

## SUMMARY

The work described in this thesis deals with the hot corrosion studies carried on stainless steels and nickel-base superalloys (Nimonic alloys) in presence of ash-deposit from coals of Indian origin. A comparative study of the hot corrosion behaviour has also been carried out in presence of  $\text{Na}_2\text{SO}_4$ .

Chapter 1 reviews literature on hot corrosion, special emphasis has been laid on the mechanistic aspects of hot corrosion.

Chapter 2 describes some aspects of fossil fuel corrosion with special reference to coal-ash deposit corrosion. Latest literature on coal ash deposit corrosion has been referred. The need of systematic hot corrosion studies on Indian coals, in the light of the introduction of high efficiency thermal power generating units in this decade and that of coal gasification in the 90's has also been emphasized.

Chapter 3 describes experimental part of the work and is mainly devoted to sampling and grading of the coal and its analysis. A detailed description of the procedures involved during the analyses of coal and coal ash is also given.

Nine samples of Indian coal of different grades were selected for the oxidation studies. The samples were graded on

the basis of moisture and ash contents. The coal samples were analyzed for moisture, volatile matter, fixed carbon and ash. The ash samples were analyzed for soluble and insoluble matter, metallic and non-metallic constituents (elemental and constituents) using a wide variety of techniques including chemical analysis, flame photometry, atomic absorption spectrometry, thermogravimetry, u.v. and visible spectrophotometry, X-ray diffraction analysis and infrared spectroscopy.

Indian coals are found to be rich in minerals and have relatively high ash contents. The ash content of the coal varies from 11% to 38%. In coal ash residues sulfur varies 2500 ppm to 10,000 ppm and vanadium 100 to 230 ppm. Some trace elements like Mo(1960 - 2830 ppm), Pb(400 - 4450 ppm) and Zn(700 - 3760 ppm) have abnormally high concentrations in the ash.

Chapter 4 deals with the ash deposit corrosion of stainless steels.

Chromium steels: S-110, austenitic 18:8 and AISI 303 were used for corrosion studies. The ash-coated steels were oxidized at 800<sup>o</sup> and 1000<sup>o</sup>C in air for 8 to 24 hours.

In general, coated steels exhibit increasing oxidation rates with increasing sulfur and vanadium contents. The effect is more pronounced at 1000<sup>o</sup>C. Studying the combined effect of sodium, potassium magnesium and calcium in ash on the oxidation rates of the steels with increasing concentration of Na + K +

Ca + Mg there is a gradual decrease in oxidation rates of the alloys. Ash from high moisture - low ash coals containing higher alkali contents have relatively less aggressive effect than the ash from low moisture - high ash having lower alkali contents. At 800°C, the scales formed on ash-coated steels have found to be protective and ash does not seem to be aggressive at this temperature. At 1000°C except S-110, the other two steels have higher oxidation rates than the ash-coated steels. Furthermore, the steels coated with ash residues from high ash-low moisture coals have higher oxidation rates than the steels coated with ash from low ash-high moisture coals.

During high temperature oxidation of ash coated steels two different types of scale morphologies are developed depending upon the nature of the ash.

Ash residues from low moisture - high ash coal are rich in free silica interact with protective chromium oxide scales to form fused complex chromium iron calcium aluminum silicates and on cooling are appeared as compact silicate scales. At scale/alloy interface the consumption of oxide in the formation of silicate results in an increasing sulfur activity and therefore, internal sulfidation occurs though on limited scale due to the presence of relatively small amount of sulfur present in the ash.

With steels coated with ash from high moisture - low ash coal and oxidized in air, oxidation reactions seem to be predominant and slag type reactions have minor role. The ash from high moisture - low ash coal has most of the silicon in the form of complex silicates ( $\text{CaAl}_2\text{Si}_6\text{O}_{16}$ ,  $\text{MgAl}_2\text{Si}_6\text{O}_{16}$ ,  $\text{NaAlSi}_3\text{O}_8$  etc.) and relatively small concentration of free silica. The oxygen activity at ash/alloy interface is sufficiently low and is capable to oxidize chromium and to some extent iron to form chromium rich iron oxide scales. In general, the alloy coated with ash from high moisture - low ash coal contains scales in which chromium enriched oxide is present as an inner porous layer followed by a silicate layer.

Temperature and the amount of free silica present in the ash seem to be the most important factors in influencing the oxidation rates and the morphologies of the scales of ash coated chromium steels.

Chapter 5 describes studies on ash deposit corrosion of superalloys. Nickel - base superalloys (Nimonic 75, 80A, 90 and 105) coated with ash and were oxidized at  $800^\circ\text{C}$  and  $1000^\circ\text{C}$  up to 36 hours in air.

At  $800^\circ\text{C}$ , the coated alloys show parabolic or nearly parabolic behaviour and the oxidation rates are substantially lower than the uncoated alloys. It appears that at this temperature the ash coating which mainly contains silica and

silicates as a protective film and there is no appreciable interaction in between molten constituents of the ash and the  $\text{Cr}_2\text{O}_3$  film present on the alloy.

Like steels, at  $1000^\circ\text{C}$ , the nimonic alloys coated with high ash coal residue have higher oxidation rates than those coated with low ash coal residues except N-105 which shows an opposite behaviour.

The high ash coal residue has relatively high concentration of silica and presumably undergoes slag type reactions with chromia, alumina and other oxides present in the scales. On the other hand, low ash coal residue is richer in silicates (containing relatively small amount of free silica) do not undergo slag type reaction and oxidation reactions seem to be predominant. In fact, low ash coated N-80A and N-90 have even much lower oxidation rates than the uncoated alloys. It sounds convincing that in such cases, the silicate film forms on the alloy acts as a protective layer.

In general, two types of scale morphologies are distinguished in ash coated alloys. In low ash coated alloys, a protective chromia or mixed oxide layer which is originally formed retained on the alloy surface and the outer layers formed from ash coating contain silicates (mixed Ca - Mg or Mg - Fe complex silicates) and there is a possibility of some combined sulfur remained on those layers in the form of  $\text{CaSO}_3$  or  $\text{FeS}$ .

In alloys coated with high ash coal residue, due to the presence of higher free silica contents in the ash slag formation takes place with the result that oxide layers on the alloys is replaced by a silicate layer adjacent to the metal. During slag reactions,  $\text{CaSO}_3$  and  $\text{FeSO}_3$  (or  $\text{FeS}$ ) could undergo decomposition reaction to release sulfur for the reaction.

Chapter 6 contains results of high temperature oxidation studies carried out on four Nimonic alloys, e.g., N-75, N-80A, N-90 and N-105, coated with varying amounts (0.5 to 11.0  $\text{mg}/\text{cm}^2$ ) of  $\text{Na}_2\text{SO}_4$  at three different temperatures, 650°, 800° and 1000°C in air.

Apart a few exceptions, the oxidation rates of the  $\text{Na}_2\text{SO}_4$  coated alloys in general, have been found to be less than those of the corresponding alloys without coating in the temperature range 650 - 800°C. At 1000°C, however, the coated alloys in majority of cases have slightly higher oxidation rates than the uncoated alloys. In general, the oxidation rates of the alloys decrease gradually with increasing salt deposition. It appears that  $\text{Na}_2\text{SO}_4$  is not aggressive at least up to 800°C if present as thicker films the latter act as a barrier against corrosion. Similar results have been reported by other workers. The thinner deposits of  $\text{Na}_2\text{SO}_4$  facilitates fluxing reaction as is evident by the higher oxidation rate of the alloy coated with relatively small amount of the salt.

With a thin deposit of  $\text{Na}_2\text{SO}_4$  ( $\sim 0.5 \text{ mg/cm}^2$ ) the oxidation rates follow the sequence (in order of decreasing oxidation rates).

### 650°C

Uncoated alloy : N-80A > N-75 ~ N-90 > N-105

Coated alloy : N-80A > N-75 > N-105 > N-90

Oxidation rates of  $\text{Na}_2\text{SO}_4$  - coated N-105 and N-75 are higher than the uncoated alloys where N-90 and N-80A have the same rates as that of uncoated alloy.

### 800°C

Uncoated alloy : N-80A > N-105 > N-90 > N-75

Coated alloy : N-80A > N-105 > N-90 > N-75

Oxidation rates of the coated alloys are invariably lower than the uncoated alloys.

### 1000°C

Uncoated alloy : N-90 > N-80A > N-75 > N-105

Coated alloy : N-105 > N-80A > N-90 > N-75

N-105 which has the lowest oxidation rate without salt deposition is otherwise most severely attacked in presence of the  $\text{Na}_2\text{SO}_4$  coating. The coated N-105 and N-80A have much higher rates than the uncoated alloy whereas N-75 and N-90 have lower oxidation rates.

With a relatively thick deposit of  $\text{Na}_2\text{SO}_4$  ( $5 \text{ mg/cm}^2$ ) the oxidation rate follows the sequence (in order of decreasing oxidation rates):

### 650°C

Uncoated alloy : N-80A > N-75 > N-90 > N-105

Coated alloy : N-105 > N-75 > N-90 > N-80A

N-80A which is severely attacked in presence of a thin deposit is least attacked in presence of a thick deposit. The oxidation rates of N-105 and N-75 are higher than that of uncoated alloy at 650°C.

### 800°C

Uncoated alloy : N-80A > N-105 > N-90 > N-75

Coated alloy : N-80A > N-90 > N-75 > N-105

The behaviour is similar to that observed with alloys with thin deposits. The oxidation rates of the coated alloys are always lower than the uncoated alloys.

### 1000°C

Uncoated alloy : N-90 > N-80A > N-75 > N-105

Coated alloy : N-105 > N-80A > N-75 > N-90

The behaviour of alloys in presence of thick deposit is similar to that observed in alloys coated with the salt deposits.

From the oxidation studies of the  $\text{Na}_2\text{SO}_4$  - coated Nimonic alloys it may be concluded that N-90 and N-75 have better corrosion resistance than N-80A and N-105 in the temperature range of 650-800°C. N-105 perhaps is most vulnerable to  $\text{Na}_2\text{SO}_4$  induced hot corrosion attack.

The oxidation behaviour of N-75, N-80A, N-90 and N-105 has also been studied in presence of  $\text{Na}_2\text{SO}_4 + \text{CoSO}_4$ ,  $\text{Na}_2\text{SO}_4 + \text{NiSO}_4$  and  $\text{Na}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3$  at 800°C and 1000°C in air.

The presence of  $\text{CoSO}_4$  in the deposited mixture is found to be beneficial to the corrosion resistance of the alloys and the oxidation rates are markedly lowered at 800°C and 1000°C. With the exception of N-75, the addition of  $\text{NiSO}_4$  increases the oxidation rates of the alloys. This is perhaps due to the formation of Ni rich sulfides resulting in accelerated corrosion. The presence of  $\text{Cr}_2(\text{SO}_4)_3$  has either beneficial or marginal effects on the oxidation rates of Nimonic alloys. In case of N-90 and N-105 alloys coated with mixtures of  $\text{Na}_2\text{SO}_4$  and  $\text{Cr}_2(\text{SO}_4)_3$  the oxidation rate is decreased whereas N-75 and N-80A show little or no effect on the oxidation rates at 1000°C.

The general morphological features of the  $\text{Na}_2\text{SO}_4$  coated Nimonic alloys consist of an outer porous layer of NiO followed by an intermediate layer of mixed oxides containing NiO and  $\text{Cr}_2\text{O}_3$  with some spinel and an inner layer of grey light or steel grey particles of  $\text{Cr}_2\text{O}_3$ . Light grey particles of chromium sulfide

appear in the form of stringers at grain and sub grain boundaries.

In the initial stages  $\text{Cr}_2\text{O}_3$  is formed (i.e., N-75, N-80A, N-90 and perhaps N-105) which interacts with oxide ion released from  $\text{Na}_2\text{SO}_4$  to form chromate ion. The reduction in oxide ion activity results in an increased S-activity in the  $\text{Na}_2\text{SO}_4$ . Sulfur may penetrate into the alloy to form  $\text{Cr}_2\text{S}_3$ . With the formation of  $\text{Cr}_2\text{S}_3$  the chromium content of the substrate will be depleted with a resulting local increase in the activity of Ni in this region. The depletion in the subscale zone may lead to Ni activity sufficiently high for the formation of NiS or  $\text{Ni}_3\text{S}_2$  (m.p.  $797^\circ$  and  $790^\circ\text{C}$ ) liquid.

The heavy corrosion of Nimonic alloys coated with thin films of  $\text{Na}_2\text{SO}_4$  can also be explained by considering the formation of chromium rich sulfide at grain and subgrain boundaries.

The sulfides then oxidize and the resulting oxide entered into the alloy as the scale, the Ni-rich particles also incorporate into the scale. The sulfur released by the oxidation of the sulfides penetrates into the alloy in advance of the oxidation front to form fresh sulfides, as a general rule no sulfur is lost to the atmosphere, hence the hot corrosion attack will continue without further introduction of  $\text{Na}_2\text{SO}_4$ .