Hot Corrosion of B-1900 in CaSO₄/Na₂SO₄ Salt Mixtures in Reducing Atmospheres

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Hot corrosion of B-1900 in CaSO₄/Na₂SO₄ salt mixtures was performed at 900 °C under a host of reducing/sulfidizing atmospheres. Substantial differences were noted as the oxygen pressure was reduced from 10⁻⁷ to 10⁻¹⁵ Pa. In all cases the resulting morphologies were different from those noted under corresponding oxidizing conditions. Substantial alloy sulfidation was noted when the Pₒ₂ = 10⁻¹⁵ Pa and the Pₛ₂ = 10⁻⁷ Pa. Hot corrosion was found to be maximized at higher oxygen potentials, i.e., above 10⁻¹⁰ Pa. In all cases studied, the corrosion was less extensive than pure Na₂SO₄ at 900 °C in air or in pure O₂. Segregation of CaSO₄ and Na₂SO₄ was noticed; this contributed to the formation of localized regions of extensive hot corrosion while other regions corroded by simple oxidation.

I. INTRODUCTION

Sulfur emissions from fluidized bed coal combustors (fbcc's) can be minimized by adding lime (CaO), which reacts with sulfur impurities to form the stable compound, CaSO₄. However, CaSO₄ has been shown to form dense, adherent deposits on experimental fbcc heat transfer tubes. For example, a 50-micrometer thick deposit formed after 500 hours in one test fbcc. Molten Na₂SO₄ deposits are known to cause catastrophic hot corrosion in gas turbines. Because of this, it is suspected that CaSO₄ may also induce accelerated corrosion under the proper conditions. Indeed, accelerated corrosion has been observed on test fbcc tubes. In one test fbcc, nickel alloy and stainless steel tubes corroded at an approximately linear rate. A significant bed deposit was found adjacent to the corrosion scale. CaSO₄ deposits were also found in another test fbcc, in which 304 stainless steel tubes developed sulfur-rich corrosion scales and exhibited evidence of pitting. However, the extent to which CaSO₄ itself is responsible for the observed corrosion in fbcc's is not clear.

Under experimental oxidizing conditions, we have shown that while Na₂SO₄ is indeed a severe corrodent of the nickel-based superalloy, B-1900, additions of 40 to 60 wt pct CaSO₄ greatly mitigate the corrosive effects of Na₂SO₄. When exposed to a salt mixture high in CaSO₄ concentration (90 to 100 wt pct) the corrosion scale morphology resembled simple oxidation of B-1900. This suggests that a different or additional mechanism was responsible for the observed fbcc tube corrosion. Also contributing may be a reducing/sulfidizing environment, which may result from a low oxygen potential at the deposit/scale interface or from a high carbon potential due to uneven coal/air distribution in the fbcc. The reducing/sulfidizing environment may be solely responsible for the observed corrosion, or may increase the corrosive nature of the CaSO₄ deposit.

The nickel-based superalloy, B-1900, was chosen as the test alloy in this study, because it is extremely susceptible to Na₂SO₄ hot corrosion, and its corrosion kinetics and reaction morphology are well known. Previous studies of Na₂SO₄-induced hot corrosion of B-1900 in O₂ or air have clearly shown that the acid/base nature of the deposit has a critical influence on the degradation process. In particular, the role of molybdenum and tungsten in the alloy and SO₃ in the atmosphere in generating acidic fluxing conditions. B-1900 was found to be particularly susceptible to catastrophic hot corrosion by acidic fluxing. The generation of acidic conditions was attributed to the 6 wt pct Mo present in B-1900 dissolving in the Na₂SO₄ melt. This catastrophic attack of B-1900 was preceded by massive internal sulfidation beneath a porous complex outer scale.

The objective of this investigation was to characterize the hot corrosion of B-1900 superalloy as a function of salt concentration and atmosphere. Additions of CaSO₄ salts to Na₂SO₄ were studied in a single reducing/sulfidizing atmosphere representative of possible fbcc conditions. The corrosion due to CaSO₄ additions relative to pure Na₂SO₄ was assessed by comparing the magnitude and character of the corrosion microstructure, using optical and scanning electron microscopy in conjunction with energy dispersive X-ray analysis.

The reducing/sulfidizing conditions possible in an fbcc may vary widely, so that no one combination of oxygen and sulfur pressures is strictly representative. To determine the effects of variations in oxygen and sulfur pressures, a series of experiments was also performed in which the gas pressures were varied. A few selected salt mixtures were used. Variations in B-1900 hot corrosion as a function of gas pressure was assessed using the analytical techniques described above.

II. METHODS

Approximately 4 mm × 4 mm × 2 mm samples were cut from cast B-1900 bars supplied by United Technologies, Inc. (B-1900 composition given in Table 1). These were polished to 600 grit with silicon carbide paper and washed in acetone and ethanol. Samples were coated with mixtures of reagent grade Na₂SO₄ and CaSO₄ from aqueous solution. The solubility of CaSO₄ is only about 2.09 g/1 of H₂O; thus, to obtain a homogenous solution, the ratio of the salts to...
water was closely controlled. Samples were heated to 300 °C and sprayed with the aqueous salt mixture to form a salt layer coating corresponding to 2 ± 0.3 mg/cm². In one standard reducing/sulfidizing atmosphere (see below), a range of salt mixtures was used from pure Na₂SO₄ to pure CaSO₄. Pure Na₂SO₄ and a mixture of 10 wt pct Na₂SO₄/90 wt pct CaSO₄ (a model deposit composition) were chosen to test effects of changes in the atmosphere.

Coated samples were heated in a tube furnace at 900 °C for 24 hours in a flowing gas stream. The B-1900 samples were suspended from an alumina fixture placed in the tube furnace. A mixture of hydrogen, hydrogen sulfide, and water vapor, in a balance of argon, was used to set the oxygen and sulfur partial pressures, using equilibrium constants at 900 °C for the following reactions:

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \]
\[ H_2 + \frac{1}{2}S_2 \rightarrow H_2S \]

Flow rates and gas mixtures were set to provide the proper \( H_2/H_2O \) and \( H_2/H_2S \) ratios. A gas mixture of 600 ppm \( H_2 \), 180 ppm \( H_2S \), balance argon, was obtained from the gas supplier (gases supplied by Matheson). This mixture was preheated before entering the main furnace to tie up trace oxygen as \( H_2O \). A second argon gas stream was first run through an auxiliary furnace packed with titanium powder suspended in a quartz wool, to remove oxygen. This argon stream was subsequently run through a humidifier to introduce a calibrated water pressure, and then introduced into the main furnace.

When five percent water vapor was mixed in the proper ratio with the \( H_2/H_2S \)-argon mixture, the calculated oxygen and sulfur pressures were \( 10^{-7} \) and 10 Pa, respectively. This combination of oxygen and sulfur pressures was selected as a standard reducing/sulfidizing atmosphere for testing the effects of variations in salt mixture in the model deposits. These pressures were chosen so as to form a reducing/sulfidizing atmosphere for nickel, the major component of B-1900. At these pressures at 900 °C, nickel sulfide is stable. This sulfur pressure is also above that necessary to form chromium sulfide, a commonly observed hot corrosion product; the oxygen pressure was somewhat high for the latter sulfide, but the activity of oxygen was expected to drop off within the corrosion scale product.

Since the atmosphere in an fbcc may vary widely, a number of other atmospheres were also tested with pure Na₂SO₄ and a single salt mixture, 10 wt pct Na₂SO₄/90 wt pct CaSO₄. The former was chosen because the Na₂SO₄ hot corrosion of B-1900 has been extensively studied thus lending comparative analysis, while the latter was chosen to model a deposit in an fbcc treated for emission control. The atmospheres were varied from standard by adjusting the \( H_2/H_2S \)-argon/\( H_2O \)-argon ratio and by adding additional hydrogen to the \( H_2/H_2S \)-argon mixture.

Subsequent to the exposures, the samples were mounted in epoxy, polished to 3 micrometer diamond polish, and subjected to metallographic examination. Numerous samples were also gold coated and examined by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX).

### III. RESULTS

#### A. Effects of Variations in \( Na_2SO_4/CaSO_4 \) Ratio

In the standard reducing/sulfidizing atmosphere \( (P_{O_2} = 10^{-7} \text{ Pa}, \ P_{S_2} = 10 \text{ Pa}) \), pure Na₂SO₄ caused severe hot corrosion after 24 hours, as shown by SEM in Figure 1. This is in contrast to the protective aluminum and titanium oxide scales which formed in B-1900 simple oxidation. In Figure 1, the outer scale labeled “a” was nickel rich (as

![Fig. 1 — SEM and EDAX of B-1900 coated with 100 wt pct Na₂SO₄, in oxygen and sulfur pressures of 10⁻⁷ and 10 Pa, respectively, at 900 °C for 24 h: (a) outer scale, (b) upper porous scale, (c) smooth surface, (d) dark stringers, (e) within crack, and (f) alloy within stringers.](image-url)