THIN FILM HOT CORROSION STUDIES
OF OXIDISED AND CARBURIZED TYPE 310 STAINLESS STEEL

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ABSTRACT

During hot corrosion in fossil-fuel-fired power plants a molten salt layer, around 1 mm thick, forms on the leading superheater and reheater tubes, under fly ash, and dissolves some of the metal surface. First time studies using 1 mm thick layer of molten sulfate at 650 °C for up to 2000 h under a synthetic flue gas are here reported, employing a specially designed ceramic holder to retain a thin even film around metal coupons. The content, concentration and penetration of the components of type 310 stainless steel, (iron, chromium and nickel), in the thin molten salt layer, were determined at 200 h intervals. Both oxidised and carburized samples were investigated. The results showed evidence for a repeated pattern of initial rapid attack followed by a period of passivity, and significantly faster corrosion of carburized specimens.

INTRODUCTION

For the electricity generation industry to be economic and efficient unplanned shutdowns must be minimised. In plants that burn fossil fuels a major cause of power outages and shutdown is hot corrosion, which can bring about the failure of one or more tubes in a boiler, Fig. 1. Hot flue gases, at 900 to 1100 °C, impinge upon first the banks of superheater and then the reheater tubes, depositing sulfates and fly ash on the leading tubes in each bank. In the 10 o’clock and 2 o’clock positions from the direction of flue gas flow the fly ash is thin, allowing better heat transfer to the tube, and thus maintaining the sulfate deposit in the molten state, Fig. 2 (A). This then dissolves SO3, formed from SO2 from the sulfur in the coal and converted to the trioxide due to the presence of excess air and the (mild) catalytic effect of the ferric oxide, Fe2O3, in the fly ash. This pyrosulfate-containing melt slowly attacks the superheater tube, thinning the tube in these two positions, generally by a combination of pitting corrosion and spalling, if subjected to temperature cycling. The steam inside such tubes is around 650 °C and at 2000 psi. Eventually the weakened tube bursts, and the power station has then to be shut down. Fig. 2 (B) shows diagrammatically a section of a tube experiencing hot corrosion and the temperature gradient from flue gas to tube through the molten salt layer. Maintenance shutdowns, to identify and replace those sections of tubing experiencing hot corrosion attack, should thus be timed to take place before a tube fails. Part of the information
required by plant operators is the rate of attack by the deposited molten salt layers, but other parameters also enter the equation.

These parameters include the composition of the fuel burned. Its sulfur content, while important for emission regulations, is not so critical for hot corrosion as its chlorine content. Not all the parameters can be obtained from laboratory experiments, on site experience is important too, and here it has been found that as a rough rule-of-thumb, a doubling of the chlorine content in the coal causes up to a ten-fold increase in the rate of hot corrosion attack.

This study, however, focuses on a more recently recognised factor and compares the extent of the thin film hot corrosion of pre-oxidised and pre-carburizes coupons of 310 stainless steel, an austenitic steel commonly used for superheater and reheater tubes. Although these tubes are neither deliberately oxidised or carburized before start-up, one or other of these conditions will take place before the sulfate layer is laid down and hot corrosion commences. Extensive thinning, and tube failure, appear to be linked with generating plant in which carburization is likely to have occurred.

Under normal start-up conditions the slightly oxidising nature of the flue gas will oxidise the metal surfaces. However, the start-up procedure involves the burning of injected oil before the fuel is switched to pulverised coal (PF). Sometimes when this is done the fire goes out and the interior of the furnace, essentially miles of tubes, is sprayed and coated with oil. When re-lit the oil coating is incompletely burned, leaving a carbon residue on the tube surfaces that can then carburize the surface before the sulfate layer arrives. It was thought that carburized surfaces would suffer faster and more severe hot corrosion, and our objective was thus to establish if this was so, and provide quantitative data if possible.

A common source of hot corrosion information has been electrochemical measurements. These are generally made in the laboratory, using steel samples as electrodes in molten sulfates. However, as indicated in Fig. 2 (B), there is a thermal gradient across the molten sulfate layer, and electrochemical studies have been made in isothermal baths, because anode and cathode have to be at the same temperature for meaningful measurements.

Some years ago we developed at Leeds a spectroscopic technique that investigated and essentially measured continuously the hot corrosion of metal coupons in a simulated molten sulfate melt, over which was passed synthetic flue gas, and, particularly, a thermal gradient was maintained from the coupon to the melt-gas interface (1,2). This technique, termed EASE, Electronic Absorption Spectroscopy Experiments, identified and followed the sulfate complexes formed by the transition metals in the coupon as they entered the melt and diffused to the melt-gas interface. This was achieved by recording the spectra of 1 mm thick layers of the melt, parallel with the upper surface of the coupon, Fig. 3. This procedure, carried out in essentially a standard 10 mm path length optical silica cell, replicated closely the situation in fossil fuel fired plant except that the thickness of the molten sulfate layer above the metal was around 40 mm, compared with the plant situation of 1-2 mm thick.
Although our results confirmed and clarified the experience and expectations of plant managers, we recognised the need to investigate thin, 1 mm thick, films. Little work has been done using thin films coupled with analysing the corrosion products in the film as a function of time. The extent of penetration of corrosion products into the salt layer also as a function of time is reported for the first time. Previous studies have been largely confined to metallographic and other analyses of the surface of the metal.

EXPERIMENTAL

For effective thin film studies the requirements are:

- Replication of the 1 mm molten sulfate layer between superheater tube and fly ash deposit.
- Replication of the molten sulfate composition
- Conduct experiments up to 700 °C
- Reproduce metal surface conditions
- Multi-sample experiments for time-dependency studies
- Design apparatus capable of heating the samples in a synthetic flue gas atmosphere containing both SO₂ and SO₃, be able to analyse the exit gas and allow periodic sample removal
- Follow the corrosion of the steels with respect to time and the elements, Fe, Cr and Ni.

These items can be achieved, and an account of preliminary experiments and results has been given (3). To create a 1 mm thick layer around our steel specimens we designed a special holder, and made it by machining it out of a special ceramic, Macor, Fig. 4. Macor is impervious to attack by molten sulfate over prolonged exposure. A set of 20 holders was prepared, ten containing pre-oxidised and ten pre-carburized samples of 310 stainless steel and the required weight of sulfate eutectic, which were then loaded into a carousel. This was located in the large uniform hot zone of a furnace under a flow of synthetic flue gas and maintained at 650 °C, and two holders, one from each group, were removed every 200 h for analysis.

After cooling, the holders were cut vertically with a diamond-edged wafering saw, under oil to prevent the sample being exposed to moist air. The two halves were then cleaned ultrasonically in acetone and stored in a dry-box.

One half was then examined by EMPA (Electron Microprobe Analysis), after polishing down to 0.25 μm by a technique that excluded water and gave a polish with no relief at all on both metal and salt. The other half had the salt picked out, ground into a fine powder and divided into two, for chemical analysis, using ICP-AES, (Inductively Coupled Plasma - Atomic Emission Spectroscopy) and absorption spectroscopy. This latter required the development of a computer-based technique for enhancing absorption spectra such that quantitative data was obtained. Samples were around 0.3 g and concentrations of Fe, Cr and Ni below 1 g dm⁻³ were reliably determined. The results were close to, and paralleled, the ICP-AES data, and this is the first time that absorption spectra...
have been used to determine the individual concentrations of iron, chromium and nickel entering the corroden.

RESULTS AND DISCUSSION

Certain general trends were observed for all three elements. After an initial attack, passivity occurred for up to around 900 h, followed by spalling of the chromium oxide layer and further attack, until more chromium diffuses to the steel surface and forms another protective layer. This layer now lasts for less than the time of the first passive period before spallation occurs again and the corrosion rate slows down considerably, but not now completely because the available chromium has been further depleted. This stop-start mechanism has been favoured as occurring (4) during the hot corrosion of superheater and reheater tubes, but has not had previously any evidence in support until now. Evidence for the contribution of the expected spallation to this mechanism was discernable in the appropriate sectioned crucibles.

Fig. 5 shows the results for iron by ICP-AEC analysis for type 310 steel. The carburized samples are more readily attacked by a factor of about two to three. The chromium protection is lost from the carburized samples much earlier than from the oxidised coupons, which show little spalling. Similar behaviour was observed in the results for chromium. Again a carburized surface is more readily attacked by a factor of 2-3 than oxidised surfaces, Fig. 6. Fig. 7 compares the results for the amounts of nickel found in the molten sulfate layer. Very little nickel is lost over 2000 h from the oxidised coupons but the passivation-spallation pattern can be detected. The carburized coupons, however, clearly show the established pattern. Also included for these samples are the results from the analysis of the spectra obtained after dissolving some of the quenched melt in water. The spectra were separated into the profiles for iron, chromium and nickel by a process that will be described in detail elsewhere. Fig. 8 shows some of these profiles, from which the nickel concentrations were obtained, the concentrations from the oxidised samples were too low for spectra that could reliably be resolved into their component profiles. The concentrations from absorbance data are thus very similar in magnitude to the ICP-AES data, and certainly parallel the changes in slope between successive data points. Improved and commercial computer programs, that should be able to separate out known overlapping profiles with better precision that was possible with the programs we had much earlier developed, are now available. The precision of the concentrations from spectra should be improved, and a closer correspondence with the ICP-AES data above 1000 h anticipated.

The polished halves of the sectioned ceramic holders that survived the necessary pre-treatment and preparation were examined by EDAX (Electron Diffraction X-ray Analysis). Depth profiling of the quenched melts was hereby undertaken. The concentration of the elements iron, chromium and nickel was determined as a function of distance away from the metal-melt interface. To do this, elemental distribution maps were created by repetitive scanning of an electron beam over a 100 µm square. The progressive movement of this square from an initial position on the steel coupon into the adhering salt would eventually create a picture whereby, as a function of distance, the elemental distribution resulting from corrosion could be followed. Fig. 9 shows a plot for the 310
steel components, iron, chromium and nickel, and aluminium and sulfur, from the (Na,K,Al)SO₄ eutectic melt. This shows clearly that the products of corrosion had penetrated around 100 µm from the steel surface into the thin sulfate layer. Beyond this distance the iron and nickel concentrations were dropping quickly to their minimum values around 140 µm, which then remained constant until the edge was reached, at 700 µm. Some nickel has entered the melt, and has probably spalled off with the iron. The iron level has a maximum at the front of the corrosion products moving into the melt and so does the chromium, but it also indicates falls and rises, probably reflecting the periodic passivating effect that it has.

The profiles for sulfur and aluminium are interesting. The peak for sulfur in the advancing front, and near the steel surface, indicates the presence of sulfide, and this distance also corresponds with minima in the iron and chromium profiles but with the maximum for nickel. There is essentially no sulfur in the edge of the front, but its concentration rises as fast as that for iron and nickel falls, and then remains constant, as do all the other elements, from 160 to 600 µm, corresponding to the region of the melt layer not participating in or contaminated by the hot corrosion process. No aluminium is detected near the steel coupon surface but its concentration rises to a maximum just in front of the advancing edge, and just as the chromium level drops to zero. As with most of the other elements it has dropped back to a constant level at 160 µm. It does however rise to a maximum between 600 and 700 µm, the range over which the sulfur level is dropping. We can therefore suggest that this latter indicates the decomposition of sulfate or, more likely, a wall effect of the Macor container or slight penetration of the sulfate melt into the Macor material while at the same time a deposit of alumina is formed on the wall, possibly as a protective skin. A layer of alumina would also appear to precede the advancing front of corrosion products. This can be understood in terms of the oxide ions generated in the melt reacting with the aluminium ions present, and consequently, not unexpectedly, the concentration of sulfur, in the form of sulfide ions, is particularly low.

Fig. 10 shows the concentration profiles for iron in the thin layer after 400, 1000 and 1400 h, and allows a comparison between carburised and oxidised steel. After 400 h the carburized sample shows that it has been readily attacked and iron can be located up to about 75 µm into the sulfate layer, but the oxidised sample has been but little affected, and there is no indication of any spalling during this time period. After 1000 h iron from the carburized coupon has travelled nearly 200 µm into the melt layer and iron from the oxidised specimen is now evident but considerably less in concentration. One spallation event appears to have recently occurred. Four hundred hours later evidence for spallation is strong for both types of pre-treated samples and the front is now beyond 200 µm. A more systematic account will be published later.

When comparing these profiles with those in Figs. 5-7 it is important to note that although they all contain the same basic information they are and cannot be identical. The latter, because the quenched melt was ground up and a sample taken for elemental analysis, provides an average or overall picture of the concentrations of the main components of 310 steel over the 2000 h of the experimental run. The former provides a snapshot of the concentrations in the melt of the corrosion products as a function of distance at 200 h intervals. Also, the values depend upon from where on the metal coupon the measurements were taken on the sectioned and polished Macor crucible. Fig. 4 also
indicates the position chosen as the most representative site for determining the data in Fig. 10. It should be noted that in order to enable the synthetic flue gas, containing SO$_3$, to enter the melt and participate as it does in boilers the site cannot be too far from the melt surface exposed to the gas. Hot corrosion also generates SO$_2$, which is insoluble in molten sulfate and so is slowly released as gas bubbles around the coupon in the melt that rise very slowly to the surface to escape. Evidence for quenched bubbles could be seen in certain sectioned Macor holders, together with spalled particles that were also moving to the upper surface. For each sample, therefore, it was necessary to determine the optimum site on the coupon for EDAX studies into the melt.

Thus, although we had replicated for the first time thin sulfate films, and measured their individual components and their concentrations as a function of distance and time, one feature had to be ignored. In achieving thin film hot corrosion conditions with the newly designed sample holder it was impossible to maintain a thermal gradient across the molten sulfate layer. However, we consider that these results and this approach, coupled with our earlier technique for making distance and time dependent measurements across a much thicker melt layer, does provide detailed information concerning hot corrosion occurring in PF boilers. From this study, a comparison of carburized and oxidised 310 steel, we have been able to determine that carburised samples are much more susceptible to hot corrosion attack and that plant operators should take every precaution to prevent start-up failures that result in oil-coating furnace interiors and cause subsequent carburization.

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Deposit layers on a corroding superheater or reheater tube

A schematic representation of the temperature distribution through a superheater deposit