REVIEW

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An overview of problems and solutions for components subjected to fireside of boilers

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Abstract

In engineering applications, there are various types of boilers such as water tube boilers, fire tube boilers, packaged boiler, fluidized bed combustion boiler, pulverized fuel boiler and waste heat boilers. These boilers are used in different industries such as power plants, paper, and chemical. The present paper reports various problems (such as agglomeration, slagging, fouling, caustic embrittlement, fatigue failure and high temperature corrosion) related to boilers and their possible solutions. Some of the controlling parameters for high temperature corrosion has also been studied viz use of inhibitors, varying temperature and pressure, sol–gel coating and thermal spray coating. Thermal spraying has emerged as a main tool for improvement in surface. Problem of corrosion, wear resistance, electrical or thermal insulation can be altered using different coating techniques and materials. Deposition of ash in biomass-fired boilers also causes severe problems of agglomeration. The problem of agglomeration can be solved using kaolin or NH_3 in the bed of boilers. Some important processes such as pulse detonation wave technology, intelligent soot blower, chemical treatment technology can be used to minimize the effects of fouling.

Keywords Boilers · Fuel · Slagging · Hot corrosion · Coatings · Thermal spray

Introduction

A boiler is a closed vessel producing heat by the combustion of fuel which is transferred to water for its conversion into steam at desired temperature and pressure [1]. They are vastly used in power plants, paper industry, chemical industries, water treatment plants, textile industry, building material industry and food industry. They are also being used in the tobacco industry, food packaging, refineries, metal work industries, hospitals, distilleries, waste incinerators, print offices and many more [2]. The efficiency of these industries is very much dependent upon boiler's efficiency. Hence, it is necessary to carry out the maintenance of boiler at regular intervals so as to avoid any unwanted shutdown. However, operation of boiler leads to number of problems such as agglomeration, slagging, fouling, caustic embrittlement,

fatigue failure and hot corrosion which are responsible for their unwanted shutdown [3]. Moreover, fireside of boilers suffers maximum damage. Hence, it is necessary to find the solutions either to avoid or to remove such type of problems in the boiler. Therefore, in the present paper effort has been made to discuss the problems as well as their possible solutions according to the available literature.

Types of boilers

Boilers can be basically classified into water tube boilers, fire tube boilers, packaged boilers, fluidized bed combustion boiler (FBC), Pulverized fuel boiler and waste heat boilers.

In water tube boilers, the water to be heated flows in the tubes and the combustion gases flows around the tubes, thus converting the water into steam. These types of boilers are used where high steam and pressure are required. The capacity of these boilers varies from 4500 to 1,20,000 kg/h [3, 4]. Habib reported that if the fuel is burnt in pure oxygen rather than in air, then the exhaust gases produced consist of only H_2O and CO_2, which could further be separated with the help of condensation. It was also opined that consumption of

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oxygen is relatively slower compared to air–fuel consumption. He also observed a higher heat transfer rate in case of oxyfuel compared with the use of air–fuel [5].

Fire tube boilers are the least used boilers now-a-days. In this, combustion products and high temperature gases flow in the tubes and water to be vaporized flows around these tubes [6]. The capacity of these boilers is up to 12,000 kg/h. They produce low to medium steam pressures up to 18 kg/cm^2 [7, 8].

Packaged boilers are the types of boilers in which the tubes for the flow of steam are enclosed in a capsule. This is mainly the shell type boiler in which only water supply, electrical supply and fuel is required when delivered to the desired area. It only requires oil as a fuel for combustion to take place. These boilers have high evaporation rate due to restricted combustion space. So, the thermal efficiency of these boilers is higher than other boilers [9, 10].

In fluidized bed combustion boiler (FBC) (Fig. 1), a high velocity air is passed through finely divided bed covered with sand. The sand gets suspended in air due to high turbulence. These sand particles are then heated in this fluidized state. When the fuel such as coal is fed into the bed, the coal burns instantly as the sand is heated to ignition temperature of the fuel. The temperature ranges from 850 to 950 °C in the combustion chamber [4]. It has been reported that if metal oxide particles such as Fe_2O_3 has been used on the bed as oxygen carrier then CO_2 and H_2O can be obtained without any energy loss [11]. Any type of fuel whether solid, liquid or gas can be used in fluidized bed combustion. They mainly use coal, wood, biomass and even slurry as a fuel [12]. The amount of sulfur and nitrogen oxide produced during fluidized bed combustion is comparatively less as produced in conventional boilers [13]. Fluidized Bed Combustion Boiler can be further divided into Atmospheric Fluidized Bed Combustion

Boiler (AFBC), Pressurized Fluidized Bed Combustion Boiler (PFBC) and Circulating Fluidized Bed Combustion Boiler (CFBC).

In Atmospheric Fluidized Bed Combustion Boiler (AFBC), crushed coal of size 1–10 mm is supplied to the fluidization media. As the temperature of furnace becomes equal to the ignition temperature of the coal it starts burning. Coal supply is also controlled so that the temperature of the fluidized bed can be kept between 750 and 850 °C. Heat exchanger tubes present in the fluidized bed recover the heat from the combustion chamber. If limestone is used as the fluidizing medium then SO_x can be removed during the combustion of coal [4, 14–16]. In Pressurized Fluidized Bed Combustion Boiler (PFBC), a highly compressed draft air is supplied through the fluidizing bed. This type of boiler is mainly used in the power plants for the generation of steam which strikes on the turbine thus producing electricity. In this, the steam generation tubes are fed on the fluidizing bed as well as above the bed [4]. On the other hand if combustion products such as gases are also struck at the gas turbine, they will also help in generation of electricity [17, 18]. Jensen reported that the injection of NH_3 into the system leads to 50–60% reduction in NO_x [14, 15]. Coal along with biomass and other wastes such as straws, switch grass and willow chips can be used as a fuel which is further used for running a combined cycle [19]. Circulating fluidized bed combustion boiler (CFBC) is the system in which steam is produced after burning of fossil fuels in furnace which operates under special hydrodynamic condition known as Fast bed. The boiler is divided into two sections: first section consisting of furnace, gas–solid separator, solid recycle device and external heat exchanger and is known as solid circulating loop. The other section is known as convective section. The major advantages of these boilers are fuel flexibility, high combustion efficiency, efficient sulfur removal and low NO_x emmission [20, 21]. Leckner investigated that if we are using wood as a fuel there is a production of large amount of nitrogen oxide. But if we use char on the bed then there is a reduction in formation of NO in the combustion products. There were no signs of N_2O found during the combustion of wood [22].

In Pulverized fuel boiler system, powdered coal is used for combustion, out of which 2% is nearly of + 30 microns size and 70–75% is below 75 microns. A different variety of coal can be used in these types of boilers. In pulverized boilers, coal is reduced to a fine powder with the help of grinding mills and projected into combustion chamber with the help of hot air current. Pre-heated air from PA fan helps the coal to flow from the bowl mill to the boiler. A fire ball is created when the coal is fired inside the furnace where the temperature rises up to 1300–1700 °C. About 90% of the coal power plants use these types of boilers
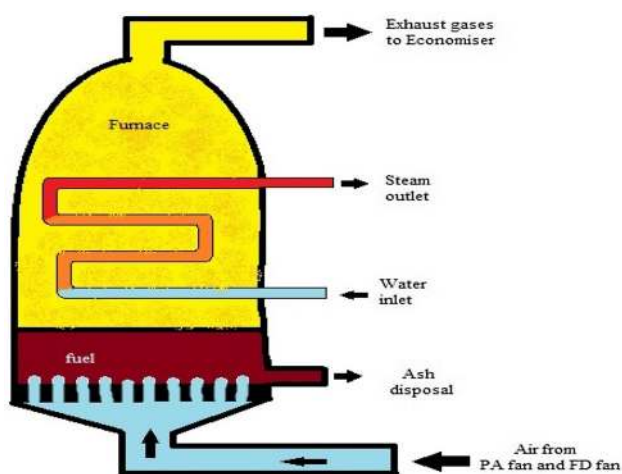

Fig. 1 Working of Fluidized bed combustion boiler

for power generation [4, 23]. Small proportion of wood, biomass and agricultural materials can also be used as fuel in pulverized fuel boilers [24].

In waste heat boilers, the heat of exhaust flue gases coming from combustion process is used to generate steam. They may also be called as economizers as they help in saving the fuel, thus reducing the cost of production of electricity. This system consists of tubes, i.e. the heat pipes, and convection heat transfer chamber which is finally connected to the boiler chamber. Steam is generated when the hot flue gases flow outside the pipe due to convection. These hot gases transfer their heat to the water present in the tubes and come out with a lower temperature [24–26].

Problems being faced in the boilers

Major problems occurring in the boilers are agglomeration, high temperature corrosion, slagging, fouling, caustic embrittlement and fatigue failure.

Agglomeration

Agglomeration problem mainly occurs on the fireside in the fluidized bed boilers [27]. Agglomeration is basically the ash-related problem of biomass-fired boilers. Ashes which are formed from high-sulfur and low-ash fuel agglomerate, if they are prone to sulfating condition for long time. The degree of sulphation varies with both time and temperature. It varies proportionally with increase in temperature and time. Ashes agglomerate when there is a production of 50–60% or more amount of calcium sulfate and Ca–K-silicates in the deposit. Loop seal and bed ashes are more prone to agglomeration than fly ash. Fly ash produces weaker deposits than bed ashes, but they all will agglomerate with respect to time [28]. The rate of agglomeration increases if the temperature increases from 850 to 950 °C. Agglomeration occurs first due to carbonation and then due to sulphation at lower temperatures [29]. The agglomeration tendency of ash increases with the increase in iron or alkali metal content [27]. Silvennoinen reported that alkali silicate mixture of low melting point is produced when alkali-rich ash reacts with the free quartz which is present in the sand and this mixture forms an adhesive bond between the fluidizing bed particles, thus leading to agglomeration [30]. The low-melting alkali chlorides may enhance the stickiness of fly ash particles and increase the ash deposition rate on the superheater tubes. The deposited alkali chlorides may increase the corrosion rate of super heaters, as the chlorides

may form low melting point eutectics and cause aggressive liquid-phase corrosion [31].

Possible solutions for agglomeration

Additives such as sulfur, kaolin and ammonia sulfate can be used to reduce agglomeration on superheater tubes. Davidsson reported that if kaolin is added to the bed material before the combustion, then this would surely resolve the problem of agglomeration. In one of the study, it was reported that the agglomeration temperatures for wheat straw and bark were determined to be 739 and 988 °C, respectively [32]. However, if kaolin is added to the bed, the initial bed agglomeration temperatures increased to 886 and 1000 °C, respectively. When kaolin was added to the bed, the compositions of the coatings were altered toward higher melting temperatures, mainly because of their decreased potassium content as kaolin absorbs the major potassium species. However, Kaolin is expensive to be used commercially against deposits [29]. The problem can also be counteracted if ammonium sulfate or sulfur is added as a substitute of kaolin [28–33]. The reactions between the additives such as sulfur and alkali chlorides form alkali sulfates and the chlorine is released into gas phase as HCl. The alkali sulfates have higher melting points than the corresponding alkali chlorides and will, therefore, have a smaller tendency to stick to the superheaters as deposits. The deposit formation and the corrosion potential of the superheaters can, therefore, be minimized [31].

Slagging

Based on the different methods involved in ash deposit over the heating surface, two types of ash deposition are observed, i.e. slagging and the fouling. Boiler slagging and fouling are two main factors that adversely affect the efficiency of boilers [34, 35]. Fireside of the boiler is mainly affected by these problems. These two processes lead to frequent non-operation of soot blowers. Slag is the molten ash and incombustible by-product that remains as residue after coal combustion. Slagging is the deposition of partially fused residues on furnace walls or surfaces exposed to radiant heat. It takes place in the hottest parts of the boiler. Slag is formed when molten softened ash particles are not cooled to solid state when they reach with the hot surface [36, 37]. It reduces the heat absorption in the furnace, increases furnace exit gas temperature, decreases boiler efficiency and availability due to unplanned shutdowns leading to losses in the operation [37]. It has been found, that serious slagging mainly occurs on the walls of the furnace. Flue gases in the center of the furnace make it to deflect on other two sides of the walls; thus leading to the impingement of the pulverized-coal flame on to the side walls of the furnace. Due to this

process, slagging on side walls takes place. It leads to slight slagging on the arch burner regions and to the front and rear wall regions of the lower furnace [38].

Possible solutions for slagging

The process of slagging cannot be prevented completely. It can, however, be reduced using several ways such as ensuring even distribution of heat to avoid localized temperatures. It can also be minimized by adding a conditioner to the molten ash particles carried by the flue gas which is taken up by those molten particles and produces a nucleating effect when those particles cool, causing them to solidify more rapidly, thereby preventing deposit formation or resulting in considerably more amount of friable deposits [39]. Formation of deposits on the convention surface can be reduced by keeping appropriate temperature at the exit of the furnace and also by removing sufficient amount of heat. Apart from the above stated solutions, height, width and depth ratio of the furnace should be proportional so that potential of ash particles impacting on the furnace surface is limited [40].

Fouling

Fouling is the formation of sintered ash deposits on conventional heating surfaces such as reheaters and super heaters [40] that are not directly exposed to flame radiation. It takes place as the suspended fly ash cools down along with flue gases [41]. Excessive fouling may lead to an increase in gas temperature and deposition rate which leads to continually changing conditions in the boiler, hence, reducing its efficiency [42]. Temperature variation for high temperature fouling lies in the range from 900 to 1300 °C, and for low temperature fouling, this range is from 300 to 900 °C [38]. Fouling in boilers is caused due to reduction in heat transfer, which further leads to sufficient loss of superheat and hot flue gas temperatures [43, 44]. Major factors that lead to the removal of fouling are the deposit strength and the adhesive bonding between the heat transfer surface and ash deposit. Deposit removal process involves breaking of deposit matrix and/or breaking of adhesive bonding. In coal-fired power plant boilers a lot of production problems are generated due to fouling. Lack in timely maintenance and cleaning can also lead to fouling problem [45].

Possible solutions for fouling

There are no permanent solutions for fouling, but there are certain technologies which can help in minimizing the deposition problems in boilers. Some of these processes are pulse detonation wave technology, intelligent soot blower, chemical treatment technology, anti-fouling coatings, etc [35]. These technologies can help in reducing the fouling problem to some extent in boiler tubes depending upon their efficiency. Finishing remarks and recommendations can be drawn according to the results shown. Soot blowers can be used to clean the heated plane of boilers during operations, with blowing medium as water and steam. Water or steam is directed at the deposit through a nozzle which causes the deposit to fracture and corrode away. There are some ash actions prediction tools such as AshProSM used to review the slagging and fouling situation in coal-fired boilers. Integrated boiler with computational fluid dynamic (CFD) simulations with ash actions models is used to determine ash development, transport, deposition, deposit growth and strength development [36]. Some of the other methods, which are used for prevention from fouling in boilers, are wet pretreatment of brown coal-fired power utility boiler, using mineral additives in coal-fired utility boiler, monitoring of fouling tendencies, chemical treatment technology: targeted in furnace injection (TIFI) technology, etc. [44].

Caustic embrittlement

The process of caustic embrittlement occurs in boilers and leads to formation of cracks on the riveted mild steel plates. The temperature ranges from 200 to 250 °C, which further leads to deposition of concentrated hydroxide on the waterside of the boiler [46]. We can also explain caustic embrittlement as a phenomenon where boiler becomes brittle, due to accumulation of caustic soda [47]. Caustic embrittlement is also known as stress corrosion cracking [46]. Caustic embrittlement is caused due to the presence of caustic soda in the boiler feed water, which is in direct contact with the steel and drums of the boiler [48]. In the boiler, when the water evaporates, the concentration of sodium carbonate increases. Sodium carbonate is used for the softening of water via. lime soda process. During this process, there are chances that some of the sodium carbonate particles may be left behind. With the passage of time, the concentration of sodium carbonate increases, and it undergoes hydrolysis to form sodium hydroxide. When the concentration of sodium hydroxide increases by a certain amount, it makes water alkaline. This alkaline water enters into small cracks of inner walls of the boiler. Evaporation of this water leads to a continuous increase in the amount of sodium hydroxide present in the boiler tubes. This sodium hydroxide attacks the iron present on the boilers and dissolves it; thus, forming sodium ferrate, which further leads to caustic embrittlement [49].

Possible solutions for caustic embrittlement

Caustic embrittlement in boilers is a natural process and can be prevented temporarily by adding a combination of chemicals consisting of a sufficient amount of sodium sulfate

in normal boiler water [50]. Caustic cracking occurs in solutions, where mixed active and passive control of corrosion is operative [51]. We can prevent caustic embrittlement by adding compounds such as sodium sulphite, tannin, lignin, and phosphate, because it blocks the cracks presented by infiltration of alkali [52].

Fatigue failure

The propensity of a material to fracture by means of continuous brittle cracking under repeated alternating or cyclic stresses of intensity fairly below the normal strength is known as fatigue failure [53]. It may affect a vast majority of materials, mainly crystalline solids such as metals and alloys. Fatigue process may be divided mainly into three stages. First step is initiation. Intersection of the surface with the slip bands formed due to production and movement of dislocations caused by excessive application of stress leads to initiation of fatigue. Then comes the Stage II, i.e. crack growth. Stage II fatigue crack is necessarily a small crevice associated with thin folds of metal pushed out of the surface. These crevices are known as intrusions. The cracks may develop and grow on interfaces of all types as well as it may grow on grain boundaries. Last stage is the Stage III crack growth. It is the most important aspect of fatigue failure and is caused by gradual macroscopic rotation of the crack to a non-crystallographic plane [54]. During the initial phase of boiler operation, a variety of tube failures are seen, including short-term overheating, weld failures, material defects, chemical excursion failure and occasionally fatigue failures. Fatigue failure is caused by high value of maximum tensile strength, high amount of variation in applied stress, attachment of corrosion welds, improper flexibility, improper heat treatment, contouring of welds, large number of cycles of applied stress and cold-bend restriction to thermal expansion [55].

Possible solutions for fatigue failure

Managing boiler tube failures is important as it can help in reducing forced outages, minimize risk of failures and hence, improve plant availability as well as reliability. One of the most important causes of boiler tube failure, that is, fatigue failure, can be prevented by following the given measures: avoid stress concentrations, pay careful attention to the details at design stage to make sure that cyclic stresses are sufficiently low to attain the required endurance, use stronger and more capable materials with high fracture toughness and slow crack growth, choose good surface finishes, monitor temperature variations, increase symmetry, resolve simplicity of design and ensure firm as well as thorough routine maintenance [56].

High temperature corrosion

High temperature corrosion can be defined as the accelerated oxidation of materials that is induced by salt film deposition at elevated temperatures on fireside of the boiler. The elevated temperature ranges from 700 to 1300 °C. Various types of high temperature corrosion are nitridation, chlorination, carburizing, oxidation, sulphation, flue gas and corrosion deposit. Fused alkali sulfates are deposited on the hot substrates by the oxidation of metal contaminants such as sulfates and vanadium in the fuel [34].

Possible solutions for high temperature corrosion

a) Use of inhibitors Corrosion inhibitors are substances, which when added to an environment in small concentration reduces the rate of corrosion of the metal [57]. The main factors responsible for corrosion inhibition are composition of fluid, quantity of water and flow regime. We use inhibitors in oil extraction and processing industries, because there they proved to be best defensive agent against corrosion [58]. We can also call the corrosion inhibitors as the additives to the fluid surrounding the metal.

The selection of inhibitors depends on the type of metal and the environmental conditions [59]. They can be mainly classified into two types such as environmental inhibitors and interface inhibitors. Environmental conditioners or (scavengers) inhibitors have the ability to decrease the corrosivity of a particular substance by scavenging (clearing) aggressive substances [59]. In interface inhibitors, the process of controlling corrosion is done by the formation of film on the metal/environment [60].

Interface inhibitors can further be classified into two subtypes, i.e. liquid-phase inhibitors and vapor-phase inhibitors. Liquid-phase inhibitors are those inhibitors that are categorized on the basis of their electrochemical reactions [58]. Vapor-phase inhibitors are temporary inhibitors which are used to prevent corrosion; especially in closed environments. They are environment-friendly and do not contain any harmful chemicals such as nitrates. They also have low cost, are easily affordable and last for long time thus yielding reliable results [58–60].

Liquid-phase inhibitors can be further divided into three subtypes that are anodic, cathodic and mixed inhibitors. Anodic inhibitors are those inhibitors that prevent corrosion by forming a protective layer of oxide film on the metal surface. They are also known as passivators, and these inhibitors alter the anodic reactions in the cell [61]. The process of controlling corrosion either by decreasing the reduction rate or by precipitating selective areas of cathodic region (cathodic preceptors) are termed as cathodic inhibitors. In simple words, we can also describe cathodic inhibitors as the chemical compounds that can decrease the corrosion

rate of a metal or an alloy, when added to a certain liquid or gas [58–62]. The compounds which are neither anodic nor cathodic, i.e. compounds which show the characteristics of both anodic and cathodic inhibitors are termed as mixed inhibitors. On an average 80% organic compounds are mixed inhibitors. They protect metal by the process of physical adsorption, chemisorption and film formation. They also reduce the cathodic and anodic reactions to work [58, 59].

Cathodic inhibitors are further classified into cathodic poison and cathodic precipitators. The compounds that can cause hydrogen embrittlement and hydrogen blisters due to the adsorption of hydrogen into steel are called cathodic poison and the compounds that help in increasing alkalinity and precipitation in insoluble compounds of metallic surface are called as cathodic precipitators [58].

Mixed inhibitors can also be classified into two subtypes that are physical and chemical inhibitors. Physical inhibitors are those that are adsorbed physically and interact rapidly; however, a major disadvantage about them is that they also get removed easily. In chemical inhibitors, as there is a chemical reaction involved, it slows down the process in comparison with physical inhibitors [58].

b) Sol–gel coating Sol–gel coating is widely used method for protection against corrosion. It has shown better chemical stability, oxidation control, and enhanced corrosion resistance for metallic substrates [63, 64]. It is a method for producing solid materials from small molecules. It converts the monomers into a colloidal solution (sol) which acts as the precursor to an integrated network (or gel) which is either of discrete particles or network polymers [65]. Sol–gel coating is a wet technique which can be used for making ceramic and glassy materials. Deposition of sol–gel coating to the metals is relatively recent and it has not been investigated sufficiently [66].

The synthesis of gels at room temperature is done mainly in two ways. First step is a common reaction that occurs in nature when chemical species of silica is diluted in aqueous solutions. This solution then condenses and leads to the formation of silica network. This condensation can occur in various aqueous solutions depending on salt concentration and pH. The second step is producing silica from the solution which corresponds to a chemical reaction by implying metal alkoxides and the water in an alcoholic solvent [67]. The disadvantage of sol–gel technique is that the cost of raw material (chemicals) is high. As an example, MgO powder with a purity of 98% is available in small quantities for $32/kg. Magnesium ethoxide which is a chemical substrate for making MgO, costs about $210/kg. There is often cracking and large volume shrinkage during drying thus is avoided by ceramists whenever possible [68].

c) Varying temperature and pressure The temperature can be defined as the comparative measure of cold or hot system [69]. Several research studies show that their exists many relationships between variation in corrosion rate at different range of temperature for different materials. Corrosion can, however, be defined as the deterioration of the properties of a material because of its interaction with the environment. Corrosion can lead to failures in various plant infrastructure or machines which are usually costly and usually take much time to repair. Figure 2 shows the comparison between corrosion rates with the increase in temperature. Some of the losses of contaminated products are environmental damage that may be costly in terms of human health [70]. There is a rule of thumb that the rate of corrosion of a metal gets double for every 10 °C increase in temperature. Thus, if the rate of corrosion is 30 mpy (mils per year) at 30 °C, it is expected to be 60 mpy at 40 °C, 120 mpy at 50 °C, and so on [71]. This rule is applicable in many situations, but it is necessary to recognize situations where it should not be applied. There are some places where this rule is not applicable. The rule is based on the fact that rate of corrosion is under control of a chemical reaction when subjected to dilute sulphuric acid attacking carbon steel. Even in these kinds of situations, the rate of corrosion increase with temperature, this may vary from 1.5 to 2 times with each 10 °C rise in temperature. But if the corrosion rate is under control of some other factors, such as the presence of oxygen gas in the corrosive environment, then the above statement may not be true. Oxygen plays very important role in corrosion. For example, if we consider a closed system constructed of carbon steel, then the corrosion reaction rate depends on the presence of oxygen gas. Element such as iron which is present in carbon steel has high affinity towards oxygen. Hence when carbon steel comes in contact with oxygen, it develops the oxide layer (Fe_2O_3 or Fe_3O_4) either protective or unprotective, thereby increasing the corrosion rate [72]. Once the oxygen gas in the environment of the system is used up by the corrosion of carbon steel, the rate of corrosion falls to very
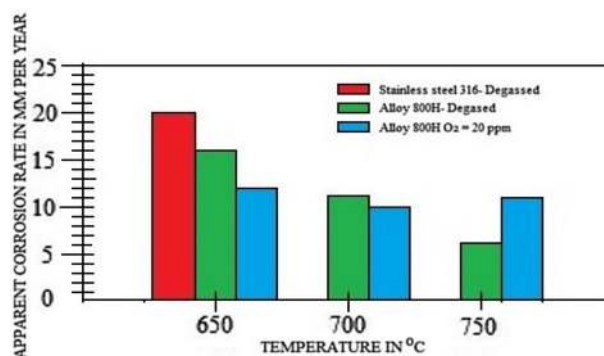

Fig. 2 Comparison between corrosion rates with the increase in temperature

low values regardless of the temperature. This is because no oxygen is left in the chamber which can react with elements to form oxide. Hence, the oxide which has already formed on the surface of components becomes passive in nature. The same follows in an open system as oxygen is driven off at an increased temperature. The final consideration is the nature of alloys. Some of the alloys develop a protective or passive film in a specific environment, such as carbon steel in conc. sulphuric acid; or they may develop it naturally, such as in case of stainless steels and titanium. As the temperature increases, and as long as passive film remains intact, the rate of corrosion does not increase. But as soon as the passive film is overcome by an increase in temperature, the rate of corrosion increases rapidly. The actual surface temperature of a metal in contact with the process environment should be known. As the hot wall affects the re-boiler tubing, it makes the inner diameter of tubing much hotter than the bulk process environment. Consequently, the rate of corrosion may be higher than predicted. With condensers, where refrigerant is sometimes cooling water present on the shell side, the reduction in temperature might lead to condensation of a corrosive species and this is sometimes called the cold finger effect or the shock cooling [73].

Pressure is represented by P and it is the force applied perpendicular to the surface area of an object per unit area over which the force is distributed. The gauge pressure (sometimes also spelled gage pressure) is the pressure relative to the local atmospheric pressure or ambient pressure [74]. The various units which are used to express pressure are the pascal (Pa) (it is one newton per square meter), the atmosphere (atm), bar. Pressure too plays a very important role in deciding the rate of corrosion [75]. Increasing the total pressure

or decreasing the volume will also result in a higher rate of reaction, because increase in pressure causes the molecules to collide with greater force.

This leads to more effective collision and, therefore, products will form at a faster rate or the rate of corrosion will be high. If partial pressure of oxygen and carbon dioxide are high, then the corrosion rate will also be higher [76]. Adding an inert gas, such as argon, neon, and krypton, will not affect the rate of corrosion because the partial pressures of the reacting gases remain the same [77]. Figure 3 shows the comparison between corrosion rate and partial pressure of CO_2.

d) Coating Coatings have been widely developed to provide protection against erosion and corrosion. They help in shielding the material from several chemical and physical damages which can occur due to direct contact of material with environment. As corrosion results in dilapidation, it eventually leads to failure of components both in manufacturing and processing industries. Therefore, corrosion and erosion difficulties are of great significance in many industrial application and products. Coatings can be used as an engineering key to improve surfaces against corrosion, wear, thermal deterioration and other surface phenomena. Good adhesion, low porosity and substrate compatibility are the various important characterizing factors for acceptable coatings. There are various coating technologies available which can be used to deposit suitable material on the substrate. They are generally illustrious by coating thickness: deposition of thick films (20–400 μm) and deposition of thin films (below 10–20 μm) [78].

Fig. 3 Comparison between corrosion rate and partial pressure of CO_2
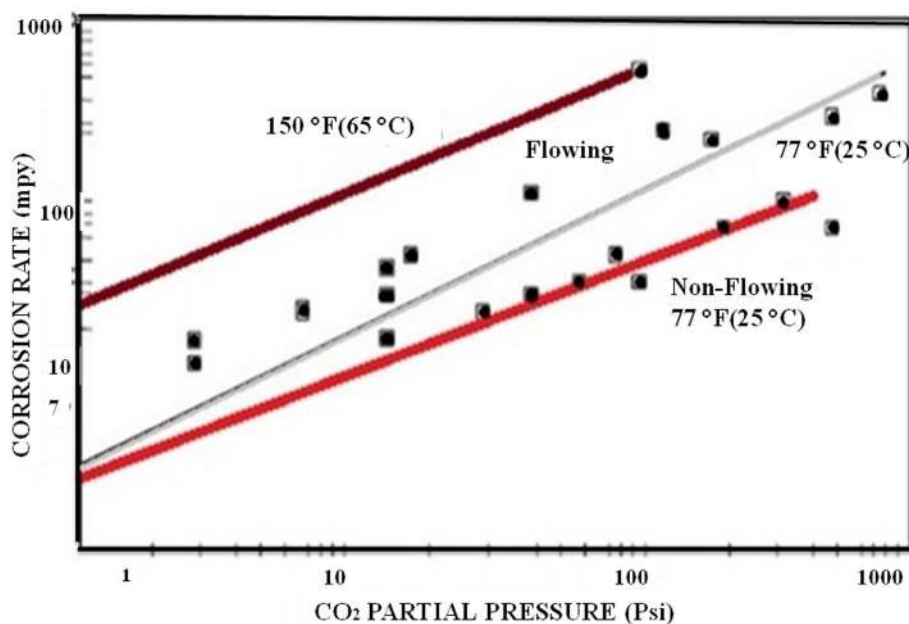
Types of coating methods

Thermal spray coating

Thermal spraying is a deposition method where a spray of molten particles is focused on a portion to form the coating. It is used for the protection of new parts against corrosion, wear and high temperatures, thereby improving the properties of engineered surfaces. Thermal spray coating processes are also applied for fixing damaged and worn parts. At times, the thermal spraying can be useful for the decoration thus improving the esthetical properties of parts. Coating material can be either in powder, wire, rod, cord or molten-bath form. Using thermal spraying process basically composite, ceramic, polymer and thick metallic coatings can be deposited. Operations of the process can be manual, mechanized and fully automated. Thermal spraying was mentioned for the first time in the patents of the Swiss engineer Max Ulrich Schoop (1870–1956) at the beginning of the 20th century [79]. The various advantages of thermal spray coatings are low porosity, excellent coating, good adherence to substrate, low permeability, excellent corrosion or wear resistance, reliability, long-lasting protection, improved electrical properties (resistance and conductivity), clearance and good dimensional control [78].

All thermal spraying processes work on the same principle of heating a feed stock, (powder or wire) and then accelerating it to a very high velocity and then permitting the particles to collide on the substrate. The particles will deform and freeze onto the substrate. When millions of particles are placed on top of each other, then coating will form. Mechanical or metallurgical bondings are main cause of adhesion between the particles and substrate [80].

There are various steps in thermal spraying technique (Fig. 4). Surface activation is the first step of any thermal spraying process. This includes cleaning and grit blasting of surface to be coated. Masking methods are generally adopted for components that require only definite coating areas. In the second step, the material is melted. The feed stock material is introduced in the hot gas stream. The hot gas stream is either produced by physical reaction (plasma) or by chemical reaction (combustion). In the third step, the particles are accelerated to the substrate by hot gas and particles deform to form the coating. Finally, the coatings are examined and evaluated for excellence either by microstructural or mechanical evaluation [81].

The family of thermal spray processes is generally grouped into four major categories, i.e. flame spray, electric arc spray, plasma arc spray and kinetic spray (cold spray) with many subsets falling in each category. Cold spray process is the latest advancement of thermal spray process. Selection of suitable thermal spray process is determined by desired coating material, economics, coating requirement performance, part size and portability [80]. Figure 5 shows the classification of thermal spray coatings.

Flame spray process

Flame spraying uses the heat produced from burning of a fuel gas (acetylene, propylene, propane, hydrogen) and oxygen combination to heat the consumable, either a wire or powder. Compressed air/inert gas is used to drive consumable to the substrate. These coatings can show low bond strength, high oxide content and high porosity. The process has a reasonable spray rate and low cost. Flame Spraying comprises low-velocity powder flame, wire flame and rod flame process, and high velocity processes such as HVOF and the detonation gun process [82].

a) Flame powder process In flame powder process, powdered feed stock is introduced in the oxy-fuel flame, melted and then driven by the flame along with air jet onto the workpiece. Particle speed is comparatively low (100 m/s) and they possess low bond strength of deposits compared with high velocity processes. Cohesive strength is generally lower and porosity can be high. The spray rates are generally
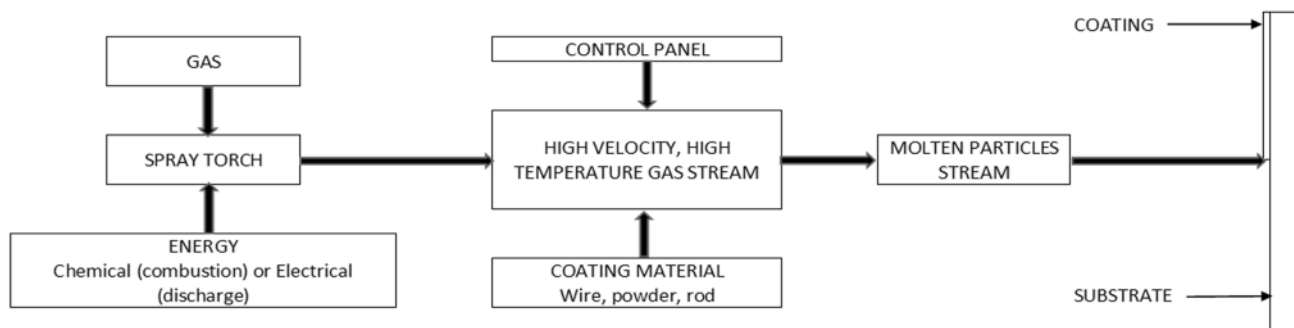

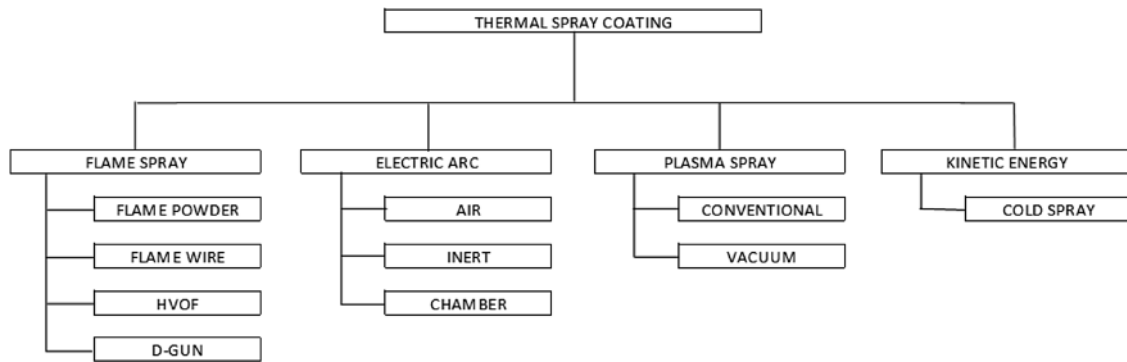**Fig. 4** Schematic diagram of thermal spraying technique

Fig. 5 Classification of thermal spraying coatings

in the range of 0.5–9 kg/h. But the spray rate is higher for lower melting point material. Due to flame impingement, the substrate temperature can run quite high. The process depends on the chemical reaction between oxygen and a burning fuel to generate a heat source. This heat source produces a gas stream with a temperature in excess of 3000 °C with balanced conditions between acetylene and oxygen. The feed stock material which is to be sprayed is put into the flame in the form of powder to melt and then the thermal expansion of the combustion is used to atomize and accelerate the particles onto the substrate [82]. Powder flame process is simple in design and easy to operate. The flame powder spraying equipment is portable, easy to operate and equipment cost is much lower than other processes. The dust and fume levels are also low in comparison with other processes. Flame powder process is restricted with material having higher melting temperature which the flame can provide or if the material decomposes on heating [83].

b) Flame wire process In wire flame spraying, the main purpose of flame is to melt the feedstock material which is then driven with the stream of atomized air onto the workpiece [84]. The spray rates are generally in the range of 0.5–9 kg/h. Again, the material such as zinc and tin alloys which have lower melting point sprays at much higher rates. Substrate temperature varies from 95 to 205 °C because of the extra energy input essential for flame melting. Less than 10% of the input energy is actually used to melt the feedstock material in most of the thermal spray processes. The spraying cost is low and the particle velocity is from 50 to 100 m/s. The efficiency of spray is quite low due to overspray and other losses. With this technique, coatings with high porosity are obtained [85].

c) High velocity oxy-fuel (HVOF) The high velocity oxy-fuel technique is a high-velocity process which was invented only 20 years ago. In HVOF, a combustion jet is

created at a temperature of 2500–3000 °C using mixture of fuel gas (such as propane, hydrogen, or propylene) and oxygen. Burning takes place at very high pressure, leaving through a small diameter (generally 8–9 mm) barrel to produce a supersonic gas jet with high particle speeds. Also powder or wire feedstock can be scattered, at typical rates of 2.3–14 kg/h [86]. The process produces well-bonded and extremely dense coatings due to higher impact velocity. These coatings have better wear resistance due to harder, tougher coatings and higher hardness due to less degradation of carbide phases with improved corrosion protection due to less porosity. It has lower oxide content due to less in-flight exposure time and smoother as-sprayed surface because of smaller powder sizes and higher impact velocities [87]. HVOF-sprayed coatings can be very complex, with their microstructures and properties depending upon many processing variables. Powder sizes are limited to a range of about 5–60 μm, with a need for narrow size distributions. Deposition of coatings is difficult to achieve on to internal surfaces of small cylindrical components, or other limited access surfaces, because HVOF spraying wants line-of-sight to the surface and a spray distance of 150–300 mm [88].

d) Detonation gun spray process Detonation gun is considered as the high velocity thermal spray process. It contains a long, water-cooled gun barrel closed at one end and open at other end. Mixture of oxygen and fuel gas (acetylene most common) is introduced into the barrel together with coating material, which is in powder form. A spark plug ignites the gas mixture [89]. Detonation liquefies and speeds up the particles to the velocity of 600 m/s. Barrel is flushed with nitrogen after each detonation. Depending on the equipment used, there are 1–15 detonations per second. Low oxide content and high bond strength densities can be achieved using this process [90]. Figure 6 shows the detonation gun technique.
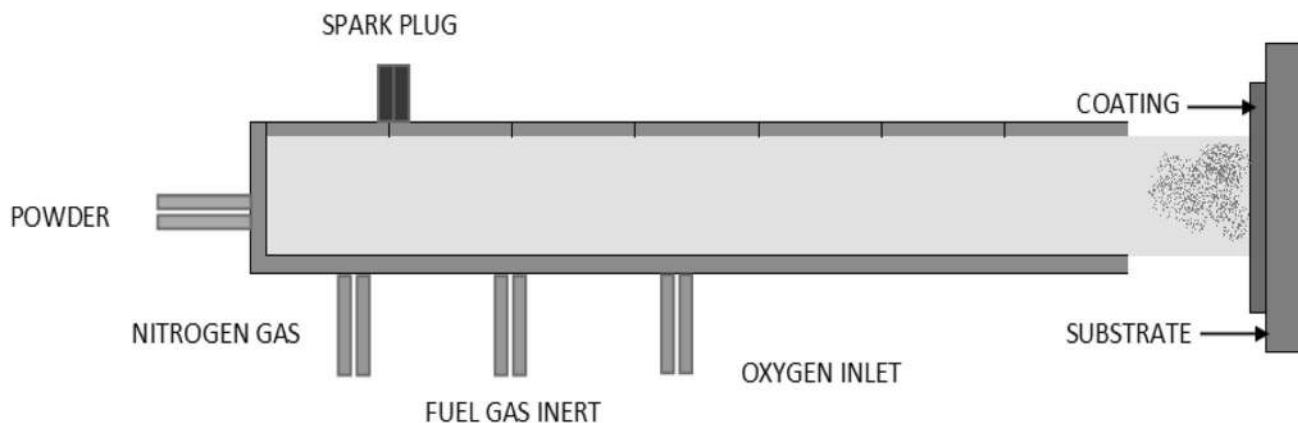
Fig. 6 Schematic diagram of detonation gun technique

Electric arc process

In electric arc spray process (also called as the wire arc process), a high direct-current is connected with two consumable wire electrodes which are fed into the gun. This establishes an arc between them which melts the tips of wire. Atomized molten metal is propelled towards the substrate through a stream of air. As all the input energy is used to melt the metal, therefore, the process is energy efficient [91]. Spray rates are driven mainly by operating current and vary as a function of both conductivity and melting point. Normally, materials such as iron-base and copper-base alloy sprays at 4.5 kg (10 lb)/100 A/h are used. Since no jet of hot air gas is directed towards the substrate, substrate temperature is low. Electric arc spraying can also be done using inert gases or in a controlled-atmospheric temperature [92]. Greater bonding strengths, lower porosity and higher spray rates are attained using flame spraying technique. However, it produces ozone, arc light and fume which may cause problems in many situations. Arc spraying has the maximum deposition rate, with rates of 15 kg/h or higher. The process offers lesser-cost coatings when compared with plasma and HVOF spraying. This is because of high deposition rates, lesser energy cost and lower material costs which is incurred compared with a wire consumable technique. Arc spraying is beneficial in metallizing thermally sensitive substrates such as capacitors and other similar electronic components because of the low heating of substrate. Two dissimilar wires can produce an intimately mixed coating which can be sprayed. Lower porosity levels can be attained by flame spraying. Arc spraying process does not make use of combustion gases or do not generate high-energy plasma, thus possessing lesser health and safety risks than other thermal spray processes [93]. This process can be used to spray only electrically conductive materials that are accessible in an appropriate wire form. It is not fit for spraying cermet or ceramics. Arc-sprayed coatings usually contain extra porosity and higher amounts of oxide and have lesser bond strengths compared with coatings deposited by HVOF and Plasma spraying [94].

Plasma spraying

Plasma spraying is generally regarded as the most versatile of all the thermal spray processes. In this technique during operation, gases such as argon and hydrogen are delivered through a torch. An electric arc dissociates and ionizes the gases. Beyond the nozzle a huge amount of heat is generated. Actually, the plasma core temperature is greater than 10,000 °C which is more than melting temperature of any material. In this method, powder is introduced into the flame, melted and accelerated towards the workpiece. Wide range of coating material is available to fulfill different applications. Plasma spraying has better coating quality than other conventional thermal processes such as flame or electrical arc spraying. Many substrate material, such as metals, ceramics, glass, plastics and composite materials can be coated by plasma spraying. High temperature of a plasma jet makes it mainly suitable for being sprayed as coatings on ceramics and refractory metals, including ZrO_2, B_4C and tungsten. A wide powder particle size range can be used, normally 5–100 µm compared with HVOF spraying. Plasma spraying is a coating process that is extensively obtainable and well understood [95]. Plasma spraying gives high-quality coating by a combination of high-energy heat source, high temperature, inert spraying medium and high particle velocity, generally 200–300 m/s. Air plasma spraying equipment inclines towards the need of more asset than arc and flame spraying. Equipment used for low-pressure plasma, vacuum plasma and the controlled atmosphere plasma spraying technique makes use of high capital cost. It is a line-of-sight process, like all other thermal spraying processes, making it hard to coat internal bores of small diameters or limited access surfaces. Plasma spray gun experiences fast

deterioration of electrodes of inner gun and other internal components. This leads to regular replacement of gun electrodes, and the necessity for quality control to sustain coating consistency. High temperatures linked with the plasma jet can effect in carbide decomposition or extreme oxidation when spraying in air, thus leading to carbide coatings with higher oxide levels or with lesser metallic coatings compared with HVOF-sprayed coatings [96].

a) Conventional plasma Conventional plasma spray process is generally known as atmospheric or air plasma spray (APS). Temperature of plasma in the region of powder heating range from 6000 to 15,000 °C which is nearly above the melting point of any material. To create plasma, an inert gas—generally argon or argon–hydrogen mixture—is superheated by DC arc [97]. Through inert carrier gas, powder feedstock is introduced and accelerated towards plasma jet which is further directed towards workpiece. Commercial plasma guns operate in the range of 20–200 kW. Accordingly, spray rates are mainly dependent on plasma gases, gun design, powder injection system and material properties. Figure 7 shows the flow chart of physical vapor deposition process.
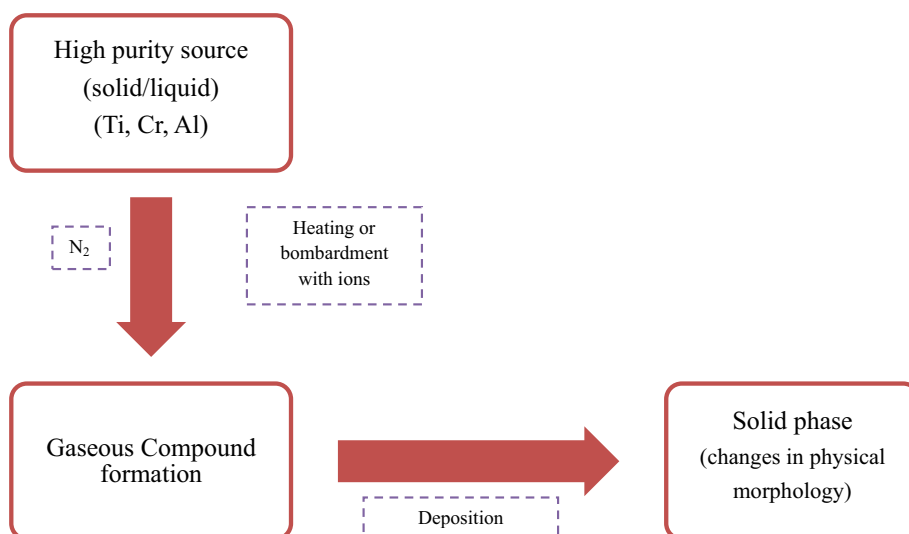
b) Vacuum plasma Vacuum plasma spraying (VPS) is known as low-pressure plasma spraying (LPPS) which uses advanced plasma spray torch in a chamber with the pressure in the range of 10–50 kPa. Plasma becomes larger in diameter and length due to low pressure and higher speed of gas which is due to the presence of convergent/divergent nozzles. Lack of oxygen and capacity to operate with higher substrate temperature makes it denser, thus making more adherent coatings with lesser oxide content [98].

Kinetic energy process

In thermal spray process, kinetic energy has been an important factor from the beginning. With the introduction of HVOF, detonation gun and high-energy plasma spraying, kinetic energy becomes a more significant factor. Cold spray is the latest advancement in kinetic spraying.

a) Cold spray Cold spray is a method of material deposition in which coatings are applied by accelerating powdered feedstock of ductile metal to speeds of 300–1200 m/s via gas-dynamic techniques using nitrogen or helium as the process gas. Due to relatively low temperature (0–800 °C) of the expanded gas, it is also known as cold gas-dynamic spraying. Powder feed rate up to 14 kg/h [99] is generally used. Cold spray coatings also show better adhesion, reduced material loss by vaporization, low gas entrapment, non-uniform grain growth, recrystallization, low residual stress and better surface finishes. Cold spray is restricted to the deposition of ductile metals, alloys (Zn, Sn, Ag, Cu, Al, NiCr, Ti, Nb, Mo, Cu-Al, MCrAlYs and nickel alloys), polymers and blends of > 50 vol% ductile materials with brittle metals or ceramics. Disadvantages of cold spray process include the increased gas costs, and use of high gas flows; especially in the case of helium, recycling would be needed. Therefore, lesser-cost gases such as nitrogen are being examined as an alternative. Also, high gas pressures leads to the development and modification of feeders. Solid materials traveling at high velocities are abrasive, so the dimensional and lifetime stability of key components are emphasized [100]. Cold spray coating applications include corrosion protection, where the lack of process-induced oxidation may offer better performance; the application of metallic coatings to glass substrates and deposition of ceramics for solders and electrical conductors. It is difficult to coat the inner surfaces

Fig. 7 Flow chart of physical vapor deposition process

High purity source (solid/liquid) (Ti, Cr, Al)

N₂ | Heating or bombardment with ions

Gaseous Compound formation

Deposition

Solid phase (changes in physical morphology)

of small diameter bores and other limited access surfaces. Also the usage of flammable gases, with acetylene, needs to be used safely and storage of gases should be done carefully [101].

Physical vapor deposition (PVD)

Physical vapor deposition uses thermodynamic or mechanical means to produce thin film. Sputtering is a principal technique among all the mechanical method, where energetic noble gas ion, mostly argon, is bombarded on the surface of a material made from the preferred film material. Thermal evaporation (thermodynamic means) is a process in which a solid piece of the desired film material is heated until it melts and then evaporates or until it sublimes. The vapors follow a direct line-of-sight path to the substrate in a high vacuum where it condenses to form a thin film. The temperature in the region ranges from 70 to 500 °C [102].

This technique has excellent adherence, uniform coating thickness and typical coating thickness of 3–5 μm. The various applications are cutting tools, forming tools, components, medical devices and decorative items. In this process, there is no environmentally harmful material, emissions and no toxic reaction materials [103]. There are great varieties of coatings which can be produced. The coating temperature lies below the final heat treatment temperature of most of the steels. It produces small, precisely reproducible coating thickness. This process has low friction coefficient and high wear resistance. Slots, bore holes, etc. can only be coated down to a depth equal to the width or diameter of the opening. To attain a uniform coating thickness, the parts to be coated should be rotated uniformly during processing [104].

Chemical vapor deposition (CVD)

In chemical vapor deposition (Fig. 8), the substrate is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the preferred deposit. Regularly, volatile by-products are also formed, which are removed through the reaction chamber by gas flow. The growth of the film is often improved either by a plasma, or by heating the substrate to increase the density of reactive species (free radicals). In some cases, both are used, like in the deposition of diamond-like carbon (DLC) where carbon is deposited at very high temperatures (normally more than 800 °C in dense Hydrogen plasma) from a methane precursor [105, 106].

The temperature in this process ranges from 800 to 2000 °C in the region. This process has excellent adherence and coating thickness up to 20 μm. Coating has high wear resistance, economically viable for thicker coatings and also suitable for slots, bore holes, etc. But coating with several metals is not possible such as TiAlN. It is also seen that due to thick coatings sometimes edges become round [107–112].

Conclusion

i.   The main problems faced by the boilers are agglomeration, slagging, fouling, caustic embrittlement, fatigue failure and high temperature corrosion.

ii. Corrosion inhibition is one of the methods that has been used to protect and increase the life of metallic cultural heritage. A large amount of scientific literature is available on corrosion inhibitors, but majority of it deals with fundamental studies of corrosion inhibition or industrial applications.

iii. Sol–gel protective coatings on the metal and alloys surfaces can decrease the rate of corrosion in various corrosive mediums. They can also provide a high oxidation, abrasion, water resistance, and many improved properties. However, this coating cannot be used at very high temperature.

Fig. 8 Schematic diagram of chemical vapor deposition process
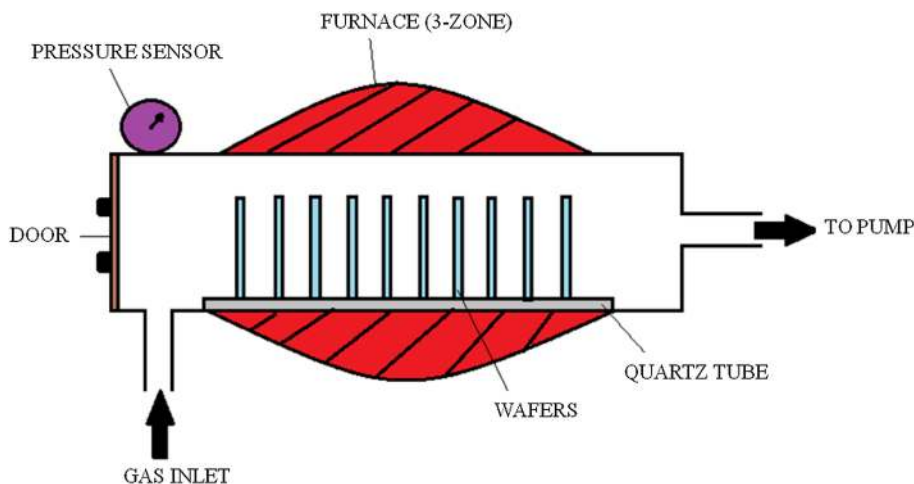
iv. Rate of corrosion increases with the increase in temperature. Increase in pressure also implies increase in corrosion rate. However, the rate of corrosion also depends on the nature of gas. With the increase in partial pressure of oxygen the rate of corrosion increases, and moreover carbon dioxide partial pressure is less sensitive to the rate of corrosion. On the other hand, noble gases do not change the rate of corrosion rate at all.

v. Physical vapor deposition techniques for deposition of multilayer coatings ensure high wear and corrosion resistance. CVD process is a versatile process which can be used for coating of nearly any metal as well as non-metal such as carbon or silicon. These techniques provides extra layer of material on the substrate, hence increasing the life of boiler tubes.

vi. Thermal spray coatings can be used for wear, corrosion and erosion resistance. They are used to resist almost all forms of wear, including erosive, abrasive, and adhesive, in nearly every type of industry. The materials used range from hard metals to soft metal alloys to oxides to carbide-based cermet. Flame-sprayed aluminum and zinc coatings are frequently used for corrosion resistance on bridges, ships, and other structures. Other thermal spray coatings are used for their corrosion resistance, often coupled with their wear resistance. Thermal spray coatings are used in some applications to provide specific frictional characteristics to a surface, covering the full spectrum from low friction to high friction. Textile industry provides an application covering the complete range of friction characteristics and surface topography to handle very abrasive synthetic fiber.

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