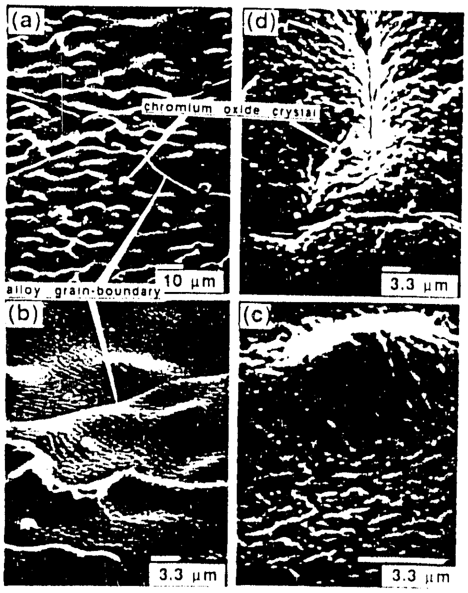

Fig. 2. (a)–(c): Fe–25Cr alloy surface after removal of spalled oxide scale; (d): scale side of alloy/scale surface.

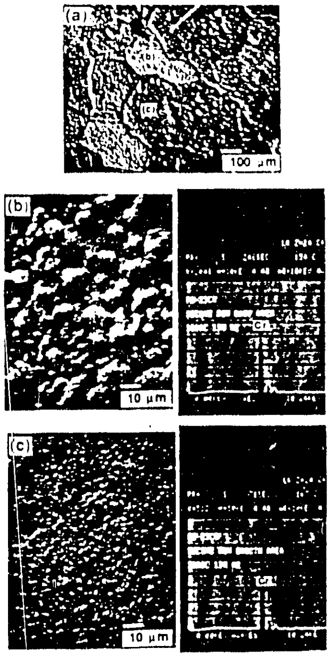

Fig. 3. SEM photomicrographs and EDX analysis of surface of Fe–25Cr alloy reoxidized: (a) overall oxide surface, (b) rough area in (a), and (c) smooth area in (a).

Cr in Y is 0.70 at.%. However, on the basis of the difference in the respective atomic radii of Cr and Y, the solid solubility of Y in Cr is reported to be $<0.005$ at.%.[6] The compound $Y_2Fe_{17}$, with a hexagonal crystal structure, has been identified in a Fe-Y phase diagram.

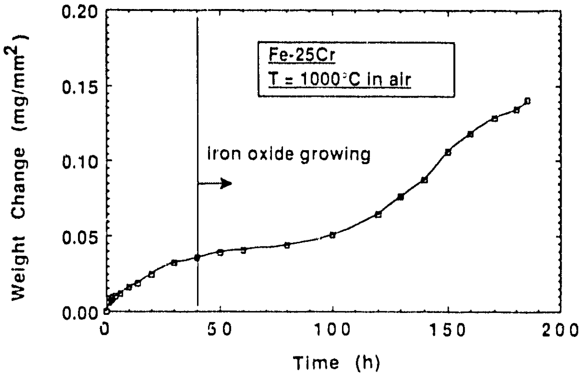

Fig. 4. Weight change versus time for second oxidation of Fe–25Cr alloy at 1000°C.

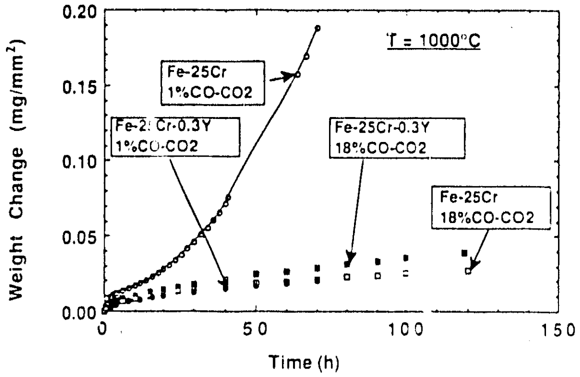

Fig. 5. Weight change versus time for Fe–25Cr and Fe–25Cr–0.3Y alloys exposed at 1000°C in a low-$pO_2$ environment.

EDX analysis allowed detection of Y in the grain boundaries of the scale and in the scale/alloy interface regions of the oxidized Fe-25Cr-Y alloy that contained Y at 1.0 wt.% but not at 0.3 wt.%.

Figure 6 shows TGA data for Fe-25Cr, Fe-25Cr-1Y, and Fe–25Cr-1Ce alloys oxidized at 1000°C. The rate of weight change is similar for the base alloy and that containing Ce; the rate for the Y–containing alloy is somewhat lower. Measurements of scale thickness showed no appreciable difference between the Ce- and Y-containing alloys. The difference in weight change between the two alloys is probably due to the increased level of internal oxidation in the Ce-containing alloy. One striking difference in the scaling behavior of these alloys is the total spallation in the base alloy and fully adherent scale in the doped alloys. Repeated oxidation of the samples (with removal of spalled scale from the Fe-25Cr alloy and of adherent scales from the doped alloys) showed that the scales formed during the second exposure were adherent in all the samples even after thermal quenching. Further, grain growth, which was large during the first oxidation of the base alloy, was much smaller during the second exposure. The alloy grain growth in the doped-alloys was small during both exposures. Figure 7 shows the variation in grain size for an alloy with and without Y as a function of exposure temperature. It is evident that, at 700°C, the lowest temperature of this study, reactive–element addition has almost no effect on grain growth.

## Alloy Grain Growth

To evaluate the role of reactive–element addition in the grain–growth process in the absence of oxidation, samples of Fe-25Cr, Fe-25Cr-1Ce, and Fe-25Cr-1Y alloys were

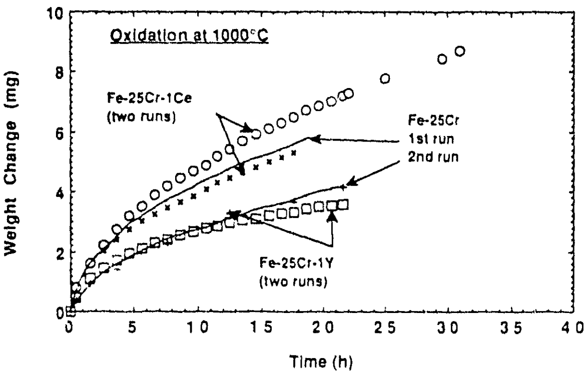

Fig. 6. Thermogravimetric test data for Fe-25Cr, Fe-25Cr-1Ce, and Fe-25Cr-1Y alloys oxidized at 1000°C in a low-$pO_2$ environment.

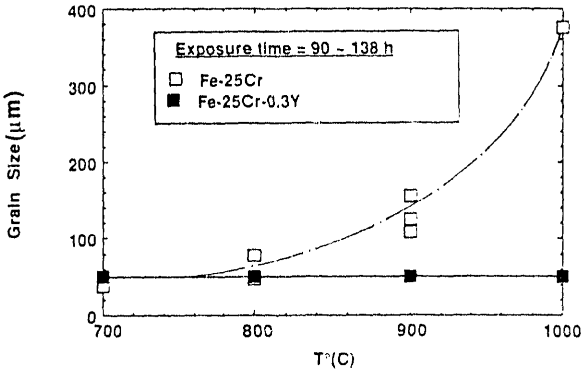

Fig. 7. Grain size variation for Fe-25Cr and Fe-25Cr-0.3Y alloys during oxidation at temperatures from 700 to 1000°C.

wrapped in Ta foil, vacuum-sealed in quartz capsules, and annealed at 1000°C for 44 min, 2 h 52 min, 8 h 20 min, and 24 h 40 min. Microstructures of the annealed samples were examined by SEM and EDX analysis. In the initial stages of the annealing treatment, grain growth in the base alloy was much greater than in the doped alloys. The presence of Ce in the alloy causes the boundaries to be less mobile, leading to smaller grain growth. Figure 8 shows the variation in grain size as a function of annealing time for the base and doped alloys. Lack of grain growth in the substrate alloy is probably the major reason for the better adhesion of the oxide scale to the substrate in the doped alloys.

To examine the effect of alloy grain growth on the scale spallation behavior of Fe-25Cr alloy, specimens of the alloy that had been annealed at 1000°C in vacuum were oxidized in the TGA test facility. Also, the spalled scale was removed and the specimen was reoxidized. The results showed that, during the first oxidation experiment, the alloy developed an oxide scale that was accompanied by substantial grain growth in the substrate alloy. Upon cooling of this oxidized specimen, the scale spalled completely. When the same specimen was reoxidized in a second run, the alloy again developed an oxide scale of essentially the same morphology, but grain growth in the underlying alloy was negligible. This seemed to enhance the adhesion of the scale to the substrate, and oxide spallation was rarely observed.

## Oxidation Mechanisms

In general, to depict morphological changes in a scale growing as a function of oxidation time, a mechanism of oxidation should incorporate both thermodynamic and kinetic factors. From the thermodynamic standpoint, oxidation experiments were conducted over a wide range of temperatures and $pO_2$s, and scale morphologies were

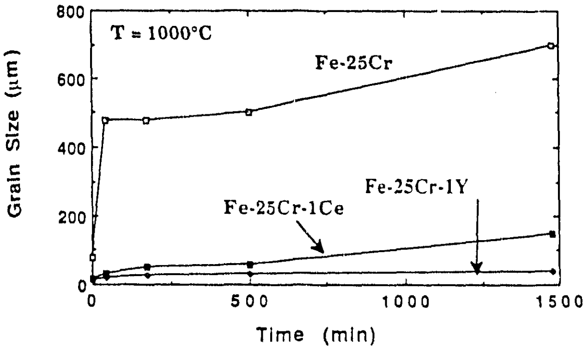

Fig. 8. Grain-size variation in Fe-25Cr, Fe-25Cr-1Ce, and Fe-25Cr-1Y alloys during annealing at 1000°C, as a function of exposure time.

determined. From the kinetic standpoint, scale and alloy grain growth were examined by oxidation experiments of differing duration and by determining the morphological development of scales.

In the oxidation of the Fe-25Cr alloy, the mobile species are two cations (Cr and Fe) and one anion (O). Oxide scale forms and grows by transport of one or more of these mobile species through the scale and subsequent chemical reactions. The oxide growth kinetics and associated morphological development are primarily dependent on the transporting species and their properties. However, it is difficult to determine the transport properties of each and every species because of the influence of scale microstructure, defects, alloy fabrication procedure, and exposure conditions of the oxidation experiment. In this section, oxidation mechanisms are proposed for Fe-25Cr alloys without and with reactive-element additions, based on results from the present study.

### Without Reactive Element

First Oxidation. When a specimen of Fe-25Cr alloy was oxidized at 1000°C for 24 h and quenched to room temperature, separation of scale from substrate alloy resulted in total spallation of the scale. The primary cause of the separation seemed to be grain growth in the underlying alloy during oxidation. From the beginning of oxidation, a thin chromia scale formed on the specimen surface. Based on thermodynamics, chromia is expected to form because its stability is higher than that of iron oxide. As the oxidation continued, chromia scales grew in a wavy and partially folded fashion. In the early stages of oxidation, the scale was thin and completely covered the alloy surface. The scale/alloy interface was fairly uniform, and adhesion of the scale to the substrate was good. As oxidation continued, grain growth in the substrate alloy caused the oxide to separate from the alloy at several locations; the separated oxide buckled and appeared wavy in cross section (see Fig. 9a). The scale exhibited only a few points of contact with the substrate alloy and adhesion to the substrate was tenuous at best. When the sample was quenched to room temperature, the scale spalled primarily because of the mechanical weakness of the buckled scale.

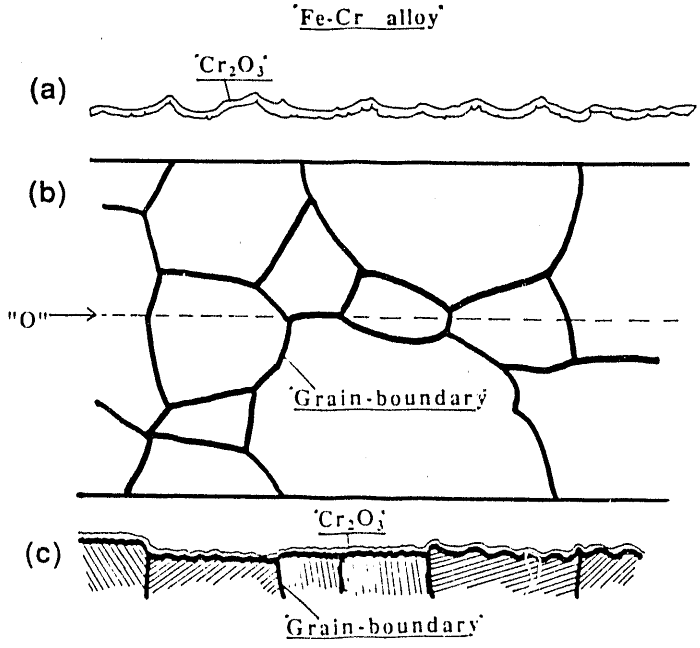

Fig. 9. Schematic representation of oxidation of Fe-25Cr alloy: (a) chromia scale totally spalled (b) alloy side of scale/alloy interface after spallation, and (c) cross section of specimen at plane "O" shown in (b).

Thermal-expansion mismatch may have also contributed to scale spallation but it is not the primary cause of the scale failure. Lack of cracks in the scale also indicates that the scale had mostly separated from the alloy during oxidation rather than on cooling from the oxidation temperature. Separation distance between the scale and the underlying alloy was ≈1 µm. Figure 9b is a schematic representation of the surface of the alloy side of the scale/alloy interface. The grain structure of the base alloy is evident but the surface also exhibits a thin layer of oxide. Figure 9c is a schematic representation of the cross section of the sample taken along the plane "O" shown in Fig. 9b.

Second Oxidation. After removal of the spalled oxide from the sample, the specimen (with a thin chromia layer) was reoxidized under the same conditions as in the initial oxidation experiment. The second oxidation was also conducted for 24 h at 1000°C and the sample was quenched to room temperature. Figure 10 is a schematic representation of the cross section of the specimen after the second oxidation. The thin layer of chromia left behind after scale spallation (from the first oxidation) did not prevent Fe migration outward from the alloy. In addition, Cr activity at the surface (for the second oxidation run) was much lower and Fe activity was high relative to the unexposed alloy. The migrated Fe oxidized on the gas side of the interface, whereas an intermediate layer of (Fe,Cr) oxide and a chromia layer developed at the alloy/scale interface. Even though the morphology of the scale layers that developed after the second oxidation was complex and thicker than that after the first oxidation run, scale adhesion to the substrate was extremely good. The superior adhesion and lack of spalling can be attributed to negligible grain growth in the substrate alloy after the second oxidation.

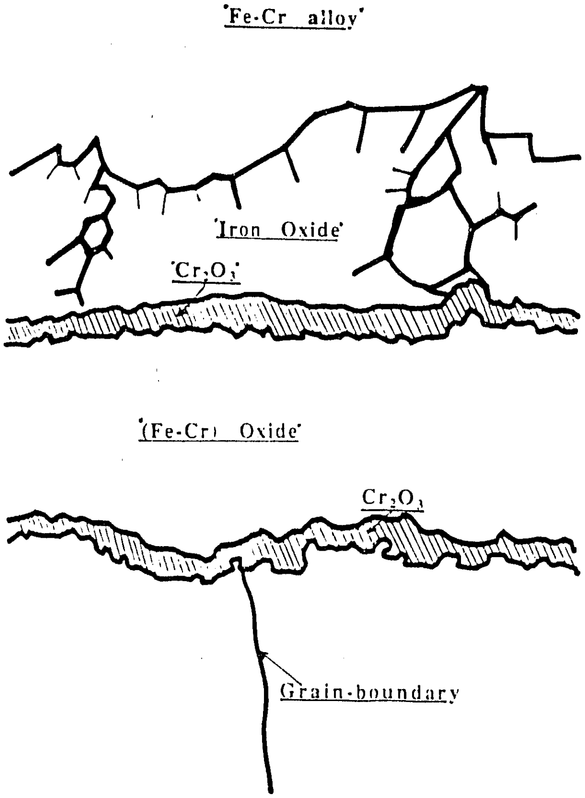

Fig. 10. Schematic representation of scale morphology developed during reoxidation of Fe-25Cr alloy at 1000°C.

## With Reactive Element

The oxidation rate of reactive–element–containing alloys containing reactive elements at 1000°C for 24 h was negligibly different; however, the additions had some beneficial effect over longer oxidation periods (>120 h at 1000°C). The composition of the scale in the reactive-element–containing alloys was pure chromia, and no trace of Fe was detected in the scale. Morphological analysis of scale layers indicated that Fe diffusion outward was suppressed in the doped alloys. There is some evidence, even though not conclusive in this study, that O transport inward may also contribute to scale growth. Parabolic rate constants for the oxidation of doped alloys were similar to those for undoped alloys. The major difference in the performance of the doped and undoped alloys was in scale adhesion. Adhesion was much superior in the doped alloys and virtually no spallation of scale was observed, even under thermal quenching. The improved adhesion can be attributed to smaller grain growth in the doped alloys than in the undoped alloy.

Figures 11 and 12 show schematic representations of scale morphologies in Ce- and Y-containing alloys after oxidation. These doped alloys developed pure chromia scales at high temperatures and the dopants had a tendency to oxidize internally and segregate in grain–boundary regions of the substrate alloy. The presence of these

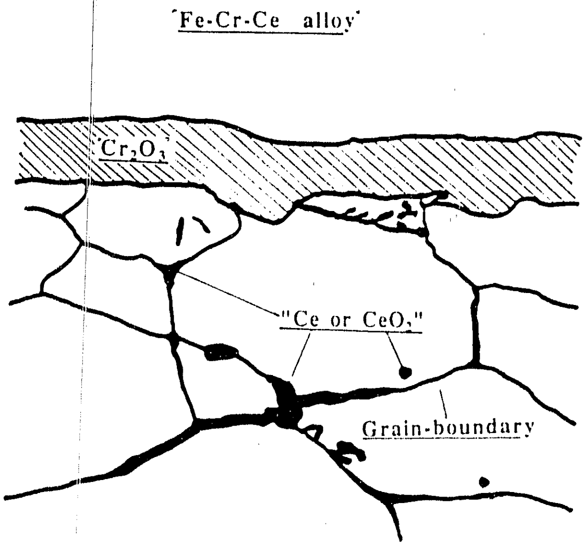

Fig. 11. Schematic representation of scale morphology developed during oxidation of Fe-25Cr-1Ce alloy at 1000°C.

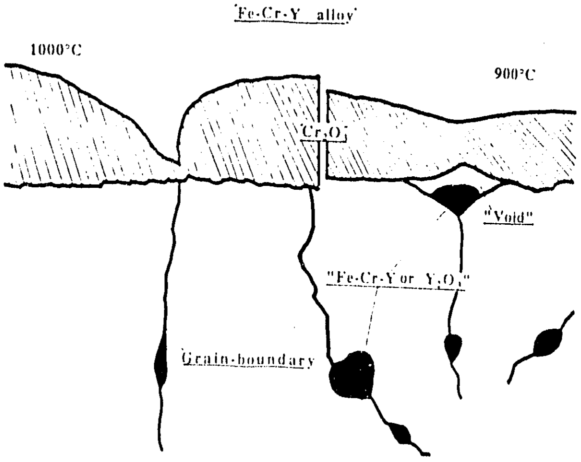

Fig. 12. Schematic representation of scale morphology developed during reoxidation of Fe-25Cr-1Y alloy at 1000°C.

internally oxidized particles seem to pin the grain boundaries, thereby minimizing grain growth in the substrate alloy during oxidation. Lack of grain growth in the alloy results in improved adhesion of the scale to the substrate and virtual elimination of scale spallation. Even after thermal quenching of the two dopants used in the present study, Y seems better than than Ce because the Ce-containing alloys exhibited much higher weight gain, primarily due to increased internal oxidation. Further, Ce can combine with Fe to form a low-melting (640°C) eutectic that decreases oxidation resistance.

## SUMMARY

Alloy samples of Fe-25Cr, Fe-25Cr-0.3 and 1.0Y, and Fe-25Cr-1Ce were subjected to oxidation tests in a microbalance at temperatures from 700 to 1000°C for time periods of 24 to 120 h in $pO_2$s ranging from $10^{-4}$ to 1 atm. Tests in which oxidized samples were quenched from oxidation temperature to room temperature in ≈20 min were also conducted. Thermal-quenching test results showed total spallation of oxide scale from Fe-25Cr alloy, whereas no spallation was observed in Y- and Ce-doped alloys. After removal of spalled oxide, the Fe-25Cr alloy specimen was reoxidized a second and third time by the procedure used in the first oxidation. Test results showed substantial improvement in adhesion of the scale to substrate after these runs; however, the totally spalled scale from the first run was pure chromia whereas that after the second and third runs comprised a multilayer scale with Fe oxide as the dominant phase at the gas/scale

interface. Even though the scale thickness after repeated oxidations was somewhat thicker than during the first oxidation, the oxidation resistance of the alloy seems to have improved.

The primary cause of scale spallation was identified as grain growth in the alloy substrate during the oxidation process. The extent of grain growth during the first oxidation step was substantially larger than in following oxidation steps. Additions of reactive elements, such as Y and Ce, seem to pin the grain boundaries in the substrate alloy, thereby minimizing grain growth even during the first oxidation step. As a result, Y- and Ce-doped alloys developed pure chromia scales that were resistant to spallation and exhibited superior oxidation resistance even under thermal quenching.

## ACKNOWLEDGMENT

Work was supported by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program, Work Breakdown Structure Element ANL-3, under Contract W-31-109-Eng-38.

## REFERENCES

1. K. Natesan, "Oxidation of Alloys in Bioxidants," Proc. Symp. Oxidation of Metals and Associated Mass Transport, eds. M. A. Dayananda, S. J. Rothman, and W. E. King, TMS-AIME, Orlando, FL, October 6-7, 1986, p. 161.

2. P. Kofstad, High Temperature Corrosion (Elsevier Applied Science, England, Essex, 1988); Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley Interscience, New York, 1972.

3. A. Rahmel, G. C. Wood, P. Kofstad, and D. L. Douglass, "International Workshop on Critical Issues Concerning the Mechanisms of High-Temperature Corrosion," Oxid. Met., 23 (5/6) 251, 1985.

4. L. B. Pfeil, Improvements in Heat Resistant Alloys, Brit. Pat. No. 459848, 1937.

5. J.-H. Park and K. Natesan, Oxidation Behavior of Iron-Chromium Alloys at Elevated Temperatures: A Reactive-Element Effect, Argonne National Laboratory Report ANL/FE-92/1, in press.

6. J.-H. Park and K. Natesan, "Transport Properties of Chromium and Fe-Cr Alloys Exposed to Oxygen/Sulfur Environments," Proc. Fourth Berkeley Conf. on Corrosion-Erosion-Wear of Materials at Elevated Temperatures, January 31-February 2, 1990, Berkeley, CA, NACE.

DATE
FILMED
8112192