Corrosion of Alloy 800H and the Effect of Surface-Applied CeO_2 in a Sulphidizing/Oxidizing/Carburizing Environment at 700°C

M. F. Stroosnijder,^{*†§} V. Guttman,^{*} T. Fransen,[‡] and J. H. W. de Wit[†]

Received October 2, 1989; revised November 27, 1989

The corrosion behavior of a wrought austenitic Fe-20Cr-32Ni steel, Alloy 800H, was studied in a simulated coal-gasification atmosphere at 700°C for exposure times up to 2500 hr. The influence of preoxidation and CeO_2 -surface application followed by preoxidation on the corrosion resistance of this material was assessed. The improvement in the corrosion resistance due to preoxidation of the blank material was small, whereas the effect of the CeO_2 -treatment was significant. This difference is thought to be due to better scale adherence in the case of CeO_2 -surface application.

KEY WORDS: Alloy 800H; oxidation/sulphidation; preoxidation; reactive elements.

INTRODUCTION

In several high-temperature technical processes, such as coal-gasification, the structural components are exposed to environments of low-oxygen and high-sulphur activities. Sulphur especially, can significantly reduce the service life of metallic components. The ability of alloys to resist attack by S in these situations normally depends upon their potential to form and maintain a protective oxide scale (e.g., Cr_2O_3 or Al_2O_3). In this context the addition of reactive elements, such as yttrium and cerium, is of interest for an improved protectiveness of the scale (see, e.g., Ref. 1) The present paper

^{*}Commission of the European Communities, Institute for Advanced Materials, Petten Establishment, P. O. Box 2, 1755 ZG Petten, The Netherlands.

[§]Present address: Commission of the European Communities, Institute for Advanced Materials, Ispra Establishment, 21020 Ispra (Varese), Italy.

[†]Laboratory for Materials Science, Delft University of Technology, The Netherlands.

[‡]Department of Chemical Technology, Twente University, The Netherlands.

deals with the corrosion behavior of a 20Cr-32Ni wrought austenitic steel, Alloy 800H, under conditions simulating a coal-gasification environment. The material has been tested in the blank condition and after preoxidation following a previous Ce sol-gel treatment. For comparison a few tests were performed on material preoxidized only.

EXPERIMENTAL

The alloy investigated came from a commercial heat and had the composition as shown in Table I. The material was given a solution anneal of 0.5 hr at 1150°C followed by water quenching. Cylindrical corrosion specimens of 20 mm length with a 6 mm diameter were machined and mechanically polished with silicon carbide paper up to 800 grit. Sometimes flat specimens of 10×8×6 mm were used. For final surface cleaning the specimens were degreased in acetone.

Preparation of the samples by the Ce sol-gel technique was performed as follows². Cerium hydroxide $\text{Ce}(\text{OH})_4$ was prepared from ammonium cerium nitrate and ammonia:

and washed with water until a pH of 7 was obtained. The precipitate was stirred in dilute HNO_3 at 60°C, yielding a sol with a pH value of 0.3:

For the electrophoretic deposition on the specimens the sol concentration was adjusted to 0.4 M by the addition of water, while the applied current density was 1 A/m². After a deposition duration of 1.5 hr, followed by drying in air, the ceria deposit was sintered in air by heating the test specimen first to 150°C at a rate of 6°C/hr followed by further increasing the temperature to 850°C at a rate of 30°C/hr. Directly after reaching the maximum temperature the specimen was cooled at a rate of 30°C/hr to ambient temperature.

Testing was generally performed in a mixture of 0.4 v/o H_2S , 7 v/o CO , and 1.2 v/o H_2O in H_2 . The water concentration was obtained by

Table I. Chemical Composition (wt.%) of the Tested Alloy 800H

C	Cr	Ni	Si	Mn	Fe
0.085	19.60	32.2	0.45	0.69	bal.
S	N	Al	Ti		
0.006	0.02	0.38	0.46		

(i.e., Fe, Ni, and Cr as well as for Al, Mn, and Ce). Also shown is the range of possible potentials for coal-gasification atmospheres.

Heating of the samples to test temperature was performed in about 2 hr in the active gas, whereas cooling was in argon. After exposure, the specimens were examined gravimetrically and by metallography. Bulk identification was carried out by X-ray diffraction (XRD).

Microstructural examinations were made using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDX). Additionally, electron probe microanalysis (EPMA), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary neutral mass spectroscopy (SNMS) were performed.

RESULTS

Gas Characterization

In order to control whether equilibrium conditions were attained in the applied gas system, a three-fold approach was applied. In order to determine semiquantitatively the actual S- and O-potentials, pure Fe, Ni, Cr, Co, Nb, and Cr_2O_3 were exposed. Secondly, analyses of the inlet and outlet gas were performed. Finally, the effect of removing individual gas components (e.g., CO and H_2O) from the standard atmosphere on the corrosion behavior was studied.

XRD and XPS results obtained on the pure components after exposure showed sulphidation of Fe and Ni and oxidation of Nb leading to Nb_2O_5 . Cr formed both oxide and sulphide on exposure. No reaction could be observed for Co and Cr_2O_3 .

Inlet and outlet gas compositions as well as the calculated thermodynamic values at 700°C and 150°C (operating temperature of the gas chromatograph) are presented in Table III. It can be seen that if the gas reaches thermodynamic equilibrium at 700°C it will contain up to 2.5 v/o

Table III. Calculated Composition (at 700°C and 150°C) and Analyzed Inlet and Outlet Composition of a H_2 -7CO-1.2 H_2O -0.4 H_2S Gas Mixture with a Total Pressure of 1.5 Bar

	CO (v/o)	CH_4 (v/o)	H_2S (v/o)	H_2O (v/o)
Inlet	7	—	0.4	1.2
Equilibrium 700°C	2.5	5	0.44	6
Equilibrium 150°C	0	8	0.47	9.5
Outlet (150°C)	7	0.01	0.4	1.2

Fig. 2. Mass gain vs. time for corrosion of Alloy 800H at 700°C in two gas mixtures both having $\log P_{O_2} = -23, 2$, and $\log P_{S_2} = -9, 2$.

CO, 5 v/o CH₄, and 6 v/o H₂O. With decreasing temperature, the equilibrium fraction of CH₄ and H₂O increases and decreases for CO. The measured CO, CH₄, and H₂O levels indicate that equilibrium was not achieved for the present system. For example, the measured CO level was 7 v/o, which equals the inlet fraction of CO, but the equilibrium value at 700°C is 2.5 v/o CO. Reversal of the gas reaction, due to the lowering of temperature (150°C) should lead to even lower CO levels. A similar approach can be used for CH₄ and H₂O. Note that from the measured H₂S content, it can be deduced that no starvation of H₂S occurred.

A further control of the actual gas conditions was carried out by studying the corrosive attack caused by different gas mixtures. In this context the influence of CO was of primary interest because of its contribution to the P_{O_2} level. It was found that leaving CO out of the standard gas (gas B in Table II) caused the calculated P_{O_2} to drop by a factor of 35, but the corrosion pattern and extent of corrosion were very similar to those of the standard gas. However, when H₂O was omitted (gas C in Table II) resulting in a calculated P_{O_2} level of only 1.4 times lower than for the standard gas the mass gain was found to increase by about a factor of 2. Finally, for the CO-free gas (D in Table II) with calculated P_{O_2} and P_{S_2} values practically identical to the standard gas, corrosion was observed to be significantly reduced (Fig. 2).

Corrosion Kinetics

Weight-gain measurements were made on blank, preoxidized, and CeO₂-treated Alloy 800H in the standard gas mixture for exposure times

Fig. 3. Mass gain vs. time for corrosion of Alloy 800H in the standard gas at 700°C for blank and preoxidized condition and after CeO₂ treatment.

up to 2500 hr. As shown in Fig. 3, the CeO₂-treated material appeared to be significantly more resistant to corrosion compared with the blank material showing a 25-times smaller weight gain. It should be noted also that preoxidation without Ce led to an improvement in corrosion resistance, but as shown in Fig. 3 the improvement was less marked. Moreover, a rather large scatter in mass gain was observed when only preoxidation was applied. The corrosion kinetics were close to parabolic behavior for both the blank and the CeO₂-treated material, indicative of a diffusion-controlled corrosion mechanism. Determination of the exponent n in the equation

$$\Delta m/A = kt^n \quad (3)$$

where $\Delta m/A$ is the weight gain per unit area of the original surface area (in mg/cm²), t the exposure time (in hr), and k the reaction constant given n values of about 0.5 for both the blank and CeO₂-treated material. With these values the reaction constants were 1.54 and 0.042, respectively.

Corrosion of Alloy 800H

Observations of the sample surface by SEM/EDX depicted a scale that was composed of (Fe, Cr) sulphide crystals (Fig. 4). Cracks were found in the scale and appeared to be both transgranular and intergranular. These cracks might have formed during cooling because no enhanced corrosion was observed on the edges of the cracks. The scale was found to be poorly adherent. On the surface of the sulphide crystals, protrusions of a metallic (Fe, Ni) phase (Fig. 5) could be observed, with a relative frequent appearance on the grain boundaries.

Fig. 4. SEM micrograph of the scale surface of Alloy 800H after exposure for 650 hr at 700°C in the standard gas.

X-ray powder analysis of the scale indicated the presence of a cubic (Fe, Cr) sulphide (M_3S_4) and a hexagonal MS phase. Additionally, an austenitic phase, possibly related to the (Fe, Ni) protrusions, and a minor amount of pentlandite $[(FeNi)_9S_8]$ were detected. XRD analysis on the gas side and on the specimen side of the scale showed that at the specimen side Cr_2O_3 had formed also. Observations with SEM/EDX supported this by a higher Cr-signal relative to the sulphur signal compared with the gas side (Fig. 6). The (Fe, Ni) phase, which was found on the outside of the external scale, was present also in the scale itself, on grain boundaries, and in pores (Fig. 7). The atomic composition of this phase was determined with EPMA to be in the range 1 Fe to 2 Ni.

Cross-sectional examinations of the external scale (Fig. 8) revealed a large amount of porosity. The sulphides composing the scale had a lamellar structure with widths of the lamellae up to 1 μm . Polarized-light microscopy indicated that the alternate layers were, respectively, isotropic and anisotropic. This was in agreement with the XRD observations of the presence of a cubic (M_3S_4) and a hexagonal (MS) phase. SEM/EDX analysis indicated that the MS phase was richer in Fe, while the M_3S_4 phase was enriched in Cr. Figure 9 shows element distributions for the external scale. The alternate lamellae, richer either in iron or chromium, could be observed

Fig. 5. SEM micrograph of the scale surface and EDX spectra of Alloy 800H after exposure for 696 hr at 700°C in the standard gas.

as well as an (Fe, Ni) inclusion. Quantitative EPMA to determine more precisely the composition of the lamellae failed due to the poor lateral resolution and relatively high information depth of conventional EPMA.

SEM/EDX observations of the specimen after removal of the external scale showed a smooth surface with a high Cr-signal, indicative of chromia (Fig. 10). Some sulphide crystals had remained after stripping the scale. XRD analysis of the surface indicated the presence of the same phases present at the specimen side of the scale (i.e., M_3S_4 , MS, Cr_2O_3 , and austenite). In this case the austenite signal resulted from the matrix.

Fig. 6. SEM micrographs and EDX spectra of corrosion scale of Alloy 800H after removal from the specimen exposed for 1023 hr at 700°C in the standard gas: (a) and (b) gas side; (c) and (d) specimen side.

Cross-sectional examination displayed two internal-corrosion zones (Fig. 11). The outermost zone was characterized, similar to the external scale, by a lamellar appearance, but the average crystal size was smaller. The composition of the lamellae was essentially the same as for those of the external scale, but EPMA indicated that this zone contained more oxides. The innermost corrosion zone was composed of individual sulphides,

Fig. 7. SEM micrographs of scale cross-section after rupture of scale, presented in Fig. 6 (right is higher magnification of framed area in left picture).

Fig. 8. Optical micrograph showing lamellar structure of the scale formed on Alloy 800H after exposure for 163 hr at 700°C in the standard gas.

Fig. 9. Element distribution maps for the scale of Alloy 800H exposed for 650 hr at 700°C in the standard gas.

Fig. 10. SEM micrograph and EDX spectrum of specimen after removal of the external scale. Alloy 800H exposed for 1023 hr at 700°C in the standard gas.

Fig. 11. Optical micrograph showing external and internal corrosion of Alloy 800H after exposure for 575 hr at 700°C in the standard gas.

Fig. 12. Optical micrograph showing carbide precipitates preferentially along grain and twin boundaries in Alloy 800H after exposure for 1023 hr at 700°C in the standard gas.

some of them showing a lamellar structure. Deeper into the material, monophasic sulphides rich in Cr with some Mn and Fe appeared. Directly beneath the innermost corrosion zone a high concentration of carbides could be observed (Fig. 12). EPMA of this area indicated an average carbon content of 0.3 wt.%, whereas for the noncarburized bulk material an average of 0.07 wt.% carbon was identified, which is in close agreement with the chemical analysis of the material (Table I).

Surface Condition of CeO₂-Treated Alloy 800H

The morphology of the scale after application of the CeO₂ treatment (Fig. 13) was characterized by a systematically packed structure. XRD analysis indicated the presence of CeO₂ and Cr₂O₃, and EDX and EPMA depicted an enrichment in Ce, Cr, Mn, and a slight enrichment in Ti and Si. Because of the high penetration depth of these techniques, they are only semiquantitative with respect to the analysis of the scale composition. By SEM cross-sectional examination, the total thickness of the oxide layer (i.e., CeO₂ and Cr₂O₃ together) was determined to be about 0.5 μm. XPS was applied to obtain element-depth profiles over the oxide layer. The spectra were quantified by applying the elemental sensitivity factors of C. K.

Fig. 13. SEM micrograph of the surface of CeO₂-treated, preoxidized Alloy 800H.

Jørgensen and H. Berthou³. The oxidation state of the elements was deduced by comparing the peak position relative to that of Cls. The measurements (Fig. 14a) indicated a thin outer layer of CeO₂ followed by a layer of principally Cr₂O₃ with a gradually decreasing content of Ce toward the bulk alloy. It was not clear by XPS in which chemical form the Mn was present. AES measurements indicated that most of the Mn was present in connection with the Cr₂O₃, but no quantitative data could be obtained from these measurements.

Additional SNMS profiling (Fig. 14b) showed for the major elements a pattern similar to XPS profiling, but due to the higher sensitivity of SNMS, an increased amount of Ti in the oxide scale became clearly visible and also a slight enrichment of Si. The relative intensity in Fig. 14b is only indicative of the atomic percentage of the elements, since average sensitivity factors⁴ were taken for the calculations, and no standards for calibration were used. It should be mentioned that SEM observations after sputtering showed a relatively smooth surface for both the XPS and the SNMS sputtered areas, which allows one to conclude that the results are not markedly disturbed by surface roughening due to sputtering.

Comparative analyses were carried out on the oxide scale formed on blank Alloy 800H which had been preoxidized under conditions identical

Fig. 14. Element profiles of the layer formed on CeO₂-treated, preoxidized Alloy 800H obtained by (a) XPS, (b) SNMS.

to those used for the CeO₂-treated material. The total thickness of the oxide layer was about 0.3 μm . Visual examination and further SEM observations revealed significant scale spallation after the oxidation treatment on several specimens. Unspalled areas (Fig. 15) showed locally advanced oxidation, possibly related to the grain boundaries of the substrate. XRD analysis indicated the presence of both Cr₂O₃ and an oxide spinel. XPS profiling (Fig. 16) showed a high concentration of Cr and Mn in the oxide layer.

Corrosion of CeO₂-Treated Alloy 800H

After exposure to the aggressive environment (standard gas) up to about 2500 hr, the CeO₂-treated specimens appeared relatively unattacked compared to the blank material. Contrary to the latter, which showed a rather dense sulphide scale, only individual sulphide crystals of two different sizes formed on the sample surface (Fig. 17). SEM/EPMA revealed that the

Fig. 15. SEM micrograph of the surface of blank Alloy 800H after preoxidation.

smaller sulphides with dimensions up to about $4\text{ }\mu\text{m}$, consisted essentially of Mn with minor amounts of Cr and Fe, and were more or less uniformly distributed. The nucleation of such small sulphides can be seen in Fig. 18. A few sulphides larger than $10\text{ }\mu\text{m}$, containing mainly Cr and small amounts of Mn and Fe, were concentrated locally.

Fig. 16. XPS element profiles of the scale formed on blank Alloy 800H by preoxidation.

Fig. 17. EPMA of the surface of CeO_2 treated preoxidized Alloy 800H after exposure for 2252 hr at 700°C in the standard gas (bottom is higher magnification of framed area shown in upper picture). Quantitative EPMA (atomic %):

position	S	O	Cr	Fe	Ni	Mn	Al	Si	Ti	Ce
1	56	—	39	2	0.6	2	0.3	—	—	—
2	49	—	5	2	0.4	43	0.5	0.3	0.4	0.3
3	1	52	27	9	4.4	2	0.1	1.4	1.6	1.5

Fig. 18. SEM micrograph showing nucleation of a small sulphide on surface of CeO_2 -treated, preoxidized Alloy 800H after exposure for 192 hr at 700°C in the standard gas.

Cross-sectional examinations showed that internal corrosion appeared locally (Fig. 19), occurring in regions associated with relatively severe external attack. However, regions exhibiting external attack with no indication of associated internal corrosion, were also frequently observed. It should be noted that the internal attack was not specifically related with grain boundaries. Element distribution and point analysis were carried out by EPMA at a region where an external sulphide nodule was already large and associated with internal corrosion. As shown in Fig. 20, the nodule contained mainly Cr and S with minor amounts of Mn and Fe. This is in agreement with surface EPMA of the large nodules (Fig. 17). The internal-corrosion products were mainly oxides of Cr, Al, Si, and Ti, whereas a minor amount consisted of (Mn, Cr) sulphides.

DISCUSSION

Gas Characterization

The behavior of Fe, Ni, Co, Nb, and Cr_2O_3 was in accordance with the position of the calculated oxygen and sulphur potentials of the atmosphere in the related thermodynamic stability diagrams. The observation of

Fig. 19. Optical micrograph showing the corrosion pattern of CeO_2 -treated, preoxidized Alloy 800H after exposure for 663 hr at 700°C in the standard gas.

Cr sulphide next to Cr oxide is in agreement with the observations of several workers.⁵⁻⁷ Due to kinetic factors, the oxygen activity of the gas at a constant sulphur activity has to be higher than expected from thermodynamic calculations to form only oxide. This shift from the thermodynamic boundary to a “kinetic boundary” can be about 3–5 orders of magnitude.

The gas analyses have shown that under the testing conditions employed the calculated thermodynamic equilibrium was not achieved. It can be assumed that the actual oxygen partial pressure $P_{\text{O}_2}^*$ was provided by the inlet $\text{H}_2\text{O}/\text{H}_2$ ratio, whereas CO did not contribute to $P_{\text{O}_2}^*$. The $P_{\text{O}_2}^*$ for the standard gas mixture was therefore about 35 times less than the calculated one (Table II). On the other hand, the $P_{\text{O}_2}^*$ value in the $\text{Ar}-20\text{H}_2-0.1\text{H}_2\text{S}-1.2\text{H}_2\text{O}$ gas mixture equals the calculated one (i.e., was 25 times higher than the $P_{\text{O}_2}^*$ of the standard gas mixture).

Corrosion of Alloy 800H

The investigations have shown that the blank Alloy 800H suffered severe external and internal corrosion. Three corrosion zones could be distinguished: an external scale and two internal zones. The scale consisted mainly of sulphides that contained primarily Cr and Fe and small amounts of Ni and Mn with some oxygen also being present. It should be noted that

Fig. 20. Cross-sectional element-distribution maps and quantitative EPMA of a representative place of CeO_2 -treated, preoxidized Alloy 800H after exposure for 663 hr at 700°C in the standard gas. Quantitative EPMA (atomic %):

position	S	O	Cr	Fe	Ni
1	57	—	36	3	1
2	3	48	24	10	5
	Mn	Al	Si	Ti	
1	—	—	—	—	
—	—	5	3	2	

no Ni sulphides were detected, although sulphidation occurred on pure Ni. This discrepancy has to be explained by the lower Ni activity in the alloy (about 0.3), which demands an increase in sulphur partial pressure by a factor of about 30 to form Ni_3S_2 .

The (Fe, Ni) phase observed on top of the scale and at various regions inside the scale was formed very probably during cooling. This was confirmed by corrosion experiments on a Fe-50%Ni alloy, which sulphidized at a significant rate, showing that the metallic phase is not stable under the present environmental conditions. It can be argued that the scale at the actual test temperature consisted primarily of (Fe, Cr)S with small amounts of Ni, which during cooling disproportionated to iron-rich (Fe, Cr)S, FeCr_2S_4 and the metallic (Fe, Ni) phase. Both (Fe, Cr)S and FeCr_2S_4 appeared in lamellar form. It has been suggested for a sulphidized Fe-20Ni-25Cr alloy that, due to the high diffusion coefficients of Fe and Ni in the

Fig. 20. Continued.

(Fe, Cr(Ni))S phase, the metallic phase is rapidly formed at favorable locations, such as grain boundaries and free surfaces.⁸

The outermost internal corrosion zone had essentially the same corrosion appearance as the external scale, but the crystal size of the corrosion products was smaller. A possible explanation might be that because the sulphides are supposed to nucleate also on carbides, more nucleation sites are available in the interior of the sample compared to the free surface.

The innermost corrosion zone was composed of individual (Cr, Fe, Mn) sulphides. Some of them showed a lamellar appearance composed of alternating Fe-rich (Fe, Cr)S and FeCr_2S_4 phases. Toward the specimen core the sulphides were monophased and contained mainly Cr with a minor Mn and Fe content. At this stage the Fe content is not yet high enough for phase decomposition to occur upon cooling.

Beneath the innermost internal corrosion zone an increased density of carbides could be distinguished. This is thought to be due to a supplanting process during which carbides are transformed into sulphides thereby releasing carbon which penetrates further into the substrate to form new carbides.^{6,9,10} It is expected, considering the width of the zone compared to that seen after exposure in the CO-free gas, that a significant ingress of carbon from the environment occurred.

Corrosion of CeO_2 -Treated Alloy 800H

The results indicated that the scale formed on the CeO_2 -treated samples after preoxidation was composed mainly of an outer layer consisting of rather closely packed CeO_2 particles, which were positioned on a Cr_2O_3 layer. The CeO_2 particles tended to conglomerate without forming a tight continuous layer. Such a morphology (i.e., a discontinuous layer of CeO_2 on a Cr_2O_3 sublayer) causes severe difficulties for accurate determination of the composition of the various surface layers by techniques with a relatively large analysis area. For instance, the chemical state of the Mn related to the Cr_2O_3 scale could not be discerned.

On some samples a thicker layer of CeO_2 had been deposited locally. This caused severe conglomeration of the CeO_2 particles during the preoxidation treatment, which in turn led to fracturing, and the formation of a flake-like surface morphology similar to that observed by others.^{2,11} In this case the protectiveness of the scale in the present S-O-C atmosphere was very poor. Thus a very careful treatment during CeO_2 application particularly concerning the coverage must be guaranteed in order to achieve an optimized corrosion resistance.

Regarding the mechanism of preoxidation of the CeO_2 -treated material, it has been suggested that the addition of reactive elements to Cr_2O_3 -forming

alloys could result in the replacement of a cation-transport-dominated oxidation by an anion-dominated one.¹¹⁻¹⁴ The finding that CeO_2 was observed mainly on top of the scale may be considered as a preliminary indication of such a mechanism, assuming that CeO_2 acted as a marker. However, another reason for the CeO_2 being in the outermost position might be a displacement of the CeO_2 particles by the Cr_2O_3 scale growing in the usual manner (i.e., by cation diffusion). The displacement of inert markers by a growing oxide layer was observed by other workers.¹⁵ The observation of small amounts of Ce, possibly as CeO_2 , present in the underlying Cr_2O_3 layer, also indicates cation diffusion.

Analyses of the CeO_2 -treated samples exposed to the S-O-C bearing gas revealed numerous small Mn sulphides on the scale surface, which apparently formed the initial surface corrosion products. Although the Mn present in the oxide scale could contribute to the MnS formation, the high amount of MnS certainly required an additional supply of Mn from the substrate alloy. Mn is known to diffuse relatively easily through Cr_2O_3 —for example, a factor of 1000 faster than Cr.¹⁶ Diffusion probably takes place locally along fast diffusion paths (e.g., oxide grain boundaries).^{13,17-21}

After MnS has formed as the initial phase at discrete regions (e.g., regions with a less-protective quality of oxide) the evolution of the larger (Cr, Mn) sulphides occurs. It should be noted that even after 2500 hr of exposure the external sulphide nodules contained mainly Cr, whereas Fe and Ni were nearly absent. Hence, the preformed oxide layer forms a good barrier for Fe and Ni outward transport. This is consistent with observations made under oxidizing conditions.^{22,23} This confirms that through scale cracks or sulphide channels through the oxide layer did not form, because otherwise the formation of Fe and Ni sulphides should be expected.^{24,25}

Internal corrosion of the CeO_2 -treated material became clearly visible only when the larger Cr-rich external sulphide nodules were already present. EPMA showed that the internal corrosion products were mainly oxides of Cr, Al, Si, and Ti, whereas a minor amount consisted of (Mn, Cr) sulphides. The slightly increasing S level at greater depths is possibly related to release of S from the initially formed corrosion products by oxide/sulphide transformation, as has been discussed by others.^{6,26-28} The small amount of internal-corrosion products in comparison to that of the external ones shows that in spite of a relatively long exposure time the preformed oxide layer retains its good resistance against O and S inward diffusion.

For an explanation of the considerably improved corrosion-resistance of the CeO_2 -treated material compared to the blank preoxidized material, two features are thought to be relevant. Both the XRD and XPS analysis showed that the oxide layer on the untreated material contained a Mn-rich spinel, whereas on the CeO_2 -treated material this spinel phase has not been

found, although a relatively high Mn content was observed. This agrees with the work of others, showing that the addition of reactive elements reduces the amount of spinels relative to chromia.²⁹⁻³¹ Oxide spinel phases are known to form rapid diffusion paths in oxide scales.^{32,33} However, the main reason for the improved corrosion-resistance is expected to be the much better adherence of the oxide scale as demonstrated by the absence of any spalled areas after the preoxidation treatment. Samples of the blank material after preoxidation exhibited various places from which the scale had spalled and which were found to be heavily attacked upon exposure to the aggressive gas. Only slight corrosion occurred where the oxide layer was still present, although for the latter the attack was more severe than in the case of CeO₂-treated specimens. The exact reason for this is unclear, but it might be related to the presence of the spinel in the case of the untreated preoxidized specimens.

Several mechanisms have been proposed for an improved oxide adherence due to the application of reactive elements or their oxides^{1,34-36}:

- modifications of growth processes;
- graded-seal formation;
- vacancy-sink provision;
- oxide pegging;
- better chemical bonding, including tramp element gettering effect;
- enhanced scale plasticity.

Based on the observations made, some of the aforementioned mechanisms can be excluded for the system under investigation. As has been discussed before, a change from cation-dominated to anion-dominated oxide growth could not be confirmed. Results obtained with SEM as well as with XPS and SNMS profiling do not indicate a graded seal of CeO₂ but rather a discontinuous distribution of CeO₂ particles on Cr₂O₃. Since the CeO₂ was not present in the alloy, the particles could not act as vacancy-sinks. The absence of oxide pegs suggests that peg-assisted mechanical keying is not responsible for the observed adherence. Improved adhesion of the oxide on the CeO₂-treated material could be attributed to the two remaining mechanisms (i.e., stronger chemical bonding and/or improved scale plasticity). Concerning these two points, various contradicting discussions can be found in the literature. The application of CeO₂ may improve the interfacial bonding between oxide scale and alloy (e.g., by scavenging of impurity elements, particularly sulphur).³⁵⁻³⁹ This "sulphur theory" not only applies to pure reactive element additions, but also to their oxides which are known to have a strong tendency to form oxysulphides.^{40,41} Results from recent studies, however, have indicated that sulphur segregation, although it might decrease the strength of the bond, is possibly not the major cause of scale spallation.^{11,42} With respect to improved scale plasticity it has been

suggested that this is due to decreased oxide grain size caused by an increased number of nuclei present for oxidation.^{11,14,31,43-49}

SUMMARY AND CONCLUDING REMARKS

Exposure of Alloy 800H to a coal-gasification atmosphere simulating S-O-C bearing gas at 700°C was found to cause severe external and internal corrosion leading to mainly (Fe, Cr) sulphide formation. The application of CeO₂ to the surface followed by preoxidation led to a significant improvement in the corrosion-resistance, whereas only a minor effect could be achieved by preoxidation of the blank material. The main reason for the better corrosion behavior due to the CeO₂ treatment is expected to be the much better adherence of the oxide scale. From a critical comparison of the existing theories concerning this feature with the present results, it was concluded that the better adherence is probably related to either a better chemical bonding at the scale/substrate interface or enhanced scale plasticity. Corrosion of the CeO₂-treated material in the S-O-C bearing gas commenced with the external formation of more or less uniformly distributed small Mn sulphides. Later, at discrete regions, the evolution of larger (Cr, Mn) sulphides occurred. The initiation of internal corrosion, leading mainly to oxidation, was found to be retarded relative to the external attack, and only appeared at places beneath the larger (Cr, Mn) sulphides.

From the present work it is concluded that by the application of CeO₂ to the surface, followed by preoxidation, Alloy 800H can be protected in S-O-C type atmospheres, characterized by a high sulphur activity and a low oxygen activity even for periods of several thousand hours. The extent to which this also holds for superimposed mechanical deformation, which can lead to cracking of the protective oxide layer, is the subject of further investigations.^{50,51}

ACKNOWLEDGMENTS

The authors wish to thank Mr. B. Geerdink of the Department of Chemical Technology, University of Twente, for the CeO₂ surface application of the specimens.

They are grateful to Dr. H. Peters of Leybold, Cologne, for providing the SNMS facilities, to Mr. D. Schalkoord of the Laboratory for Materials Science, Delft University of Technology, for providing EPMA facilities, and to Dr. A. Manara of I.A.M. Ispra for performing the AES measurements.

Dr. J. B. Marriott, for helpful discussions during the preparation of the manuscript, and the technical assistance of the staff of I. A. M. Petten, in particular, Messrs. G. von Birgelen (XPS), P. Frampton (OM), Ph. Glaude

(XRD), A. E. Moulaert (EPMA), H. Rother (thermodynamic calculations), and K. Schuster (SEM) are kindly acknowledged.

REFERENCES

1. H. S. Hsu, *Oxid. Met.* **28**, 213 (1987).
2. T. Fransen, M. A. de Jongh, M. M. A. Perik, and P. J. Gellings, *Proc. 9th Int. Cong. Metall. Corros.* **4**, 311 (1984).
3. C. K. Jørgensen and H. Berthou, *Chem. Soc. Faraday Discuss.* **54**, 269 (1973).
4. H. Oechsner, in *Topics in Current Physics*, Vol. 37, H. Oechsner, ed. (Springer-Verlag, Berlin, 1984), p. 63.
5. T. C. Tiearny Jr. and K. Natesan, *J. Mat. Energ. Systems* **1**, 13 (1980).
6. D. S. Williams, R. Möller, and H. J. Grabke, *Oxid. Met.* **16**, 253 (1981).
7. M. H. La Branche and G. J. Yurek, *Oxid. Met.* **28**, 73 (1987).
8. D. B. Rao and H. G. Nelson, *Oxid. Met.* **12**, 111 (1978).
9. J. Barnes, J. Corish, and J. F. Norton, *Oxid. Met.* **26**, 333 (1986).
10. T. Narita and T. Ishikawa, *Mater. Sci. Eng.* **87**, 51 (1987).
11. P. Y. Hou and J. Stringer, *Mater. Sci. Eng.* **87**, 295 (1987).
12. P. Skeldon, J. M. Calvert, and D. G. Lees, *Phil. Trans. R. Soc. Lond. A* **296**, 557 (1980).
13. C. M. Cotell, G. J. Yurek, R. J. Hussey, D. F. Mitchell, and M. J. Graham, *J. Electrochem. Soc.* **134**, 1871 (1987).
14. G. M. Ecer, R. B. Singh, and G. H. Meier, *Oxid. Met.* **18**, 55 (1982).
15. E. W. A. Young and J. H. W. de Wit, *Solid State Ionics* **16**, 39 (1985).
16. R. K. Wild, *Corr. Sci.* **17**, 87 (1977).
17. K. P. Lillerud and P. Kofstad, *Oxid. Met.* **17**, 127 (1982).
18. A. Atkinson, *Rev. Modern Phys.* **57**, 437 (1985).
19. H. V. Atkinson, *Oxid. Met.* **24**, 177 (1985).
20. R. J. Hussey, D. F. Mitchell, and M. J. Graham, *Werkst. Korros.* **38**, 575 (1987).
21. E. W. A. Young, J. H. Gerretsen, and J. H. W. de Wit, *J. Electrochem. Soc.* **134**, 2257 (1987).
22. M. Yamawaki, M. Mito, and M. Kanno, *Trans. JIM* **18**, 567 (1977).
23. F. I. Wei and F. H. Stott, *High Temp. Tech.* **7**, 59 (1989).
24. S. H. Choi, doctoral thesis, University of California, 1985.
25. F. H. Stott and M. F. Chong, *Solid State Ionics* **12**, 493 (1984).
26. S. H. Choi and J. Stringer, *Mater. Sci. Eng.* **87**, 237 (1987).
27. M. F. Stroosnijder, J. F. Norton, V. Guttmann, M. J. Bennett, and J. H. W. de Wit, *Mater. Sci. Eng.* **A116**, 103 (1989).
28. J. H. Davidson, G. Beranger, F. Armanet, M. Tachikart, O. Cayla, J. Sannier, P. Fauvet, A. Lefort, and G. Silvestre, in *Proc. Conf. High Temperature Alloys for Gas Turbines and Other Applications*, Vol. 2, W. Betz, R. Brunetaud, D. Coutouradis, H. Fischmeister, T. B. Gibbons, I. Kvernes, Y. Lindblom, J. B. Marriott, and D. B. Meadowcroft, eds. (D. Reidel Publishing Company, Dordrecht, 1986), p. 1305.
29. T. N. Rhys-Jones, H. J. Grabke, and H. Kudielka, *Werkst. Korros.* **38**, 65 (1987).
30. K. Przybylski, *Proc. 10th Int. Symp. Reactivity of Solids*, Dijon, 241 (1984).
31. P. Y. Hou and J. Stringer, *Oxid. Met.* **29**, 45 (1988).
32. H. J. Grabke and P. Papaioacovou, in *Proc. 8e Congrès European Corrosion* (Nice, November 1985).
33. M. Loudjani, J. C. Pivin, C. Roques-Carmes, P. Lacombe, and J. H. Davidson, *Met. Trans.* **13A**, 1299 (1982).
34. D. P. Whittle and J. Stringer, *Phil. Trans. R. Soc. Lond. A* **295**, 309 (1980).
35. J. G. Smeggil, A. W. Funkenbusch, and N. S. Bornstein, *Met. Trans.* **17A**, 923 (1986).
36. D. G. Lees, *Oxid. Met.* **27**, 75 (1987).
37. Y. Ikeda, K. Nii, and K. Yoshihara, in *High Temperature Corrosion of Metals and Alloys*, Supplement to *Trans. Jap. Inst. Met.* **24**, 207 (1983).
38. J. G. Smeggil, *Mater. Sci. Eng.* **87**, 261 (1987).

39. D. R. Sigler, *Oxid. Met.* **29**, 23 (1988).
40. P. E. Waudby, *Int. Met. Reviews* **2**, 74 (1978).
41. W. G. Wilson, L. J. Heaslip, and I. D. Sommerville, *J. Metals* **37**, 36 (1985).
42. K. L. Luthra and C. L. Briant, in *Fundamental Aspects of High Temperature Corrosion*, Vol. II, D. A. Shores and G. J. Yurek, eds. (The Electrochemical Society, Pennington, 1986), pp. 187, 200.
43. T. N. Rhys-Jones, H. J. Grabke, and H. Kudiella, *Corros. Sci.* **27**, 49 (1987).
44. J. Stringer, B. A. Wilcox, and R. I. Jaffee, *Oxid. Met.* **5**, 11 (1972).
45. S. Mrowec, A. Gil, and A. Jedlinski, *Werkst. Corros.* **38**, 563 (1987).
46. C. H. Yang, P. A. Labun, G. Welsch, T. E. Mitchell, and M. J. Bennett, *J. Mater. Sci.* **22**, 449 (1987).
47. M. Landkof, A. V. Levy, D. H. Boone, R. Gray, and E. Yaniv, *Corrosion* **41**, 344 (1985).
48. I. Wolf, H. J. Grabke, and P. Schmidt, *Oxid. Met.* **29**, 289 (1988).
49. V. A. C. Haanappel, T. Fransen, B. Geerdink, and P. J. Gellings, *Oxid. Met.* **30**, 201 (1988).
50. M. F. Stroosnijder, V. Guttman, R. J. N. Gommans, and J. H. W. de Wit, *Mat. Sci. Eng. A* **121**, 581 (1989).
51. M. F. Stroosnijder, V. Guttman, and J. H. W. de Wit, *Proc. 9th European Congress on Corrosion* (Utrecht, October 1989, Vol. II, EG257).