Abstract
The behavior of materials at elevated temperature is gaining increasing technological importance. Understanding the behavior of metals at elevated temperatures and especially their corrosion behavior became an object of scientific investigation since long. Metallic components in coal gasification pilot plants are exposed to severe corrosive atmospheres and high temperatures. The corrosive nature of the gaseous environments which contain oxygen, sulphur and carbon may cause rapid material degradation and result in the premature failure of components. It is estimated that corrosion-related costs can be reduced more than 30% by development and use of better corrosion control technologies. It is now generally accepted practice to apply coatings to components in fossil fuel energy generation processes to provide thermal insulation, corrosion and wear resistance and in chemical process plants to protect the surface of structural steels against surface degradation processes. Plasma spraying is now a versatile technology that has been successful as a reliable and cost-effective solution for many industrial problems.

Keywords
Hot Corrosion, Plasma Spray, Oxidation, Coatings

I. Introduction
Hot corrosion is an accelerated form of oxidation which occurs when metals are heated in the temperature range 700-900°C in the presence of sulphate deposits formed as a result of the reaction between sodium chloride and sulphur compounds in the gas phase around the metals. It is a problem that man has had to face and solve from the very beginning of his existence. Understanding the behavior of metals at elevated temperatures and especially their corrosion behavior became an object of scientific investigation since long [1]. Coal gasification systems operate at temperature of up to 2000°F (1093°C) and at a pressure of up to 100 atm depending on the specific process and the product, coal gas generates the greatest problems. In addition to hydrogen and carbon-containing gaseous species, there are many undesirable species including sulphides, sulphites, sulphates, ammonia, cyanides, volatilised oils, phenols and aggressive trace elements such as potassium, sodium, vanadium and lead [2].

The coal used in Indian power stations has large amounts of ash (about 50%), which contain abrasive mineral species such as hard quartz (up to 15%), which increase the erosion propensity of coal [3]. The Indian coal proved to be exceptional in that they had significant amounts of alkali feldspars, (K, Na)AlSiO₃, and a garnet, minerals usually thought of as trace components of a coal. The garnets found in the Indian coals were found to follow the general formula (Mg, Fe²⁺),Al₂Si₃O₁₂. Table 1 indicated the Indian coal with dry ash content and mineral matter [4]. Further the coal analysis data collected from Guru Gobind Singh Thermal Plant, Bathinda (Punjab) as reported by Chawla et. al. [1], presented in Table 2. The ash and flue gases analysis of Guru Nanak Dev Thermal Plant, Bathinda (Punjab) as reported by Chawla et. al. [1], presented in Table 3, also indicates the presence of these constituents. Metallic components in coal gasification pilot plants are exposed to severe corrosive atmospheres and high temperatures. The corrosive nature of the gaseous environments which contain oxygen, sulphur and carbon may cause rapid material degradation and result in the premature failure of components [5-6]. A performance review of thermal power stations [7] indicates that erosion problems contribute significantly towards partial unavailability of power in India.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wt. %age</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total moisture (inherent + surface)</td>
<td>10.43</td>
</tr>
<tr>
<td>Inherent moisture</td>
<td>7.55</td>
</tr>
<tr>
<td>Ash</td>
<td>34.74</td>
</tr>
<tr>
<td>Ash on fire basis (actual)</td>
<td>33.64</td>
</tr>
<tr>
<td>Volatile metal</td>
<td>21.59</td>
</tr>
</tbody>
</table>

Table 1: The Ash Content and Mineral Matter in the Suite of Coals [4]
Table 3: Chemical Analysis of Ash and Flue Gases Inside the Boiler [1]

<table>
<thead>
<tr>
<th>Ash Constituent</th>
<th>Wt. %age</th>
<th>Flue Gases (Volumetric flow, 231 m$^3$/sec)</th>
<th>Constituent</th>
<th>Value relative to flue gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>54.70</td>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>5.18</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.18</td>
<td></td>
<td>SO$_x$</td>
<td>236 mg/m$^3$</td>
</tr>
<tr>
<td>Al$_2$O$_3$-Fe$_2$O$_3$/Al$_2$O$_3$</td>
<td>29.56</td>
<td></td>
<td>NO$_x$</td>
<td>1004 μg/m$^3$</td>
</tr>
<tr>
<td>Calcium oxide</td>
<td>1.48</td>
<td></td>
<td>CO$_2$</td>
<td>12%</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>1.45</td>
<td></td>
<td>O$_2$</td>
<td>7%</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.23</td>
<td></td>
<td>Na$_2$O</td>
<td>0.34</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.34</td>
<td></td>
<td>K$_2$O</td>
<td>1.35</td>
</tr>
<tr>
<td>Ignition loss</td>
<td>4.31</td>
<td></td>
<td></td>
<td>40% excess air was supplied to the boiler for the combustion of coal.</td>
</tr>
</tbody>
</table>

II. Economic Aspects of Corrosion

Corrosion of metals costs Rs. 24000 crore (Rs. 240000 million) to India due to materials corrosion in building structures, bridges, chemical plants, offshore platforms, power plants, ships, pipe lines for transportation of hydrocarbon, electrical and electronics components as reported in IIM Metal News [8]. It is estimated that corrosion-related costs can be reduced more than 30% by development and use of better corrosion control technologies. Corrosion control measures include corrosion inhibitors, cathodic protection and coatings [9]. Solid Particle Erosion (SPE) is a serious problem for the electric power industry, costing an estimated US$150 million a year in lost efficiency, forced outages, and repair costs [10]. High temperature degradation is one of the main failure modes of hot-section components in the gas turbines, so an understanding of this high temperature oxidation is very necessary [11].

Erosive, high temperature wear of heat exchanger tubes and other structural materials in coal-fired boilers are recognized as being the main cause of downtime at power-generating plants, which could account for 50-75% of their total arrest time. Maintenance costs for replacing broken tubes in the same installations are also very high, and can be estimated at up to 54% of the total production costs. High temperature oxidation and erosion by the impact of fly ashes and unburned carbon particles are the main problems to be solved in these applications. Therefore, the development of wear and high temperature oxidation protection systems in industrial boilers is a very important topic from both engineering and an economic perspective [12].

III. Preventive Measures Against Hot Corrosion

Although corrosion problems cannot be completely remedied, it is estimated that corrosion-related costs can be reduced by more than 30% with development and use of better corrosion control technologies. Corrosion control measures include corrosion inhibitors, cathodic protection, and coatings [13]. Corrosion of metals occurs when they come in electrical contact with a corrosive environment. Therefore metallic corrosion can be prevented by either changing the metal or altering the environment or by separating the metal from the environment as show in fig. 1 [14].

Depletion of high grade fuels and for economic reasons uses of residual fuel oil in energy generation systems are well known. Fuels with sulphur and other impurities bring about hot corrosion which significantly reduces the life of components [15]. The option to use low grade fuel limits the improvement in hot corrosion environment. In that case hot corrosion preventive methods to the existing environment are (a) change of metal i.e. use of super alloy (b) use of inhibitors and (c) use of coatings.

A. High Temperature Coatings

Hot corrosion is a serious problem in power generation equipment, gas turbines, internal combustion engines, fluidized bed combustion, industrial waste incinerators and paper and pulp industries. When considering coal-gasification processes, hot corrosion is expected to be a problem because the gas environment generally has large sulphur activities and low oxygen activities and also contains substantial amounts of salts.

Increasingly greater demand imposed on materials makes it more difficult or at the current stage of development, even impossible to combine the different properties required in one single material. Therefore, a composite system of a base material providing the necessary mechanical strength with a protective surface layer different in structure and/or chemical composition and supplied by a surface treatment can be an optimum choice in combining material properties. Although protective surface treatments are widely used at low temperature, the use of these at elevated temperature is more recent.
It is now generally accepted practice to apply coatings to components in fossil fuel energy generation processes to provide thermal insulation, corrosion and wear resistance and in chemical process plants or boilers to protect the surface of structural steels against surface degradation processes such as wear, oxidation, corrosion and erosion [16]. Among these coating techniques the thermal spraying has grown into a well-accepted industrial technology. Plasma spraying is gaining importance in many critical areas of application. This is mainly due to the fact that it provides increased design flexibility so that the parts made up from a combination of materials with widely differing physical and chemical properties could be employed [17].

**B. Plasma Spray Coatings**

The demand for protective coatings has increased recently for almost all types of superalloys with improved strength, since high-temperature corrosion problem become much more significant for these alloys with increasing operating temperatures of modern heat engines. Among the different kinds of coating technologies, plasma spray coating should be one of the most promising. The advance plasma techniques have many advantages such as high productivity for coating thick films of more than 100 μm and good applicability for a wide range of coating materials including ceramic powder, further the process does not cause degradation of the mechanical properties of the alloy substrate [18].

The process of Plasma Spraying as indicated in Fig. 2 is based on the generation of an electrical arc in a gun that heats upto high temperature the flux of inert gas (Ar, He, H₂) to generate plasma.

**D. Fundamentals of Plasma Spray**

Figure: 3: shows a schematic arrangement for plasma spraying using a D.C. Spray torch and in most cases (99%) plasma spraying is achieved by using plasma torches [19]. A high intensity arc is operated between a stick-type cathode and nozzle-shaped water-cooled anode. Plasma gas, introduced along the cathode, is heated by arc to plasma temperatures, leaving the anode nozzle as a plasma jet or plasma flame. Fine powder suspended in a carrier gas is injected into the plasma jet where the powder particles are accelerated and heated. As the molten powder particles impinge with high velocities on substrate, they form a more or less dense coating [20].
E. Plasma Generation and Formation

Essential components of a plasma torch are shown in fig. 4. The arc is initiated between the tip of the cathode (typically thoriated tungsten) and the water cooled anode nozzle. The working gas is introduced either axially or with an additional swirl component. The latter improves arc stability in the vicinity of the cathode and rotates the anode arc root which may be desirable for reducing anode erosion. The gas heated by the arc emanates as a plasma jet from the torch orifice. For typical plasma spray applications, the gas flow rate is sufficiently high to ensure a highly turbulent jet with a visible length of several centimeters.

Argon and mixtures of argon with other noble (He) or molecular gases (H₂, N₂, O₂, etc.) are frequently used for plasma spraying. The addition of He and in particular of molecular gases results in a drastic increase in the enthalpy of the plasma, which may be important for complete particle melting [20]. The maximum temperature in the plasma jet is a function of the design and of the operating parameters.

F. Applications of Plasma Spraying Technique

Plasma spraying is gaining importance in many critical areas of application. The main advantage of plasma spray technique is that it enables a whole range of materials including metals and alloys to be plasma sprayed on to a great variety of substrate types and geometries [21-22]. It is the most widely used technique to prepare composite structural parts providing required mechanical strength properties as well as inhibition of oxidation and other corrosive degradation processes [23]. Pfender (1988) [20] reported the application of plasma process to corrosion, temperature and abrasion-resistant coatings and production of monolithic and near net shapes which at the same time takes advantage of the rapid solidification process. During fifties the first serious attempts were reported using plasma torches for spraying of primarily refractory material. Today any material can be used for plasma spraying on almost any type of substrate. The properties of coatings are dictated by particular applications. High density coatings, for example are required to provide wear or corrosion resistance, whereas thermal barrier coatings should have a relatively high percentage of porosity to ensure thermal shock resistance. The plasma spray parameters will of course affect the properties of the coatings. The ultimate goal of research efforts in the field is to establish predictive correlation between plasma spray parameters and the properties (quality) of the coatings.

IV. Conclusion

The demand for higher performance and increased efficiency has resulted in the progressive increase in the temperatures of operation of turbines. This has been accompanied by the development of single crystal blade technology, more advanced corrosion-resistant coatings and complex cooling techniques [24-25]. The development of modern coal fired power generation systems with higher thermal efficiency requires the use of construction materials of higher strength and with improved resistance to the aggressive service atmospheres. These requirements can be fulfilled by protective coatings [26]. Coatings have been used with some success in field applications. Most of the high-chromium coatings offer some resistance to oil ash corrosion. Other coating systems, such as silicon may also be helpful. Plasma Spraying is a high-tech process that can produce coatings on components for use under severe conditions. Plasma spray techniques are widely used for coating deposition as a result of their ease of application and their ability to deposit various coating materials on to substrate alloys.

References