

Properties of Protective Oxide Scales Containing Cerium on Incoloy 800H in Oxidizing and Sulfidizing Environments. I. Constant-Extension-Rate Study of Mechanical Properties

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The mechanical properties of ceramic coatings containing cerium oxide, prepared by the sol-gel method and used to protect Incoloy 800H against aggressive environments, are reported. Deformation and cracking behavior in oxidizing and sulfidizing environments has been investigated by constant-extension-rate tests. Extension rates were between 9.3×10^{-6} and $3.7 \times 10^{-7} \text{ sec}^{-1}$ at $823 < T < 973 \text{ K}$. Under these conditions, cerium oxide sol-gel-coated specimens do not show any failure at extensions of 1.0% or more, but in hydrogen, sulfide failure is found at lower extensions than in air.

KEY WORDS: constant-extension-rate tests; Incoloy 800H; sulfidation; oxidation; sol-gel method; cerium; ceramic coatings.

INTRODUCTION

The intensification of coal-conversion-processes such as atmospheric fluidized-bed combustion (AFBC) and coal gasification results in an increasing need for materials resistant to aggressive environments. Plants built for these purposes produce temperatures in the range 1100–1200 K, which minimizes the formation of NO_x and SO_2 . Even if cooling of the components to 823 K is possible, most construction materials cannot be used in practice where useful lifetimes of at least one or usually more years are required. This means that protective coatings (metallic or ceramic) could be the

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solution to increase the lifetime of the components. Under practical conditions, high-temperature components always undergo a certain deformation, because of mechanical and/or thermal stresses. These stresses are transferred to the protective coatings, which are probably susceptible to cracking under stress.

Protective ceramic coatings were applied to metal surfaces using a sol-gel technique roughly similar to that developed at the Materials Development Division, AERE Harwell.^{1,2-4} This technique is based on the use of sols consisting of colloidal units of hydrous oxides or hydroxides. The sol is applied by electrophoresis or dipping, then dried, and finally fired up to 1123 K. On drying, i.e., removing the water between the colloidal units, the sol is converted to a gel. This is a reversible process, which means that the gel can be reconverted to the sol by the addition of water. Finally, on firing at 1123 K, the gel is irreversibly transformed to a ceramic. Thus the sol-gel technique is a three stage procedure: (1) dipping/electrophoresis, (2) drying (sol+gel), and (3) firing (gel+ceramic). In this way, cerium oxide was deposited on Incoloy 800H.

It is known that alloys with a sufficiently high chromium content, forming a chromium oxide layer in oxidizing environments, are resistant to oxidizing gases. This oxide layer is in most cases not resistant to sulfidizing conditions. The influence of superficially applied oxides of rare earth metals has been investigated only in oxidizing environments.^{1,5}

It was found that cerium oxide containing coatings significantly improve the oxidation and spallation resistance of high-alloy steels in oxidizing environments. Until now, a few studies have been reported regarding their protection against sulfidation.²⁻⁴ It was suggested that the adsorption of Ce^{4+} ions on the oxide grain boundaries hinders grain growth under oxidizing circumstances, resulting in a better adherence to the substrate due to enhanced plasticity of the oxide.^{1,5}

Deformation of the metal may finally lead to cracking of the protective layer. Schütze⁶ studied the deformation and cracking behavior of oxide scales formed in air on heat-resistant steels by constant-extension-rate tests. The deformation behavior of the oxide scale (thickness $\sim 15 \mu\text{m}$) in air under tensile strain was explained by three contributions: elastic deformation, plastic deformation, and lateral growth. The strain to cracking of the oxide scale on alloy 800H at 1073 K at strain rates between 10^{-6} and 10^{-8}sec^{-1} was observed to lie between 0.09 and 0.50%.

This paper reports on a study concerning the mechanical properties of ceramic coatings containing cerium. The ceramic coatings were applied by electrophoretic deposition from sols. The influence of cerium on the corrosion resistance of high-temperature alloys will be published in a subsequent paper. The deformation and cracking behavior in oxidizing and

sulfidizing environments has been studied by constant-extension-rate (CER) tests. This method permits evaluation of the susceptibility of metals and protective oxide scales to stress-corrosion cracking (SCC). There are two advantages to this technique⁶: (1) CER is a rapid laboratory method to evaluate SCC susceptibility in aggressive environments, and (2) CER tests can be used to determine whether the failure mechanism is either ductile or brittle, or both. The results of the CER tests can be used to find the answers to the following questions:

1. Is the oxide scale susceptible to SCC for a specific combination of temperature, gas composition, and extension rate?
2. If susceptible, how does the SCC susceptibility change with environmental conditions (process constants)?
3. What are the consequences of SCC susceptibility?

EXPERIMENTAL PROCEDURE

Constant-Extension-Rate Method

A constant extension rate, achieved by the use of different gear ratios and reduction gear boxes, was applied to the specimens, over a gauge length of 15 mm. The tension-testing machine consists of a fixed stiff frame, a carriage, a drive mechanism, a load cell, and a recorder. The use of an electrical motor and a suitable gear reducer permitted the application of extension rates in the range 1.4×10^{-4} – 5.5×10^{-6} mm/sec. The tensile load on the specimen was measured by a load transducer with an output of $1 \text{ mV} \cdot \text{kg}^{-1}$.

Material

The chemical composition of the austenitic stainless steel, Incoloy 800H, is given below, in wt.%:

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

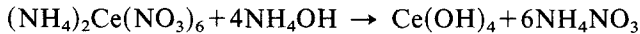
The material was annealed for 1 hr at 1373 K, water-quenched, annealed for 1 hr at 1223 K and water-quenched again. The last treatment prevents sensitization, i.e., the formation of chromium carbide particles on the grain boundaries at temperatures between 870 and 1070 K, by the formation of titanium carbide.

The dimensions of the CER test specimens are as follows: diameter, 5 mm; gauge diameter, 2.5 mm; length, 210 mm; and effective gauge length,

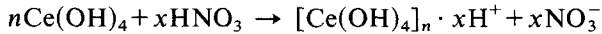
15 mm. The final surface finish was performed by grinding with 220-, 320-, 500-, and 800-grit carborundum, respectively. All test specimens were ultrasonically cleaned with hexane, ethanol, and acetone prior to coating.

Preparation of the Sols

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 333 K, yielding a sol with a pH value of 0.3:



The electrophoretic conditions were as follows: concentration of the Ce sol: 0.40 M, adjusted with water, to a current density of 1 A/m^2 , with a deposition time of 1.30 hr.

Application of the Coatings

The ceramic coatings were applied by electrophoretic deposition from ceria sols, followed by drying in air for 16 hr.

Sintering Procedure

The ceria deposits were sintered in air by heating the test specimens, first to 423 K at a rate of 6 K/hr, followed by 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/h to 293 K. Thickness of the coating was about $1 \mu\text{m}$.

Sulfidation Tests

Constant-extension-rate experiments in sulfidizing environments were performed in a furnace. The test specimens were suspended in the furnace chamber flushed for 16 hr with argon (180 ml/min). The argon was saturated with water at 288 K. Next, a flow of 5% hydrogen sulfide in hydrogen (50 ml/min) was introduced into argon. After this system was flushed, which had a volume of about 5 l, for a period of 2 hr, the temperature was raised to the desired value. After a flushing time of 5 hr with the final gas mixture, the system was closed. The conditions, i.e., 823–973 K, imply the thermodynamic stability of Cr_2O_3 , Ni_3S_2 , and FeS. CER test specimens, which were extended in air, were tested in a hydrogen sulfide–hydrogen–argon gas mixture ($T = 823 \text{ K}$) for crack detection. The partial pressures of oxygen and sulfur are given in Table I, with equilibrium assumed.

Table I. Partial Pressures (in atm) of Oxygen and Sulfur as a Function of Temperature and Composition

Gas mixture (K)		H ₂ S-H ₂ -Ar ^a	H ₂ S-H ₂ O-H ₂ -Ar
823	P_{O_2}	2.0×10^{-32}	9.3×10^{-29}
	P_{S_2}	1.2×10^{-9}	1.2×10^{-9}
873	P_{O_2}		5.8×10^{-27}
	P_{S_2}		5.2×10^{-9}
923	P_{O_2}		2.4×10^{-25}
	P_{S_2}		2.0×10^{-8}
973	P_{O_2}		6.6×10^{-24}
	P_{S_2}		6.7×10^{-8}

^aOnly used at 823 K.

Analysis

The specimens were examined after exposure, using conventional optical microscopy and scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDAX).

RESULTS

CER Tests

Strain to Cracking

For specimens in which no cerium is deposited, the strain to cracking is ~0.2% (CER = $9.3 \times 10^{-6} \text{ sec}^{-1}$, $T = 823 \text{ K}$). In Fig. 1, strain to cracking is shown as a function of the temperature and gas composition of the oxide scales of specimens on which Ce has been deposited. In all cases, the strain-to-crack values of the oxide scales in sulfidizing environments are significantly lower than those under the same conditions in air. Specimens, extended in air as well as in sulphidizing environments, tend to show a lower critical strain to fracture of the oxide scales at higher strain rates and/or lower temperatures.

Sulfidation after Cracking

The attack during sulfidation after fracture of the oxide scale (gas mixture: H₂S-H₂O-H₂-Ar, CER = $3.7 \times 10^{-7} \text{ sec}^{-1}$, $T = 923 \text{ K}$, elongation = 2.8%) is shown in Fig. 2. The external sulfides contain mainly Fe and Ni. Specimens extended in air, followed by exposure to a H₂S-H₂-Ar gas mixture for 50 hr without the application of external stress, showed the

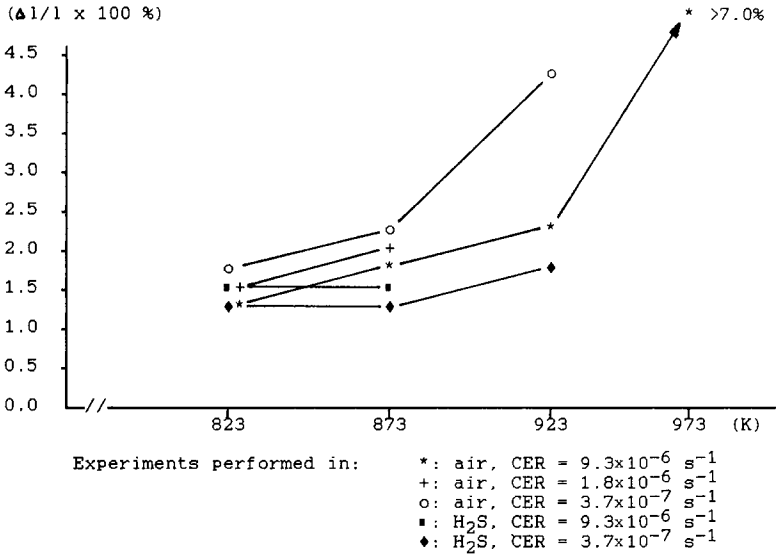


Fig. 1. Strain to cracking of the oxide scale, including ceria, on Incoloy 800H.

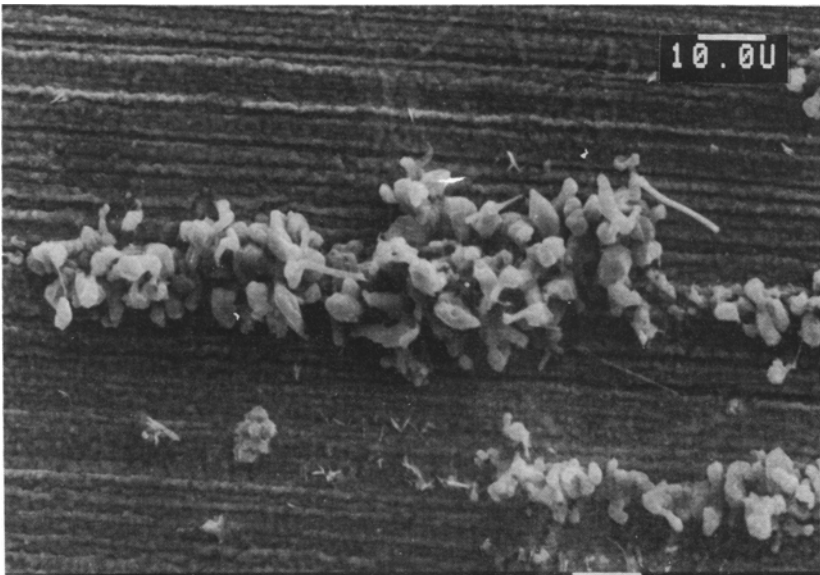


Fig. 2. SEM picture of sulfides after cracking of the protective oxide scale. The strain was applied in the vertical direction.

same attack as specimens extended in sulfidizing environments. After cracking of the oxide scale, the internal sulfidation was severe as well.

DISCUSSION

The strain to cracking of the protective Cr_2O_3 scale, expected below the transition temperature of oxide deformation if no diffusional processes affect the deformation behavior of the scale (under the assumption of purely elastic deformation), would amount to about 0.1%.⁶ This means that at room temperature no plastic deformation of the oxide scale is possible if cracking occurs after deformation. In our case, the critical strains for fracture of the oxide scale have significantly higher values than 0.1%, in oxidizing as well as in sulfidizing environments, which means that another process must take place.

Schütze⁶ reported that the strain to cracking of oxide scales did not exceed 0.5%, except when lateral oxide-growth effects in the oxide scales occurred, leading to critical strains of up to nearly 2.5%. The oxide scales on Incoloy 800H (without Ce) did not exceed a critical strain up to 0.5% ($T = 1073 \text{ K}$, $\text{CER} = 1 \times 10^{-8} \text{ sec}^{-1}$). In our experiments, the oxide scales on Incoloy 800H (without Ce) also showed critical strains below 0.5% ($823 < T < 973$, $9.3 \times 10^{-6} < \text{CER} < 3.7 \times 10^{-7}$). In contrast with these results, the cerium-oxide-coated specimens exhibited enhanced strain to cracking of the oxide scales. Possible explanations⁶ for the much larger strain to cracking are (1) plastic deformation by grain-boundary sliding, and (2) lateral oxide growth.

Oxidizing Environments

Considering these contributions, strain to cracking in oxidizing environments can be explained by plastic deformation as well as by lateral oxide growth. It is not possible to distinguish these possibilities, because the contributions of plastic deformation and lateral oxide growth are both expected to increase with decreasing extension rate and/or increasing temperature. The addition of Ce results in a higher strain-to-cracking value. Ce probably leads to an enhanced initial oxide growth because a CeO_2 molecule could act as a nucleation site, yielding reduced grain sizes, and thereby increasing the effect of plastic deformation. This is in agreement with Bennett *et al.*¹ and Ecer *et al.*,⁵ who found that an enhanced plasticity of the oxide scale was obtained by the application of ceria.

Sulfidizing Environments

The critical strains in oxidizing environments are larger than in sulfidizing environments. The plastic deformation by grain-boundary sliding will

obviously not be affected in sulfidizing environments. On the other hand, lateral oxide growth is certainly influenced by the sulfidizing environment.

The difference can be explained by the absence of lateral oxide growth under sulfidizing conditions. When fracture of the oxide scale occurs, the substrate is exposed to a sulfidizing gas atmosphere, preventing the formation of oxides, as in our experiments the thermodynamically stable phases are Ni_3S_2 , FeS , and Cr_2O_3 . The sulfides, owing to their highly defective structure, grow much faster than the oxide. This leads to overgrowth of the oxide by the thermodynamically stable sulfides because of their highly defective structures.⁷ The growth rates of FeS and Ni_3S_2 are several orders of magnitude larger than of Cr_2O_3 . A protective oxide scale cannot be formed under these circumstances. In Fig. 1, an increase of the strain to cracking under sulfidizing conditions with increasing temperature is observed as well. Plastic deformation will probably contribute more to the deformation of the oxide scale at higher temperatures.

CONCLUSIONS

An increase of strain to cracking in oxidizing as well as in sulfidizing gases is obtained by adding Ce. This increase in strain to cracking can be explained by plastic deformation. In an oxidizing environment lateral oxide growth may also contribute to the improved behavior.

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