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Hot corrosion of materials: a fluxing mechanism?

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Abstract

Hot corrosion is the accelerated oxidation of a material at elevated temperature induced by a thin film of fused salt deposit. Fused Na_2SO_4 , which is the dominant salt involved in hot corrosion, is an ionic conductor, so that the corrosion mechanism is certainly electrochemical in nature. Further, the acid/base nature of this oxyanion salt offers the possibility for the dissolution (fluxing) of the normally protective oxide scale. Non-protective precipitated oxide particles are often observed in the corrosion products. In this paper, the status of knowledge for the solubilities of oxides in fused Na_2SO_4 is reviewed, and the effects of various influences on a fluxing mechanism are discussed. An evaluation of a “negative solubility gradient” as a criterion for continuing hot corrosion is made. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hot corrosion became a topic of important and popular interest in the late 60s as gas turbine engines of military aircraft suffered severe corrosion during the Viet Nam conflict during operation over seawater. Metallographic inspection of failed parts often showed sulfides of nickel and chromium, so the mechanism was initially called “sulfidation”. However, studies by Goebel and Pettit [1] and by Bornstein and DeCrescente [2,3] showed that sulfide formation indeed resulted from the reaction of the metallic substrate with a thin film of fused salt of sodium sulfate base (but not with Na_2SO_4 vapor). Deposition of the condensed liquid film on the system

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hardware can result generally from one of two processes: (1) chemical deposition: the vapor pressure of Na_2SO_4 in the vapor phase exceeds its equilibrium partial pressure for the substrate temperature, or (2) physical deposition: some solid or liquid salt could detach from an upstream component (e.g. an air filter) and attach to a hot substrate upon impact. Thus, in hot corrosion, sulfide products are not formed by reaction with sulfur compounds in the gas phase, but rather from a metal–salt interaction.

Because corrosion by a thin electrolyte film bears some common features with “atmospheric corrosion” by an aqueous film at room temperature, the phenomenon has been renamed “hot corrosion”. While aqueous atmospheric corrosion is often controlled by the diffusion of dissolved oxygen in the water film, numerous measurements have shown that the soluble oxidant in hot corrosion is SO_3 ($\text{S}_2\text{O}_7^{2-}$) in the fused salt [4–7]. The subject of hot corrosion is divided into two sub-types: type 1 – high temperature hot corrosion above about 900°C where pure sodium sulfate is above its melting temperature, and type 2 – low temperature hot corrosion (LTHC) between about 700 – 750°C where a liquid salt phase is only formed because of significant dissolution of some corrosion products [8–12]. In the metallography of corroded components, a dispersion of tiny oxide particles in the adherent thin salt film is often observed. This observation led to the suggestion that a fluxing mechanism may be important, whereby an otherwise protective oxide scale on the material dissolves at the oxide/salt interface but precipitates as non-protective particles within the salt film. The purpose of this paper is to review some of the fundamental knowledge now available to understand hot corrosion and to assess the viability of the “fluxing mechanism”. A number of previous papers have discussed the chemistry and electrochemistry of hot corrosion [13–15].

2. Acid–base chemistry and oxide solubilities

The oxyanion sodium sulfate melt can be described by an acid–base chemistry in a manner similar to the pH of aqueous solutions, i.e.:



such that for pure Na_2SO_4 :

$$\log a_{\text{Na}_2\text{O}} + \log a_{\text{SO}_3} = -16.7 \quad (2)$$

Therefore, $\log a_{\text{Na}_2\text{O}}$ can be defined as a quantitative measure of the melt basicity, or alternatively, $\log a_{\text{SO}_3}$ can be defined as the melt acidity. By the simultaneous use of two solid electrolyte reference electrodes, based namely on a Na^+ -ion-conductor (impure silica) and an O^{2-} -ion conductor (Y_2O_3 -doped ZrO_2), the activities of Na and O_2 in the salt can be independently measured to yield specific values for $\log a_{\text{Na}_2\text{O}}$, thereby establishing the melt basicity during any given experiment. As explained elsewhere [16], the voltage between these two specific reference electrodes is given by:

$$E = -1.466 - 0.116 \log a_{\text{Na}_2\text{O}} \text{ at } 1173 \text{ K} \quad (3)$$

Thus in combination with the voltage of the oxygen sensing electrode, the pair of electrodes can accurately establish the magnitudes of the primary melt properties: its basicity and its oxidation potential.

Measurements of the solubilities of the important oxides NiO, Co_3O_4 [17,18], Fe_2O_3 [19,20], CeO_2 [21], Cr_2O_3 [22], and Al_2O_3 [23] have been determined as a function of melt basicity and oxygen activity for pure fused Na_2SO_4 at 1200 K, and for SiO_2 [24] at 973 K. A compilation of these results is presented as Fig. 1. These data also suffice to describe the solubilities of the lower oxides CoO and Fe_3O_4 . In the simplest cases, the shapes of these curves are essentially explained by the formation upon dissolution of one simple (uncomplexed) acid solute and one simple basic solute, e.g. the solubility of NiO is described by two contributions (or legs on the curve of Fig. 1):

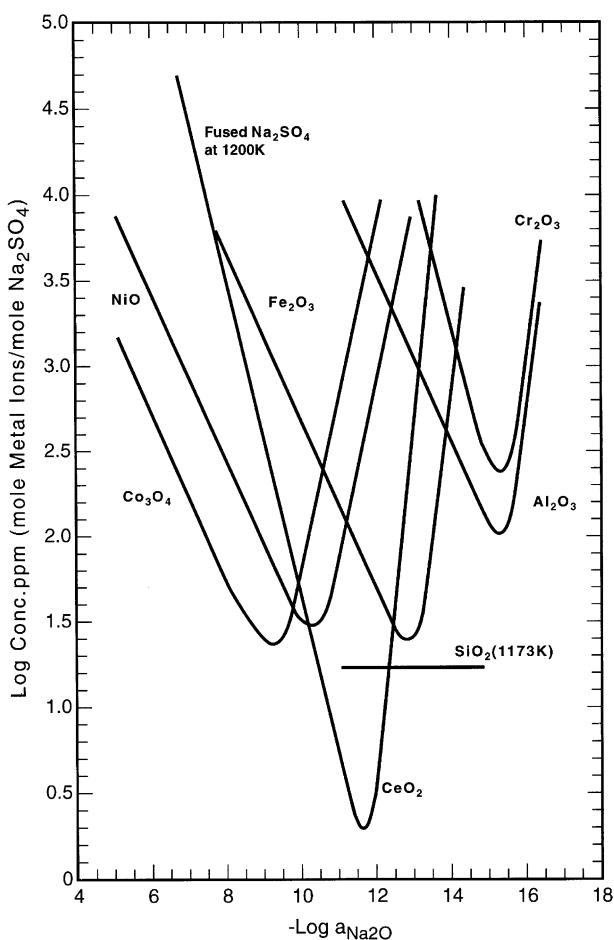


Fig. 1. Compilation of measured solubilities for several oxides in fused pure Na_2SO_4 at 1200 K [7,9–11].

Basic dissolution: $2\text{NiO} + \text{Na}_2\text{O} + \frac{1}{2}\text{O}_2(\text{g}) = 2\text{NaNiO}_2$

$$\left\{ \frac{d \log[\text{NaNiO}_2]}{d \log a_{\text{Na}_2\text{O}}} \right\} = -\frac{1}{2} \text{ at fixed } P_{\text{O}_2} \quad (4)$$

$$\left\{ \frac{d \log[\text{NaNiO}_2]}{d \log P_{\text{O}_2}} \right\} = \frac{1}{4} \text{ at fixed } a_{\text{Na}_2\text{O}} \quad (5)$$

Acidic dissolution: $\text{NiO} + \text{Na}_2\text{SO}_4 = \text{NiSO}_4 + \text{Na}_2\text{O}$

$$\left\{ \frac{d \log[\text{NiSO}_4]}{d \log a_{\text{Na}_2\text{O}}} \right\} = 1 \text{ independent of the oxygen pressure} \quad (6)$$

All of the curves of Fig. 1 (except for SiO_2) can be accurately described by such simple interpretations, i.e. the slopes of the experimental solubility curves exactly obey such simple predictions, although the oxides Fe_2O_3 and Cr_2O_3 were each found to exhibit two acidic and two basic solutes. In the range of melt basicity studied, SiO_2 does not form an ionic solute, and its measured low solubility was therefore independent of basicity. As demonstrated for NiO , if a valence change is involved in the dissolution reaction, then the solubility contribution for that solute will depend upon P_{O_2} ; otherwise there is no dependence. The range in basicity spanned between the minima for the most basic oxide Co_3O_4 and the most acid oxides Al_2O_3 or Cr_2O_3 is about six orders of magnitude. Fortunately, the operation of a gas turbine frequently establishes a P_{SO_3} in the range where both Cr_2O_3 and Al_2O_3 exhibit minima in their solubilities; alloys containing Cr and Al are therefore well suited for use as the protective coatings for gas turbine components.

3. Hot corrosion mechanism

3.1. Role of scale fluxing

Based on the expectation that oxide solubilities would generally follow the behaviour shown in Fig. 1, i.e. exhibit individual basic and acidic solutes with concentrations dependent on melt basicity and perhaps P_{O_2} , Rapp and Goto [25] proposed a “negative solubility gradient” as a general criterion for continuing hot corrosion attack. Fig. 2 shows a schematic drawing of this “fluxing” mechanism. Three specific examples which satisfy the negative solubility gradient condition are illustrated in Fig. 3. In case A, continuing basic fluxing and reprecipitation is favored because a dominant basic solute has a higher solubility at the oxide/salt interface than at the salt/gas interface. In case C, a dominant acidic solute has a higher solubility at the oxide/salt interface than at the salt/gas interface. In case B, a negative solubility gradient is realized whenever the local conditions and the corresponding solubilities straddle a minimum. In each case, the protective oxide is favored to dissolve at the oxide/salt interface and reprecipitate as non-protective particles within the salt film. In contrast, if the specific conditions should dictate that a “positive solubility gradient” exists, then the salt film should just saturate to the solute concentration established at the oxide/salt interface and the reaction should stop; no continuing hot corrosion. Because the relevant salt films are quite thin, steep