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Review article

Enhancing Resistance to Corrosion, Erosion and Oxidation of Boiler Steels by Surface Modification Techniques

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A B S T R A C T

In coal based thermal power plant, the boiler components (superheater, combustion chamber, superheater tubes, boiler walls, reheater etc.) are subjected to harsh environment characterized by high temperatures, aggressive combustion products, and abrasive particles. Corrosion, erosion, and oxidation relentlessly reduce their lifespan and efficiency, posing significant economic and safety concerns. This review explores the potential of surface modification techniques to act as a valiant shield against these destructive forces, extending the life, enhancing the performance, and ensuring the safe operation of boiler components. In this articles various surface modifications techniques including their merits and demerits are discussed with emphasis on thermal spray techniques. From established methods like thermal spraying and laser cladding to innovative approaches like nanocoatings and electrochemical treatments, each technique is meticulously examined for its effectiveness in boosting corrosion resistance, mitigating erosion wear, and minimizing oxidation at crucial boiler locations. This review culminates in a compelling vision of the future, where sophisticated surface modification techniques become an integral part of boiler design and maintenance strategies. By harnessing the power of these technologies, we can usher in an era of more efficient, reliable, and sustainable boiler operation, safeguarding investments and protecting the environment.

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1. INTRODUCTION

In most countries, the failure of boiler tubes in coal-fired power plants results in significant economic losses. Consequently, power plant operators stand to gain much financially from life evaluation of boiler tubes with the goal of prolonging their life. It is important to fully comprehend any potential damage mechanisms in order to assess the boiler tubes' residual life.

Boiler tubes may be damaged by stress/creep rupture, fatigue, erosion, steamside oxidation, and fireside corrosion. The primary process of deterioration in boiler tube components is creep. High-temperature creep or transient overheating are two potential reasons for creep failure [1]. Degradation mechanisms such as erosion, steamside oxidation, and fireside corrosion exacerbate creep damage and can cause failure before the intended life [2-4].

Various techniques for surface modification have been developed recently to counteract steel oxidation, corrosion, and erosion. Figure 1 depicts the main categories of surface modification approaches [5].

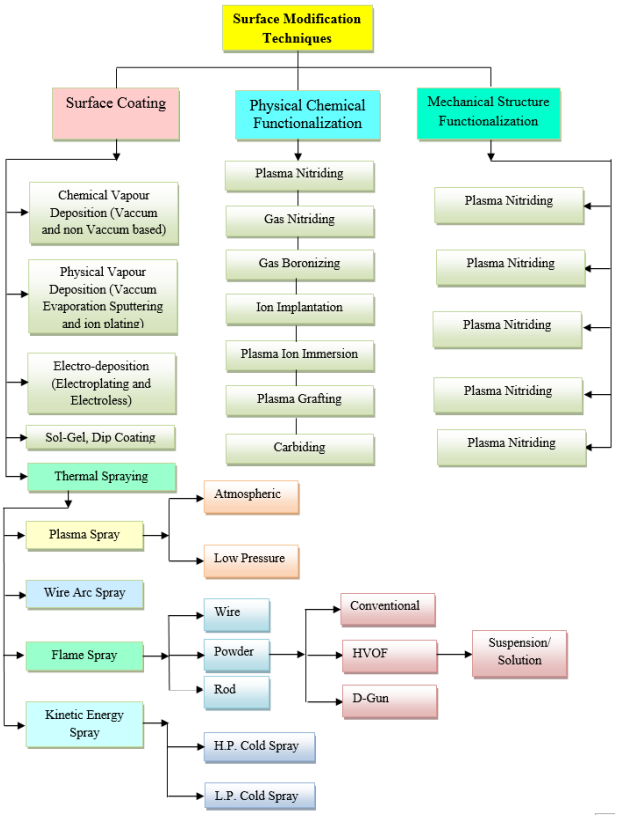


Fig. 1. Classification of surface modification techniques.

Boilers are machines that convert heat energy from water into high-pressure steam. Moreover, a turbine that produces electricity or powers machinery and facilities in the manufacturing or process sectors is powered by this steam [6]. The fuel utilised is fossil fuel, which is available in solid, liquid, and gaseous forms. The tube wall transfers heat because the water is heated indirectly. High-temperature corrosion is the result, affecting both the fireplace and the waterside [7, 8]. Fly ash and deposits such as Na2SO4, V2O5, and so forth can pose a hazard on the hearth. On the waterside, the interaction between the water and the pipe material quickens because of the high temperature. There is a tendency for salt to collect on the inside surface of the tube. The formation of deposits and the oxide layer may lessen the heat transfer from the fireside to the waterside, raising the tube wall's temperature. There are many different kinds of boiler failures, such as hot corrosion, oxidation, erosion, hydrogen damage, caustic embrittlement, oxygen pitting, fouling, agglomeration, and fatigue failure. Inadequate material selection, poor water treatment, poor maintenance, and design and manufacturing flaws can also lead to failures [9]. Figure 2 shows the schematic illustration of a thermal power plant.

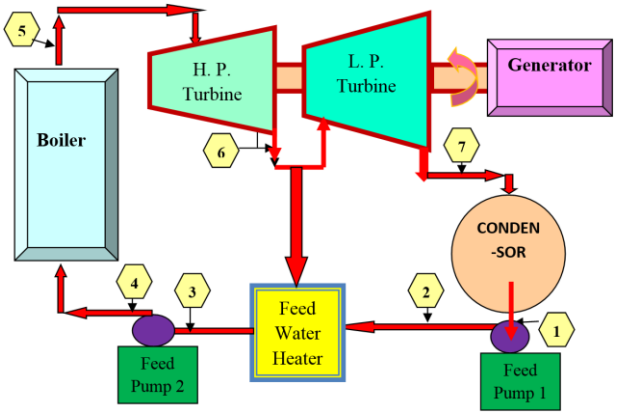


Fig. 2. Schematic diagram of thermal power plant.

2. CORROSION PROBLEM IN COAL BASED THERMAL POWER PLANT

Since coal is a naturally occurring substance, its composition varies from location to location. Moreover, burning coal would cause the oxidation process shown below:

$$C(s) + O2(g) = CO2(g) \quad (1)$$

Boiler water would be heated using the released energy. The inherent impurities in coal are the primary cause of corrosion in coal-fired power plants. Coal is a complicated and rather unclean fuel that includes a significant portion of ash—a term for noncombustible mineral constituents—as well as variable levels of sulphur. Figure 3 displays the distribution of different impurities in various coal types together with their calorie values [10].

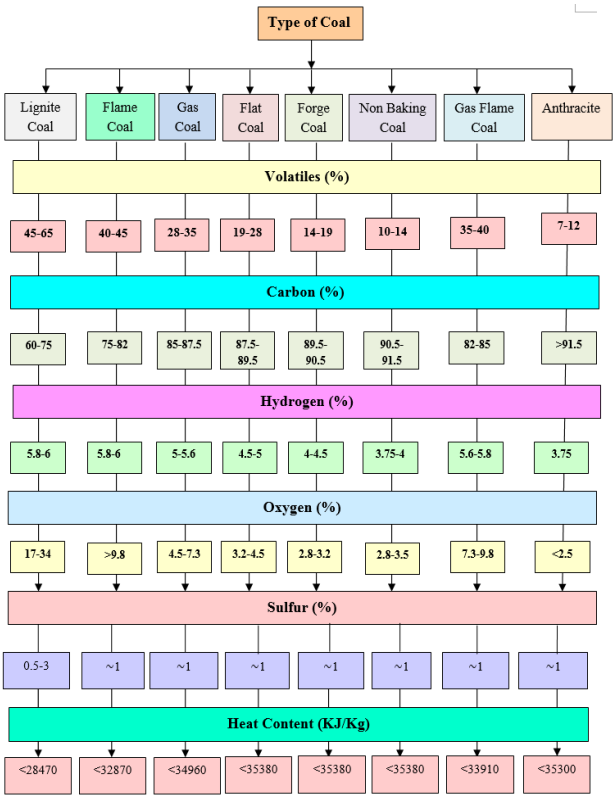


Fig. 3. Different types of coal along with impurities % and heat content.

Now let's examine how these contaminants affect corrosion:

(a) Effect of Sulfur: The contaminant that causes boiler tubes to sulfidate, oxidise, and undergo hot corrosion is sulphur. When coal is burned, sulphur dioxide (SO2) and sulphur trioxide (SO3) can be produced depending on the parts per million (ppm) amount of sulphur impurity. The air to fuel ratio determines how much of the different sulphur compounds are produced. Sulphur may react with hydrogen, which is created when water is reduced, even under reducing circumstances. This results in the creation of H2S, which interacts with steel directly and considerably more quickly than oxygen, sulphur dioxide, or trioxide [11].

(b) Effect of NaCl or KCl: Usually consisting of NaCl and KCl, salt is the second most common contaminant found in coal. These salts can react with SO2/SO3 to generate sodium sulphate, which deposits on the boiler tubes along with ash. When these salts melt at specific SO2/SO3 partial pressures, complex salts can be formed, which can cause hot corrosion. At the temperature at which the boiler operates, these complicated salts dissolve [12, 13].

(c) Effect of Silica: Coal has a well-known impurity, which ranks third in importance. This does not lead to corrosion; instead, when the coal is burned, it strikes the boiler tubes together with ash, severely eroding them [14].

(d) Effect of ash: Ash is the fourth most impurity. big ash formation causes significant fouling around boiler tubes and can cause hot corrosion when ash includes a lot of sodium sulphate or erosion with big particles of silica [15]. Ash buildup during the burning of solid fuels on heat-exchanging surfaces results in a variety of operational issues, including decreased heat transfer rates, more frequent power plant shutdowns, and an increase in soot-blowing and cleaning operations [16-18]

(e) Effect of Chlorine: Chlorine is a crafty saboteur because it creates corrosive chlorides that pierce and pit the steel, making it open to more damage. Imagine tiny crystals of salt constantly eating away at the surface of the metal [19].

(f) Effect of Alkaline Oxides: Like a chemical battering ram, sodium and potassium oxides create an alkaline environment that promotes stress corrosion cracking, causing the steel to crumble under pressure like an overbaked cookie [20].

(g) Effect of Vanadium Pentoxide: This stealthy assassin reacts with steel at high temperatures, forming brittle vanadium alloys that compromise the metal's integrity, making it susceptible to catastrophic failures [21]

(h) Effect of alumina: While not directly corrosive, these abrasive particles act like microscopic sandblasters, wearing down the steel surface and thinning its protective oxide layer, leaving it exposed and vulnerable [22].

2.1 Fireside Corrosion

Keeping the furnace's heat transmission surfaces from corroding is one of the main obstacles to burning coal consistently. Superheater and reheater tube failure is still mostly caused by fireside corrosion. Furthermore, under severe circumstances, tubes impacted by the fireside corrosion process may lose up to 15 mils annually (mpy) [23, 24].

Ash corrosion in refuse-fired boilers, oil ash corrosion in oil-fired units, and coal ash corrosion in superheaters and reheaters in coal-fired units are all examples of fireside corrosion. Hot corrosion is another name for fireplace corrosion that is occasionally used. Each example has a similar process, but it has a distinct low-melting species. Low-melting species in oil ash corrosion would be V2O5-Na2O or V2O5-Na2SO4, in coal ash corrosion they would be sodium or potassium iron trisulphates (Na3Fe(SO4)3 or K3Fe(SO4)3), and in refuse-fired boilers they would be iron and zinc chlorides among other possible species [25, 26]. These low-melting compounds are more likely to occur in a superheater/reheater with high temperatures (over 1,000F).

Vanadium, sodium, potassium, and sulphur are the corrosive components that cause oil ash corrosion. Low-melting species V2O5-Na2O, V2O5-K2O, V2O5-Na2SO4, and V2O5-K2SO4 may be produced during fuel oil combustion. Depending on their composition, these compounds have melting temperatures that vary from 1,000 to 1,550 degrees Fahrenheit [26–28].

Although fireside corrosion may also affect furnace wall tubes, low-melting species of furnace wall tubes are not like superheater/reheaters. Furnace wall corrosion has been linked to sodium and potassium pyrosulfate (Na2S2O7 or K2S2O7). These two species melt below 800F, the operating temperature of the furnace wall tubes. Na2S2O7 and K2S2O7 have melting points of 750F and 570F, respectively [29, 30].

2.1.1 Mechanism of molten salt or slag-related attack

As coal burns, certain minerals present in it (such as silica, alumina, and oxides of sodium, potassium, and calcium) melt together at high temperatures, forming molten slags. These slags can adhere to boiler surfaces, creating a dynamic interface between metal and molten salt [31]. In addition, the Slags can act as acidic or basic fluxes, depending on their composition. Acidic slags attack the protective oxide layer on the steel, while basic slags promote stress corrosion cracking, weakening the metal from within. Imagine the slag dissolving the steel's armor or causing tiny cracks to appear under pressure. Slags can act as catalysts, promoting the oxidation of the steel by oxygen at high temperatures. This accelerated oxidation further weakens the metal and makes it more susceptible to other forms of corrosion. Think of the slag acting like a bellows, fanning the flames of oxidation. Further, the molten slags can physically wear down the steel surface through abrasion, especially if they flow turbulently in the boiler. This erosion thins the steel and exposes it to further attack. Imagine the slag acting like a microscopic sandblaster, relentlessly chipping away at the metal [32-34].

Acidic Attack: Certain slag components, rich in silica and sulfur oxides, form molten silicates and sulfates with acidic properties [35]. These acidic slags react with the protective oxide layer on the steel surface, dissolving it through dissolution reactions like:

$$Fe_2O_3(s) + 3SiO_2(l) \rightarrow Fe_3Si_2O_6(l)$$

This leaves the underlying metal vulnerable to further attack and contributes to thinning of the boiler tubes [35].

Basic Assault: Other slag components, particularly oxides of alkali metals like sodium and potassium, create basic fluxes [36]. These react with the steel, promoting stress corrosion cracking through processes like:

$$Fe(s) + 2NaOH(l) \rightarrow Na_2FeO_2(s) + H_2(g)$$

The resulting sodium ferrate compound weakens the steel and makes it susceptible to cracking under pressure.

Oxidation Boost: Molten slags can act as catalysts, accelerating the oxidation of the steel by oxygen at high temperatures [37]. This reaction enhances the formation of iron oxides, weakening the metal structure:

$$2Fe(s) + 3O_2(g) \rightarrow Fe_2O_3(s)$$

This phenomenon significantly contributes to overall corrosion and material degradation.

Physical Erosion: While not strictly a chemical reaction, the turbulent flow of molten slags can physically wear down the steel surface through abrasion. Imagine microscopic grinding stones constantly buffeting the metal, thinning its protective layer and exposing it to further attack [38-42].

2.2 Steamside Corrosion Problems

Heat transport is impeded and tubes thin as a result of steamside oxidation on the inner surface of the tubes [43–46]. The power plant's operation causes an increase in metal temperature and hoop stress due to heat hindrance and tube thinning. Although an increase in hoop stress has no influence on residual life, rising metal temperatures brought on by oxide insulation shorten boiler tube residual life. Models for creep residual life assessment must take these degradation processes' effects into account [47-52]. Figure 4 illustrates the several conditions that cause corrosion on the steam side.

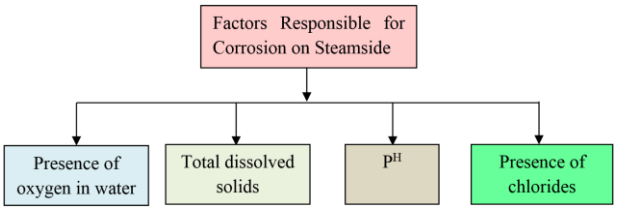


Fig. 4. Factors responsible for corrosion on steamside.

3. CORROSION CONTROL TECHNIQUES FOR COAL FIRED BOILER

3.1 Fuel and Pre-treatment

Fuel selection: Opt for coals with lower sulfur content. Sulfur oxides, released during combustion, dissolve in water to form acidic condensate, a potent corrosive agent. Pre-washing or treating coals to remove sulfur impurities can significantly reduce acid formation [53].

Flue gas desulfurization: Employ technologies like scrubbers to capture sulfur dioxide from flue gases before they condense, further mitigating acid attack on the boiler tubes.

3.2 Water Chemistry Control

Feedwater treatment: Maintain optimal pH and dissolved oxygen (DO) levels in boiler feedwater. High pH neutralizes acidity, while low DO minimizes pitting corrosion. Advanced treatment techniques like demineralization and deaeration play a vital role.

Chemical additives: Utilize specialized additives to scavenge DO, neutralize specific corrosive agents, and form protective films on the boiler tubes [54].

3.3 Boiler Design and Operation

Optimizing flow and circulation: Ensure efficient water circulation within the boiler to prevent stagnant zones where corrosion can concentrate. Proper blowdown systems remove dissolved salts and impurities, further reducing the threat.

Material selection: Choose steel alloys with inherent resistance to specific types of corrosion, such as those rich in chromium and molybdenum. These alloys withstand acidic attack and high temperatures better than standard steel.

Surface modification techniques: Consider applying specialized coatings like thermal spraying or laser cladding to create a resilient barrier between the steel and the corrosive agents. Recently, Ni based thermal spray coatings are widely employed to combat corrosion of boiler steels [55-60]. The general classifications of thermal spray methods are depicted in Figure 5.

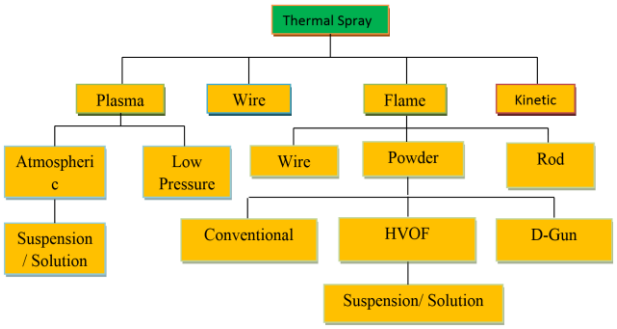


Fig. 5. Classification of thermal spray techniques.

Some of these processes are briefly explained below:

(a) Flame Spray: Flame spray, a thermal spray coating technique, harnesses the power of burning flames to transform metal wires or powders into a molten mist, propelled onto a surface to create a protective or decorative layer [61]. The schematic representation of flame spray process is shown in Figure 6.

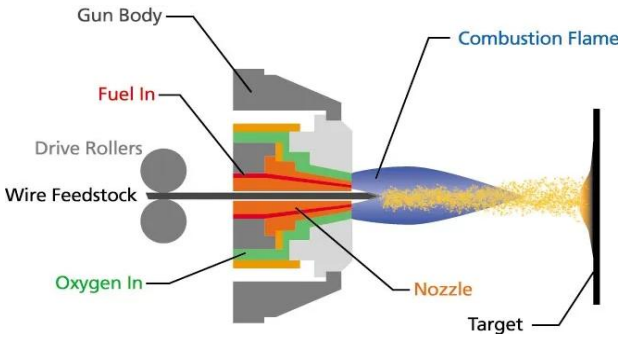


Fig. 6. Schematic diagram of flame spray.

The merits of flame spray process are: Versatility: Flame spray can coat a wide range of materials, including metals, plastics, and even wood, with various metals and alloys as coating materials.

Cost-effective: In contrast to alternative thermal spray methods, flame spray is often more affordable, making it a popular choice for various applications.

Thickness Control: Varying the spray distance and feed rate allows for precise control of the coating thickness, catering to specific needs.

Portability: Portable equipment makes flame spray suitable for on-site coating applications, offering greater flexibility.

However, this process has some drawbacks such as:

Roughness: The splattered nature of the coating results in a rough surface, requiring further finishing in some cases.

Bond Strength: While adherent, the bond strength of flame spray coatings can be lower than other thermal spray techniques.

Line of Sight: Flame spray requires direct line-of-sight access to the target surface, limiting its application for complex geometries.

Heat Distortion: The high heat involved can potentially warp or distort thin substrates, requiring careful temperature control [61-64].

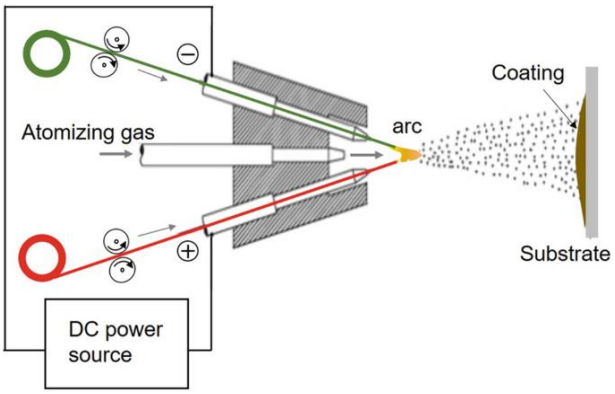


Fig. 7. Schematic illustration of electric Arc Spray process.

(b) Electric Arc Spray: Electric arc spray, another thermal spray technique, harnesses the intense heat of an electric arc to melt metal wires, transforming them into a molten mist to coat surfaces with a protective or decorative layer. Imagine a miniature lightning bolt wielding a brush of molten metal, painting a new skin onto surfaces. The schematic diagram of electric arc spray [65-70] is shown in Figure 7.

This process offer lot of benefits such as:

Finer Finish: Compared to flame spray, the finer molten droplets and higher impact velocity result in a smoother and denser coating, often requiring less finishing.

Stronger Bond: The high-velocity impact leads to better mechanical interlocking with the substrate, resulting in greater bond strength.

Precise Control: Arc spray systems offer more precise control over spray parameters like voltage, amperage, and air pressure, leading to more consistent coating properties.

Wider Material Range: Electric arc spray works with a broader range of metal and non-metal wires compared to flame spray, expanding application possibilities.

Demerits of the Electric Arc Spray

Direct Line-of-Sight: Similar to flame spray, line-of-sight access to the target surface is necessary, limiting application for complex geometries.

Heat Distortion: As with flame spray, the high heat can potentially warp or distort thin substrates, requiring careful temperature control.

Limited Porosity Control: Electric arc spray coatings tend to be denser and less porous than flame spray coatings, which might not be desirable in some applications [71-73].

(c) Plasma spray: The best technique for creating ceramic coatings over metals and composites is plasma-spraying. This method is recommended because it can provide coatings that are repeatable and long-lasting at a reasonable cost. As seen in Figure 8, plasma spraying entails injecting powders into a direct current plasma jet to melt and accelerate them. The stream of molten particles is then directed onto a substrate, where it forms a coating as it spreads and solidifies [74].

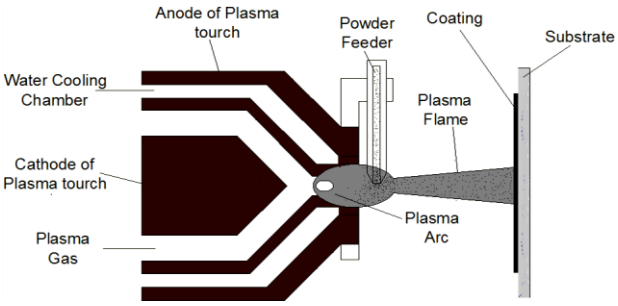


Fig. 8. Schematic illustration of plasma spray.

This process's high deposition rate and suitability for a wide range of metallic and oxide coatings are its main advantages. The difficulty of plasma spraying to provide thick, uniform, high-quality coatings is a drawback [74].

(d) HVOF Spray process: The term HVOF, which stands for High Velocity Oxygen Fuel, makes it clear that the purpose of this thermal spray method is to apply molten or semi-molten materials to surfaces quickly. Because HVOF coatings provide a variety of special coating qualities for a broad range of applications in diverse sectors, this thermal spray technique has grown to be one of the most popular ways to apply dense coatings on a variety of surfaces [75]. The schematics diagram of HVOF process is shown in Figure 9.

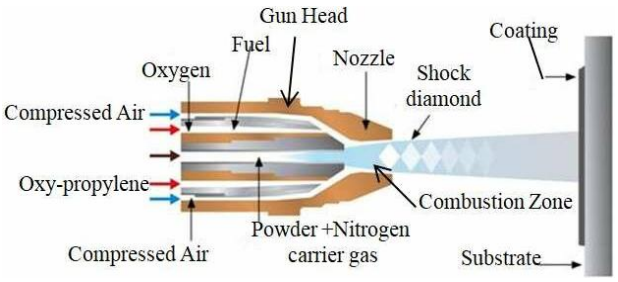


Fig. 9. Schematic diagram of HVOF process.

Improved coating quality is the primary benefit of HVOF spraying over conventional thermal spray techniques. Examples of this include:

Better wear resistance because of tougher, harder coatings; Lower oxide content because of shorter in-flight exposure times; Powder chemistry retention because of shorter temperature exposure times; Smoother as-sprayed surface because of higher impact velocities and smaller powder sizes; and Higher density (lower porosity) because of greater particle impact velocities. Thicker coating because of fewer residual stresses; • Greater corrosion protection because of less through thickness porosity; and • Higher hardness because of less carbide phase deterioration [76,77].

The following are some drawbacks of HVOF spraying: The microstructure and characteristics of HVOF sprayed coatings can be quite complicated, depending on a wide range of processing factors. The range of powder sizes is limited to around 5 - 60µm, requiring narrow size dispersion. Skilled, certified workers are needed for HVOF spraying in order to guarantee safe operation and uniform coating quality. Special attention should be paid to health and safety concerns, as with any thermal spraying procedure. HVOF spraying often requires the use of a dedicated thermal spray booth equipped with dust extraction and appropriate sound attenuation. Compared to other thermal spraying techniques, such as flame and arc spraying, HVOF equipment demands a larger initial investment. It is often not advisable to operate an HVOF spray gun manually; instead, automated gun manipulation is required. Since HVOF spraying requires a line of sight to the surface and a spray distance of 150–300 mm, coatings cannot be applied to the inside surfaces of tiny cylindrical components or other surfaces with restricted access [77,78].

(e) D-Gun Spray: The D-gun spray technique is a type of thermal spray coating that produces a coated surface with compressive residual stresses, minimal porosity, and exceptionally strong adhesive strength. Through a tubular barrel that is closed at one end, a precisely calculated amount of the oxygen and acetylene combustion mixture is delivered. A layer of nitrogen gas is permitted to envelop the gas inlets to stop any potential backfiring. A set amount of the coating powder is simultaneously injected into the combustion chamber. A simple spark plug is used to ignite the gas mixture inside the chamber. High pressure shock waves, or detonation waves, are produced as the gas mixture burns and spread throughout the gas stream. The hot gas stream's temperature may reach 4,000 degrees Celsius, and the shock wave's speed can reach 3,500 metres per second, depending on the ratio of the combustion gases. The explosion chamber produces hot gases that go down the barrel at a high speed, heating the particles to the point of plasticization (just the particle's skin melts) and accelerating them to a speed of 1200 m/sec. Following their exit from the barrel, these particles interact with the manipulator-held component to create a coating.

When the heated powder particles strike the substrate, their great kinetic energy causes an extremely thick and durable coating to form [79, 80].

The schematic representation of D-Gun spray techniques is shown in Figure 10.

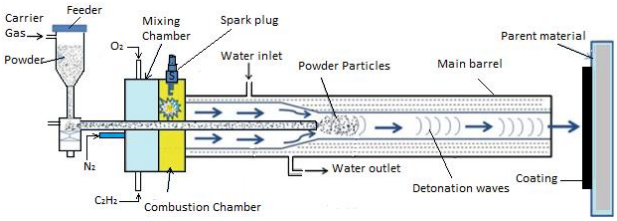


Fig. 10. Schematic representation of D-Gun spray process.

The primary benefit of the detonation spraying technique is its capacity to precisely regulate the quantity of explosive gas combination utilised for each detonation gun shot. This allows for the modification of the degree of thermal and chemical effects of the detonation products on the spraying powder particles.

However, this process is unstable for complex shapes, generate high heat, porosity etc.

(f) Cold Spray: An additional step is taken in the direction of increased velocity at lower temperature in the cold spray process. The cold spray procedure causes pure solid-state plastic deformation of the particles, resulting in the production of a splat-like morphology at or near the site of contact, by raising the particle velocities to supersonic levels and lowering the temperature to almost ambient. There are several benefits since the particle is not exposed to high temperatures, which prevents the harmful high temperature reactions mentioned above [81–83]. Figure 11 displays the schematic diagram for the cold spray procedure.

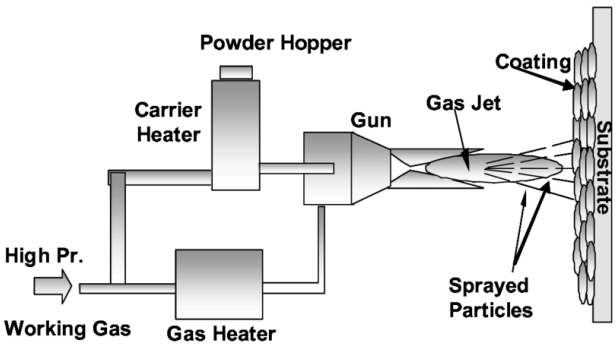


Fig. 11. Schematic illustration of cold spray process.

We'll talk about a few benefits of the cold spray method below.

High deposition efficiency: For the majority of metals, alloys, and composites, very high deposition efficiency (DE) values have been attained using the cold spray method.

High deposition rate: The cold spray beam's spray footprint is well-defined and narrow. Typically, a spray beam has sharp edges and a diameter of roughly 10 mm. A significant powder feed rate combined with a narrow spray beam results in extremely high deposition rate (DR) values. Selecting a substrate-coating with flexibility is important since many technical applications need for substrate-coating pairs made of different materials, which are challenging to create using traditional methods.

Minimal or nonexistent masking: In many cases, masking areas where overspray is prohibited is not required.

Not a grit blasting: One may think of the cold spray method as a triplex method.

High density: Only particles striking with greater than Vc can plastically deform and deposit during the cold spray procedure.

High bond strength: High binding strength is demonstrated by cold-sprayed coatings on a variety of substrate materials, such as metals and composites. In addition this coating offered High corrosion resistance, High strength and hardness. However, this process has some drawbacks as mentioned below:

In the as-sprayed state, the cold-sprayed coating has almost little ductility. It is not possible to process pure ceramics or certain alloys (such work-hardening alloys). Because cold spray is a line-of-sight procedure, like many other coating processes, it can be challenging to spray intricate forms and interior surfaces [84].

3.4 Monitoring and Diagnostics

Real-time water chemistry monitoring: Track pH, DO, conductivity, and other water parameters continuously to detect potential imbalances and take corrective action before corrosion progresses.

Corrosion rate monitoring: Employ technologies like ultrasonic testing or eddy current testing to assess the extent of corrosion in the boiler tubes and schedule timely maintenance [84].

3.5 Emerging Technologies

Advanced water treatment technologies: Research on nano-filtration membranes and advanced oxidation processes offers promising avenues for more efficient and targeted water treatment.

Corrosion-resistant materials: Development of high-performance alloys and composite materials continues, pushing the boundaries of boiler tube longevity and corrosion resistance.

Intelligent boiler monitoring systems: Integration of AI and machine learning into boiler monitoring systems can predict corrosion risks and optimize maintenance schedules for improved efficiency and safety [85-93].

4. CONCLUSION

The main cause of corrosion issues in coal-fired power plants is coal impurities. Hot corrosion, sulfidation, and erosion of superheater tubes are caused by the presence of sulphur, salts, and silica. Only improper water chemistry management can lead to corrosion issues on the steamside or waterside. Steamside issues are rare if the water has been adequately treated by eliminating oxygen, chlorides, and maintaining the right amount of dissolved solids.

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