The Properties of Protective Oxide Scales Containing Cerium on Alloy 800H in Oxidizing and Oxidizing/Sulphidizing Environments

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The corrosion protection of oxide scales formed by electrophoretic deposition in a cerium-containing sol on Alloy 800H, a 32Ni-20Cr steel, followed by firing in air at 1123 K was studied in oxidizing and mixed oxidizing/sulphidizing environments at elevated temperatures. In particular, the influence of type of sol solvent, sol concentration, and thickness of deposited layer on the protection were studied. An optimized treatment was deduced which led to a significant improvement in corrosion behavior in oxidizing/sulphidizing environments.

KEY WORDS: Alloy 800H; sulphidation; oxidation; sol/gel method; cerium; reactive elements; ceramic coatings; thermogravimetric experiments.

INTRODUCTION

Advanced coal-conversion processes, such as atmospheric fluidized-bed combustion and pressurized coal gasification, offer great potential because of several advantages, like reduced SO₂- and NO_x-emissions. However, metallic components to be used in these systems are subjected to severe conditions, resulting in high-temperature corrosion, erosion, and mechanical damage due to stresses. Although the present generation of high-temperature alloys shows generally acceptable mechanical properties,

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the poor corrosion resistance for the above-mentioned applications causes significant problems. Due to the low oxygen and high sulphur activities of the environments, the formation of a protective oxide layer may be difficult, and rapid sulphidation can be expected. Even at temperatures as low as 823 K, sulphidation can cause catastrophic failure of the construction materials, even after short exposure times, while the constructions have required lifetimes of several years.

Preoxidation can render protection to high-temperature alloys exposed to oxidizing-sulphidizing conditions,^{1,2} but in general only for a limited time. To extend the lifetime of a scale obtained by preoxidation, the addition of reactive elements, such as cerium and yttrium, is of interest because of their beneficial effects on oxide scale properties, including resistance to spallation.³ Addition of these elements is possible either by alloying or by incorporation into a surface layer (for instance, by ion implantation or by coating). A relatively cheap approach is the use of the sol/gel technique,⁴⁻⁷ based on the use of sols, which consist of a dispersion of colloidal particles of hydrous oxides or hydroxides. The sol can be applied to the surface by electrophoresis or dipping followed by low-temperature drying and firing at temperatures up to about 1123 K. On drying, water between the colloidal particles is removed, and the sol is converted to a gel. On firing, the gel is transformed irreversibly to a ceramic material and will become part of the oxide layer which is formed on the alloy. Although the influence of superficially applied oxides of reactive elements has been investigated mainly in oxidizing environments,⁴⁻¹⁴ they offer also a possibility for use of the sol-gel technique in combination with the preoxidation treatment during firing for protection in mixed oxidizing/sulphidizing environments.⁷

In this paper, the influence of CeO_2 , electrophoretically deposited from a cerium-containing sol followed by firing in air, on the corrosion behavior of Alloy 800H in oxidizing and mixed oxidizing/sulphidizing environments is reported. The influence of the coating parameters as well as the sol stability on the protective quality of the preformed oxide layers are emphasized. For comparison, some tests were performed on material which was preoxidized under similar conditions as applied during firing of the gel.

EXPERIMENTAL PROCEDURES

Material

The chemical composition of the austenitic steel, Alloy 800H, which was investigated, is given in Table I. The material was annealed in two steps: 1 hr at 1348 K, followed by water quenching, and additionally 1 hr at 1223 K, followed by water quenching again. Cylindrical corrosion specimens of 20 mm length and 5 mm diameter and disk-type samples of 10 mm

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

Fe	Cr	Ni	C	Mn	Si	Ti
Bal.	19.9	31.7	0.08	0.7	0.5	0.4

diameter and approximately 3 mm thickness were used. The final surface finish was performed by grinding with 800-grit carborundum paper. All test specimens were ultrasonically cleaned with hexane, ethanol, and acetone prior to coating.

Preparation of the Samples

Preparation of the samples by the sol/gel technique was performed according to the following procedures.

Cerium hydroxide ($\text{Ce}(\text{OH})_4$) was prepared from ammonium cerium nitrate and ammonia:

The precipitate was stirred in dilute HNO_3 at 333 K, yielding a sol with $\text{pH} = 0.3$:

To achieve different concentrations of the sol, acetone or water was added. The sol was applied on the specimen surfaces by electrophoretic deposition. The deposition conditions of the main methods are listed in Table II. Acetone, which, for example, was used in method A, is of interest as a solvent, since it is known that the hydrogen evolution during the electrophoretic deposition,¹⁵ which would hinder homogeneous deposition, is reduced by the reaction:

Table II. Electrophoretic Conditions of the Main Applied Deposition Methods

Method	Conc. Ce-sol (mol l^{-1})	Solvent	Current density ($\text{A} \cdot \text{m}^{-2}$)	Electr. time (min)
A	0.05	80% acetone	0.6	20
B	0.40	water	1.0	90

After electrophoretic deposition, the specimens were dried in air for 16 hr at 293 K, followed by sintering of the ceria deposits in air by heating, first to 423 K at a rate of 6 K/hr, and then to 1123 K at a rate of 30 K/hr. Directly after reaching the maximum temperature, the specimens were cooled at a rate of 30 K/hr to 293 K. This sintering procedure, being carried out in air, is at the same time a preoxidation treatment. In a previous investigation,⁸ the state of the cerium in the layer after this treatment has been discussed.

Testing of Specimens

Testing of the specimens was performed under purely oxidizing conditions and in oxidizing/sulphidizing gas mixtures. The oxidation experiments were carried out in a Setaram automatic recording electro-balance in pure oxygen at atmospheric pressure. The sensitivity of the balance was approximately 0.01 mg. The gas was flowing continuously through the system at a rate of about 0.3 l/hr.

For testing in the oxidizing/sulphidizing environments, spring balances were used, the design of which is shown in Fig. 1. The balance consisted of two vertical tubes. The upper pyrex tube (double-walled) was water-cooled (303 K) and controlled by means of a thermostat, to provide a uniform response along the spring. The lower quartz tube and the cylindrical furnace could be moved vertically. The balance was connected to a vacuum system, the aggressive gas source, and a manometer. The entire volume (10 l) could thus be evacuated, and the desired gas mixture was introduced

Fig. 1. Testing facility (spring balance) for the oxidizing/sulphidizing environments.

Table III. Calculated Oxygen (p_{O_2}) and Sulphur (p_{S_2}) Partial Pressures (in atm) as Function of Temperature for the Applied Gas Mixture

Temperature (°C)	p_{O_2}	p_{S_2}
550	9×10^{-29}	1×10^{-9}
600	6×10^{-27}	5×10^{-9}
650	2×10^{-25}	2×10^{-8}
700	7×10^{-24}	7×10^{-8}

into the tube. Temperature measurements were performed during the experiments with a chromel-alumel thermocouple, placed close to the specimen. The sensitivity of the spring balances used was about 0.1 mg. For testing, the spring balance, in which the sample was suspended, was first flushed with argon for 16 hr with a flow rate of 10 l/hr. The argon was saturated with water at 288 K. After this, a mixture of 5% H_2S in H_2 with a flow rate of 3 l/hr was introduced into the argon flow. After 2 hr, in order to stabilize the flow, the furnace was heated to the test temperature. The whole system was flushed for another 5 hr and then closed. Testing temperatures ranged from 823–973 K. The calculated oxygen and sulphur partial pressures of the gas mixtures at the various temperatures are listed in Table III. From the position of the calculated oxygen and sulphur potentials of the atmosphere in the related thermodynamic stability diagrams, it follows that Cr_2O_3 , Ni_3S_2 , and FeS are thermodynamically stable phases.¹⁰ Additionally, some experiments were carried out in 5% H_2S in H_2 , in which the water concentration, present as an impurity, was approximately 20 ppm.

RESULTS

Preliminary results showed that the use of acetone as a solvent was less favorable due to sol aging, resulting in a layer of poor performance. An example is shown in Fig. 2a; the formed oxide showed a flake-like morphology. The methods where water was used as a solvent gave significantly better results and no effect of sol aging was observed after 4 weeks (Fig. 2b). To find the optimum treatment, the test parameters were varied over a wider range. The results showed that method B yielded the best results upon exposure to the oxidizing/sulphidizing environments. Thinner cerium oxide deposits, obtained by decreasing the sol concentration or time of electrophoresis, gave insufficient protection. With thicker cerium oxide deposits, the protectiveness decreased also. This is obvious from Fig. 3, where an oxide scale of 0.25 mg/cm^2 , equal to an oxide thickness of

Fig. 2. SEM-micrographs of cerium oxide surface-treated Alloy 800H with cerium oxide application using sols aged for 4 weeks, following (a) method A and (b) method B.

approximately $0.5\ \mu\text{m}$, applied, following method B, gave the best protection. The optimum procedure leads to an oxide layer of rather close-packed cerium oxide particles positioned on a layer mainly consisting of Cr_2O_3 .¹⁴ However, if a thicker layer of cerium oxide was deposited, severe agglomeration of cerium oxide particles occurred, which in turn led to a flake-like morphology after firing (Fig. 4). The optimum CeO_2 treatment gave a significant improvement in corrosion resistance in oxidizing/sulphidizing environments in comparison to the untreated alloy, as can be seen from Fig. 5.

Also in oxidizing conditions the cerium-oxide-surface-treated material behaved better in comparison to specimens that were only preoxidized

Fig. 3. Mass gain vs. time for corrosion of Alloy 800H in an oxidizing/sulphidizing environment at 550°C for blank preoxidized and cerium oxide surface-treated conditions. The latter with varying thickness of the oxide layer.

Fig. 4. SEM micrographs of the scale surface of Alloy 800H after cerium oxide surface treatment with (a) optimum cerium oxide deposition and (b) too thick cerium oxide deposition.

under similar conditions as applied during firing, as depicted in Fig. 6. Both materials showed a parabolic corrosion behavior with parabolic reaction constants of 1×10^{-6} and $2 \times 10^{-6} \text{ mg}^{-2} \text{ cm}^{-4} \text{ s}^{-1}$, respectively. SEM observations revealed selective grain-boundary oxidation on the untreated preoxidized material, which was absent on the cerium-oxide-treated material, as shown in Fig. 7. Additionally, the CeO_2 -surface-treated material showed a good resistance to thermal shock. Upon cooling, the untreated alloy after preoxidation exhibited considerable spalling, which was absent in the case of the CeO_2 -surface-treated alloy.

Fig. 5. Mass gain versus time for corrosion under oxidizing/sulphidizing conditions for blank and cerium oxide surface treated (method B) Alloy 800H at various temperatures.

Fig. 6. Mass gain versus time for corrosion of Alloy 800H in oxygen at 950°C for the cerium oxide surface treated (method B) and blank pre-oxidized conditions.

DISCUSSION

The results obtained have shown that the application of cerium oxide by the sol/gel technique to the surface followed by firing in air can lead to a significant improvement in corrosion resistance in oxidizing, as well as in oxidizing/sulphidizing conditions. Thermogravimetric measurements regarding the corrosion resistance under oxidizing/sulphidizing conditions (Fig. 5) showed a clear temperature dependence: whereas no corrosion could be observed after 900 hr at 823 K, it was clearly present after 400 hr at 873 K, 240 hr at 923 K, and after 120 hr at 973 K. Three effects may contribute to this observed change with temperature:

- Increasing diffusion coefficients in the protective oxide layer with increasing temperature.
- An increase of the sulphur partial pressure (Table III).

Fig. 7. SEM-micrographs of the scale surface after exposure in oxygen at 950°C for 80 hr of Alloy 800H: (a) blank preoxidized; (b) CeO₂ surface-treated (method B).

- The formation of a low-melting Ni/Ni₃S₂ eutectic at temperatures above 918 K.

However, a very careful treatment during cerium-oxide-surface application is necessary in order to achieve an optimized corrosion resistance. For example, a too-low ceria concentration of the sol during electrophoretic deposition leads to an insufficient effect on the oxide scale quality. Using acetone as a solvent leads to the formation of a less-protective oxide scale which is probably due to insufficient stability of the sol. This may be due to a decreased thickness of the diffuse double layer, caused by a lower dielectric constant for acetone compared with water, resulting in reduced stability of the sol and rapid coagulation.^{16,17} In this way, electrophoretic deposition leads to clusters of colloidal particles on the substrate, with the consequence of a relatively poor adherence between the substrate and the superficially-applied ceria. After firing, a flake-like surface morphology is observed (Fig. 2), rather similar to the appearance after firing of a too-thick ceria layer (Fig. 4). Such a morphology leads obviously to a reduced protective action in corrosive environments, as has also been observed in the literature.¹³ Also, other parameters may be related to the corrosion resistance of the ceria-surface-treated alloy. For instance, it was found that polishing with 0.05 μm Al₂O₃, and additional treatment following method B, gave poor corrosion resistance in comparison with grinding on 800-grit carborundum paper. This may be due to a decreased adherence of the ceria particles to the smoother surface or also to cold deformation in the surface region of the metal, leading to enhanced Cr diffusion and improved Cr₂O₃ formation.

The experiments under purely oxidizing conditions showed that for the CeO₂-surface-treated material the oxidation was more uniform, and that selective grain-boundary attack, as observed for the untreated preoxidized material, was absent. This can be explained by the fact that the cerium oxide particles act as nuclei for oxidation, thus decreasing the importance of grain boundaries as selective nucleation sites, as shown in the work of Rhys-Jones and Grabke.^{18,19} Additionally, it was found that the CeO₂-containing oxide scale showed a good adherence upon thermal shock. A possible explanation might be an improved oxide-scale plasticity in combination with a decreased oxide grain size caused by CeO₂ particles acting as nuclei for oxidation. A more extensive discussion on the improved corrosion behavior due to CeO₂ can be found elsewhere.^{9,14}

SUMMARY AND CONCLUDING REMARKS

The application of cerium oxide to the surface of Alloy 800H by the sol/gel technique followed by firing in air can lead to an improvement in

corrosion resistance both under oxidizing and oxidizing/sulphidizing conditions. However, the improvement in corrosion resistance depends strongly on coating parameters, such as type of solvent and sol concentration. Acetone was found to be less favorable due to the sensitivity for sol aging. Sols based on water appeared not to suffer from sol aging. An optimum protection was obtained with an oxide layer of approximately $0.5\ \mu\text{m}$ thickness. The extent to which an improvement in corrosion protection also holds for superimposed mechanical deformation, which can lead to cracking of the protective oxide layer, is the subject of other investigations.²⁰⁻²²

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