Hot Corrosion

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Hot corrosion is an high-temperature analog of aqueous atmospheric corrosion.   A thin film deposit of fused salt on an alloy surface in a hot oxidizing gas causes accelerated corrosion kinetics.   Recognition of the problem and a search toward a mechanistic understanding and engineering abatement were initiated in response to the severe corrosion attack of military gas turbines during the Viet Nam conflict. Initially, the researchers were misled by the observation of corrosion product sulfides beneath a fused film of sodium sulfate to denote the problem and mechanism as "sulfidation".   Later, studies by Bornstein and DeCresente(1,2) and Goebel and Pettit(3,4) demonstrated that the principal corrosive environmental component was not a vapor species, but rather the contact of the fused salt with the surface. This fused salt (sodium sulfate) exhibited an acid-base character which at the time was quite uncertain and undefined. The electrolytic nature of the fused salt film and its similarity to atmospheric corrosion led to the more proper naming of the problem as "hot corrosion".

With the recognition that a fused salt deposit was critical to the corrosion mechanism, thermodynamic programs were used to predict what combinations of temperature and fuel and air compositions would cause the condensation of a fused salt as the substrate surface fell below the dew point of a component in the gas phase (5,6). In this way, a Type II Hot Corrosion was identified, Type I referring to corrosion at a temperature above the nominal melting point of pure sodium sulfate (886C). The Type II Hot Corrosion exhibited a maximum in corrosion rate at about 750C for Ni- and Co-base alloys, resulting from a lowering of the liquidus temperature of sodium sulfate upon the dissolution of oxide corrosion products from the substrate(7,8).

Progress in understanding the mechanistic aspects of hot corrosion was led by the application of phase stability diagrams (common to extractive metallurgy) and the adaptation of Pourbaix's approach to aqueous corrosion(9,10). A quantitative acid-base scale was adopted for sodium-cation salts which could be measured (in either deep melts or thin salt films) by the use of two reference electrodes: one measuring oxygen activity and the second measuring sodium activity. With such acid-base probes, the solubilities of many important oxides in fused sodium sulfate were established experimentally. These solubility curves were found to obey exactly the behavior for simple (uncomplexed) acidic and basic solutes expected from a Pourbaix sort of interpretation.

Electrochemical measurements were made to demonstrate that the principal oxidizing solute in fused sodium sulfate was dissolved SO_3, not dissolved O_2 as for aqueous atmospheric corrosion (11). Likewise, potentiometric measurements during the hot corrosion of preoxidized nickel showed that indeed the local chemical state of the salt-coated surface became highly reduced (dominated by the salt film, not the gas phase) so that sulfidation of the substrate occurred, leading to a basic dissolution of the NiO protective scale (12).

Rapp and Goto(13) proposed that the criterion for continuing hot corrosion was the existence of a "negative solubility gradient" for the protective oxide in the fused salt film. Thereby, the oxide at the scale-salt interface exhibited a higher (acidic or basic) solubility than farther out in the salt film. This condition supports dissolution of the dense protective oxide scale and reprecipitation of the oxide as non-protective particles within the salt film. Synergistic hot corrosion was also demonstrated when the basic dissolution of one oxide is coupled to the acidic dissolution of a different oxide, resulting in overall accelerated dissolution kinetics (14).

The solubilities of several oxides were measured and interpreted in a 0.70 Na_2SO_4-0.30$NaVO_3$ melt. The presence of the vanadate component led to a large increase in the acidic solubility for all oxides and a large shift in the location of the solubility minimum for any oxide on an acid-base scale (15). The further interpretation of this result led to a prediction of the dependence of the solubility for any oxide on any vanadate content(16). Indeed, the sodium sulfate-sodium vanadate system was shown to be nearly an ideal solution.

The fundamental aspects of hot corrosion via a sodium sulfate thin film can be adapted for application for similar corrosion phenomena involving other oxyanion fused salts, e.g. carbonates, nitrates, phosphates, etc.

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