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A Tracking Review on Non Arc Melting Processes for Improved Surface Properties in Metallic Materials

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Abstract

Most metallic materials lack the adequate surface characteristics to satisfactorily perform intended service functions. In such instance, the surface properties are modified by altering the chemistry, structure and/topology of the top surface of the surface via modification techniques. There exists wide options of techniques for modifying the surface properties and these are well documented in the literature. However, these techniques have different scientific underpinnings controlling them such that it is difficult to use a single mechanism to characterize the techniques. Arising from this, it is imperative that a holistic understanding of the various processes is provided. Therefore, in this paper, research status on the wide range of non-melting technique for surface modification is presented. The presentation discusses the investigation conducted on the various non-surface melting techniques and provides a comparison across the techniques. Recent developments in these techniques are equally presented. Existing challenges and emerging trends in the field are also highlighted. .

Keywords: coating composition, coating techniques, metallic materials, substrate, surface properties
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1.0 Introduction

Most bulk solid materials, particularly metals, are not directly exposed to the environment in which they are deployed rather it is the surface layer that interfaces and interacts with the environment (John and Myhra, 2009). And most often, the surface layer cannot bear the applied stimuli such as mechanical load, thermal, chemical, electrical, optical, etc. Thus, the layer arising from its sustained interaction with the environment over time become degraded or may not possess appropriate properties to serve in that particular environment. In some other instances, the bulk materials and substrate surface may by design tailored to exhibit differential properties such as a very tough core and a hard case as in the gear system. In any of these situations, the surface layer is usually manipulated to improve the surface properties of the material (Williams, 2014). The process of achieving this is known as surface modification or surface engineering; and it involves altering the surface chemistry, crystal/microstructure, topography up to certain depth to impart missing or needed features. In achieving these complex property specifications, the bulk materials are not usually touched rather the surface is twitched to offer the needed properties (Tariq *et al.*, 2013).

The twitching of the surface may involve the introduction of an extrinsic top layer material with properties different from those of the bulk materials or deliberate structural reengineering of the surface layer of the bulk material to induce differential grain and phase structure which may also involve composition change. Surface modification becomes surface coating or deposition when extrinsic top layer is deposited onto the substrate material to generate new surface composition, structure and properties (Adams and Layton, 2010). In specifics, the process can be broadly categorized into three process dynamics: (1) addition of materials of desirable functions to the surface; (2) conversion of existing surface into a more desirable composition, structure and/or topography; and (3) removal of materials from existing surface to create specific topographies/roughness. There are several imperatives for surface modifications in the development of a wide range of functional properties; and this includes improvement of aesthetics, corrosion and wear resistance, scratch resistance, biocompatibility and bio-functionality, elevated temperature strength, electrical, thermal and optical properties, etc. Surface modification particularly offers shorter process cycle for improving materials properties compared to the painstaking and laborious effort of developing novel materials with superior properties (Eker, 2010).

There is no universal surface modification technique that is applicable to all metallic materials; therefore, variation exists depending on process dynamics, intended application and the type of materials. Some of these surface modification techniques are: surface hardening via carburization or flame hardening, conversion coating, electrochemical deposition, chemical surface modification, plasma process, sol-gel techniques, chemical vapour deposition, physical vapour deposition, arc and laser based processes and chemical etching (Schneider, 2013), Most often than not, the choice of any of these techniques is influenced by the substrate material, component design and geometry, economics and target application. These techniques are widely used in the automotive, aerospace, defense and armour, power, electronic, biomedical, textile, petroleum, petrochemical, chemical, steel, power, cement, machine tools, and construction industries. Almost all types of materials, including metals, ceramics, polymers, and composites can be coated on similar or dissimilar materials. It is also possible to form coatings of newer materials, graded deposits (self-lubricating functionally graded materials) and multi-component deposits (Gautam, 2014).

The last three decades have witnessed exponential growth in the technology of surface modification ranging from the traditional thermal treatments through the medium scale processes such as conversion coating, electrochemical deposition to high end melting processes like electron beam and laser processes. Therefore, abundant literature exists on the surface modification of different metallic materials ranging from steels, titanium alloys, aluminium and super alloys for enhanced surface properties (Czerwinski, 2012; Wolf, 2010; Mandracci *et al.*, 2016; Fu *et al.*, 2000 and Gissler and Jehn, 1992). These literature are quite extensive and difficult to synchronize into seamless grouping in terms of process dynamics; microstructural evolution, incidence and presence of defects, and surface property modification (Fu *et al.*, 2000; Gissler and Jehn, 1992). In some of these works, surface modification of specific materials is discussed in relation to a particular process. For instance, some literature (Aramide *et al*., 2009, 2010; Oyetunji and Adeosun, 2012; Davis, 2002; Higgins, 1997; Ruchuan, 2005 and Atanda *et al.*, 2009) discussed carburization of metals for improved surface properties whilst nitriding and carbonitriding were also reported by several researchers (Zagonel *et al.*, 2009; Karwan- Baczewska *et al.*, 2010; Biro, 2013; Sirin and Kalue, 2013; Yang, 2012; Yatiga and Ohki, 2010; Herring, 2011; Ayodeji *et al.*, 2011; Campagna et al., 2011; Yilbas *et al.*, 2011; Yashiv, 2008). Flame hardening, induction hardening, boronizing, galvanizing, aluminizing, electrophoresis, sputtering, ion implantation, chemical vapour deposition, physical vapour deposition, sol gel deposition, plasma treatment, laser treatment, weld overlay using low energy fusion melting techniques are equally widely reported in the literature (Lee *et al.*, 2004, 2006; Heitkemper, 2003; Suzuki *et al.*,2009; Brill and Schibisch, 2015; Gopalakrishnan *et al.*,2002; Bejar and Moreno, 2006; Long *et al.*, 2004; Angeli et al.,1993; Wang and Chen, 2006; Maki *et al.*, 2010; Cheng and Wang, 2011,2012; Abdel Gawad *et al.*, 2006; Wahab *et al.*, 2013; Popoola and Fayomi, 2011; Amuda *et al.*, 2010; Popoola *et al.*, 2012; Besra and Liu, 2007; Choy, 2003; Mubarak *et al.*, 2005; Zhang and Li, 2003; Wang *et al.*, 2012; Mellor, 2001 and Geaman *et al.*, 2013). Some of these literature report exclusive treatments of some metallic materials such as stainless steels (Ruchuan, 2005), aluminum alloys (Chang *et al.*, 2006) and super alloys (Huilgol *et al.*,2013). Thus, the performance of a specific surface modification technique across different material spectra is not available and this makes it difficult to establish the flexibility and versatility of any surface modification process.

In the present paper, a review of the trends in surface modification of metallic materials for improved functionalities via non-arc melting technique is presented. The presentation discusses investigation conducted via the various non-arc melting surface modification techniques and provides a comparison across the techniques. Existing challenges and emerging trends in the field are also presented. .

2.0 Surface Modification

The surface of industrial component may require treatment to enhance its characteristics and a number of treatment techniques are commonly applied to metals to achieve this. In general, two broad methods for surface treatment are available and these are: (i) diffusing small atoms on the metal surface leading to formation of an interstitial solid solution, (ii) a chemical reaction between the diffused atoms and those of basic metal resulting in the formation of new compounds in the superficial layer (Abboud and West, 1991). Surface modification though brings about microstructural changes and/or alters the chemistry of the case of the bulk materials; there are several options of the process. These options are classified based on several parameters such as: (1) depth of modification obtained (mm, µm, nm); (2) change in composition or otherwise; (3) addition of cladding or new materials; and (4) energy source for the process. The classifications based on these parameters are illustrated in Figure 1. It is important to note that surface modification is now an alternative to more costly materials (Wolf, 2010). Figure 2a illustrates a completely worn turbine nozzle needle after some thousand hours of actual service. If this level of service life is deemed unacceptable; then either the entire component must be made of a more wear resistant material, or the area where the wear occurs must be protected to extend the service life. For cost reasons, the usual decision is the latter, the adoption of which leads to the modified surface shown in Figure. 2b.

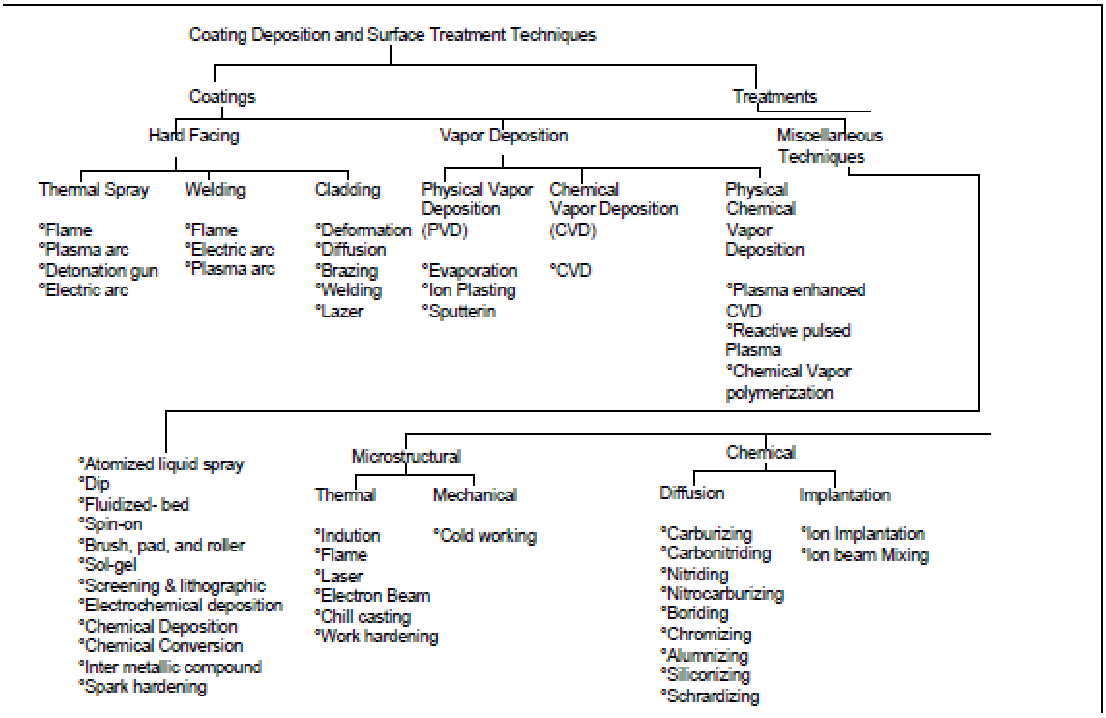
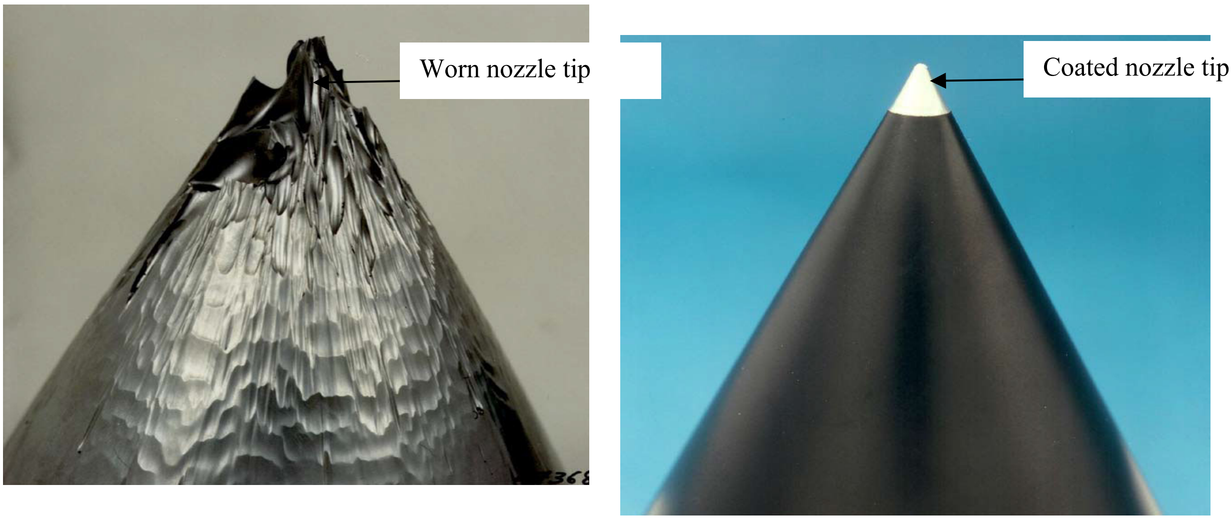


Figure 1. Classification of the various surface treatment techniques (Bhushan, 1999)



(a)

(b)

Figure 2. (a) Worn turbine nozzle needle, and (b) nozzle needle coated with chrome oxide (Sulzer Metco, 2014)

3.0 Surface Modification Techniques

Literature abounds with many variants of the techniques for surface modification. The selection of any specific technique depends on the identification of the performance requirements expected of the surface modified material in a particular application. In accomplishing this, the effect of the technique on the properties of the surface, those of the substrate and the interface between the surface and the substrate must be considered (Mandracci *et al.*, 2016). In some of the techniques, for instance in carburizing or nitriding, there is a gradual change in properties between the surface and the core of the materials, while, in some others like coating or cladding, the change in properties between the surface and the interior is very abrupt. And such differential interface characteristics do have significant influence on the performance of the surface modified material. The character of the interface is the key parameter influencing the choice of a particular surface modification technique (Mandracci *et al.*, 2016; Fu *et al.*, 2000). Since the interfacial phenomenon is different in all surface modification techniques, there are no simple guidelines for the selection of any surface modification techniques, rather selection are influenced by a combination of technical and economic considerations (Fu *et al.*, 2000; Gissler and Jehn, 1992). The variety of surface modification techniques now commercially deployed in the industry for improving surface properties of materials are subsequently discussed. In specifics, the principles, benefits and limitations of the various techniques are described.

3.1 Thermochemical Surface Treatment

Thermochemical treatment is a diffusion based technique combining simultaneous heating and injection of metal or non-metal atoms into a material's surface to modify its chemistry and microstructure. The technique which can be performed either in solid, or liquid or gaseous media permits the injection of several active chemical elements. This provides option for creating wide possibility for modifying the structural characteristics of the surface for enhanced functionalities. The mechanism of the process involves decomposition of solid, liquid or gaseous treatment species, splitting of the decomposed species into nascent atoms which are diffused into the metallic lattice of the substrate follow by chemical reaction within the substrate. The completion of the chemical reaction within the reaction chamber resulted in a modified surface layer in terms of composition, chemistry and microstructure and thus inducing differential properties in the modified layer. The traditional processes in this technique are carburizing, nitriding and their combination but there are other additions to the grouping which include boronizing, aluminizing, chromizing and thermo-reactive diffusion process for the incorporation of vanadium, molybdenum and other carbide forming elements (Gissler and Jehn, 1992). In the last few decades, the process has been extended to surface treatment of alloys with exotic chemistries, nonferrous metals like aluminum and also refractory metals (ASM International, 2001). Furthermore, several hybrid processes have been developed towards optimizing the process in which thermochemical diffusion is part of multi-steps treatment involving coating, cladding and laser processing. Thermochemical surface treatment has wide area of application including machinery, automotive, mining, defense, tooling and oil drilling (Czerwinski, 2012). A basic illustration of a typical thermochemical surface treatment is illustrated in Figure 3 with the gradient variation of composition from the surface to the core of the substrate.

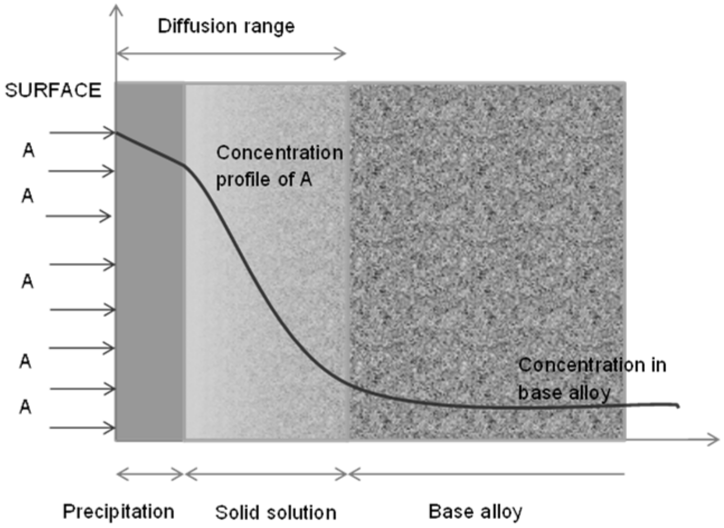


Figure 3. Illustration of thermochemical treatment showing the concentration gradient of a chemical element A in an alloy with typically modified sub- surface areas (Czerwinski, 2012)

The various thermochemical treatments and the theoretical underpinning are reviewed in the subsequent sections. Also, shown in Figure 4 are the applications and uses of the processes in steel industries. Table 1 presents some relative benefits of common surface hardening/ diffusion processes.

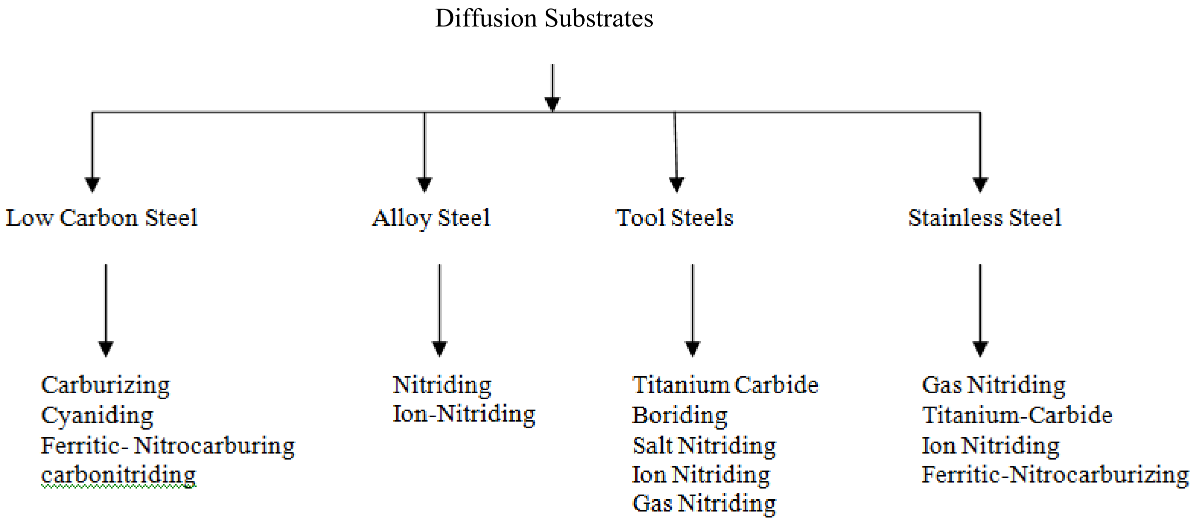


Figure 4. Thermochemical diffusion processes applicable to various types of steel (Schneider *et al.*,2013)

Table 1. Relative benefits of common surface-hardening processes (Schneider *et al.*,2013)

Process	Comparative Benefits							
	Substrate Material	Surface characteristic	Case Depth	Capacity for contact load	Bending Fatigue Strength	Geometrical Control	Susceptibility to Quench Cracks	Investment
Carburizing	Mild or medium carbon steel	Hard highly wear resistant surface	Medium case depth	Excellent	Good	Excellent	Excellent	High
Carbonitriding	Low carbon steel	Hard, highly wear resistant	Shallow case depth	Fair	Good	Excellent	Excellent	Medium
Nitriding	Medium to high carbon steel	Hard, highly wear resistant	Shallow case depth	Fair	Good	Excellent	Good	Medium
Induction hardening	Low carbon steel	Hard, highly wear resistant	Deep case depth	Good	Good	Fair	Fair	Medium
Flame hardening	Low carbon steel	Hard, highly wear resistant	Deep case depth	Good	Good	Fair	Fair	Low

3.1.1 Carburizing

Carburizing is one of the most commonly performed steel heat treatments. For perhaps, three thousand years it was performed by packing the low carbon wrought iron parts in charcoal, then raising the temperature of the pack to red heat for several hours (Aramide *et al.*, 2009) and subsequent quenching in liquid medium most conventionally water. Spent oil or synthetic oil are also used to reduce incidence of cracking arising from the residual stress that develop owing to rash cooling in water. When in solid form, it is called pack carburizing, the mild steel is packed in a well-sealed box in the presence of any carbon containing material or carburizer and then heated to a temperature within the austenitic region of the steel which generally is between 850°C and 950°C for mild steels and then held at that temperature for a period of time (Aramide *et al.*, 2010; Oluwafemi *et al.*, 2015). The fundamental principle of carburization has not changed much since its inception, but the means of introducing the carbon have undergone several improvements. Carburization can either be conducted in solid medium known as pack carburization, in liquid medium known as bath carburization or in gaseous medium known as gas carburization.

In pack carburization, the components to be treated are packed into steel boxes, along with the carburizing material, so that a space of roughly 50 mm exists between them. Lids are then fixed on the boxes which are subsequently slowly heated to the carburizing temperature (850-950ºC). They are maintained at this temperature for up to six hours according to the depth of case required (Davis, 2002; Higgins, 1997). Carburizing mixtures vary in composition, but consist essentially of some carbon- rich material, such as charcoal or charred leather, along with a carbonate energizer such as Ba_2CO_3, K_2CO_3 or Na_2CO_3 but which may account for about 10-20 percent of the total (Ruchuan, 2005). The energizer is generally a mixture of sodium carbonate (soda ash) and barium carbonate. Its function is to accelerate the solution of carbon by taking part in a chemical reaction which causes single carbon atoms to be released at the surface of the steel. The surface carbon is in the range of 0.7% to

1.3% depending on the process environment and the case depth is approximately 0.1 to 1.5 millimeters (Higgins, 1997). Control of pack carburizing is difficult because uniform temperatures may not be maintained. The influence of process parameters on mechanical and case depth of pack carburized mild steel has been studied by several researchers (Aramide *et al.*, 2010; Oyetunji and Adeosun, 2012; Atanda *et al.*, 2009; Grabke, 2002). These works indicated that mechanical properties are influenced by the carburization process, carburizing temperature, soaking time, and the percentage energizer. The case depth was established to increase with increasing percentage energizer, temperature and time. Other significant findings from these investigations include: case depth and hardness increment had a direct proportionality to the percentage energizer, carburizing time and temperature. Also, the exponential activation energy for diffusion is indirectly proportional to carburizing time or temperature. Aramide et al. (2009) established that optimum combination of mechanical properties was achieved at the carburizing temperature of 900ºC soaked for 30 minutes followed by oil quenching and tempering at 550ºC for 60 minutes. Pack carburization can make use of wide variety of furnace because it provides its own contained environment; and it is ideally suited for slow cooling of work from the carburizing temperature; a procedure that may be advantageous for parts that are to be finish machined after carburizing and before hardening. It offers a wider selection of stop- off techniques for selective carburizing (Davis, 2002). However, pack carburization is not well suited to the production of shallow case depth where a regime of strict case-depth tolerance is maintained. Furthermore, it lacks flexibility and accuracy over the control of surface carbon and carbon gradient compared to gas carburizing. Krauss (1980) identified other limitations of the process to include non-suitability for direct quenching thus requiring extra handling and processing for hardening operation which increases both processing time and cost. He equally reported that the disposal of barium containing carburizing waste post environmental problems.

Liquid carburizing is conducted in fused mixtures of salts containing from 20 to 50% sodium cyanide, together with up to 40% sodium carbonate and varying amount of sodium or barium chloride (Higgins, 1997). Ishtiaq *et al.* (2014) reported that the cyanide- rich mixture is melted in calorised pots containing the workpiece (in wire basket) to a temperature of 870- 950ºC for immersion times varying from 30 minutes to 15 hours for the required case depth. Higgins (1997) and Ishtiaq *et al.* (2014) classified liquid carburizing as a quick, efficient and economical carburization process that is quite flexible. The process can use different molten salts for the carburization process and is capable of producing uniform surface unlike pack carburization. Furthermore, it produces uniform surface. Mainly cyanide is used as a source of carbon in liquid carburizing process. Carburizing using cyanide is also called cyaniding. Parts to be carburized are immersed in a bath of molten salts with varying concentration of sodium cyanide between 25% and 90% (Ishtiaq *et al.*, 2014). In liquid carburizing process, sodium cyanide is oxidized to produce carbon and nitrogen in atomic form which are diffused into the surface of the part. Carbon is diffused inwards producing a hardened case by rapid quenching (Totten and Howes, 1997). The case produced by carbon diffusion is similar to that produced by gas carburizing. Cases formed by liquid carburizing have low nitrogen and high carbon content. A hard case of 0.5- 2.0 mm depth can be achieved depending upon the time. The case depth also depends upon the available carbon potential at the surface and the dimensions of the part or work-piece (American Society for Metals (ASM), 1977).

Ishtiaq *et al.*(2014) reported that case depth could be estimated in terms of the depth of carbon penetration down to 0.40%C provided that only martensite was formed on quenching. The solubility of carbon during carburization was at maximum in the austenitic region and the amount of dissolved or diffused carbon determines the final hardness, but when the carbon concentration at the surface exceeds 0.70%, the Ms-temperature falls steeply resulting in decrease in hardness because of increase in the amount of retained austenite after quenching. However, the final hardness can be controlled by regulating the amount of retained austenite in the carburized workpiece (Abboud and West, 1991). In a particular study, Ishtiaq *et al.*(2014) presented the effect of carburizing on the microstructure, hardness and case depth of 17NiCrMo6-4 steel. The work was able to achieve case depth (>1.5 mm) and hardness (>50 HRC) for 17NiCrMo6-4 steel used for gear production using liquid salt bath of composition Na_2CO_3 (30%), NaCN (40%) and $BaCl_2$ (30%) followed by post heat-treatment process, in which steel was heated to 850 °C for 2 hours followed by oil quenching. One of the main advantages of cyanide- hardening is that pyrometric control is quite satisfactory with a liquid bath. Moreover, after treatment the basket of work can be quenched. This not only produces the necessary hardness but also gives a clean surface to the components. The process is particularly useful in obtaining shallow cases of 0.10- 0.25mm, though case depths up to 0.5 mm are used. Salt- bath carburizing is used mainly for small parts requiring a shallow case depth. It is an economical process since the rate of heating is rapid due to the high heat- capacity of the liquid bath and the quick transfer of heat to the work. This reduces the total time of treatment. The main component in such baths is cyanide, which is extremely poisonous, and every precaution must be taken to avoid inhaling the fumes from a pot. However, safety issues have led to baths that are non-toxic that accomplish similar results (Ruchuan, 2005). The components are held in a molten salt that introduces carbon into the metal.

Gas carburizing is a thermochemical carburizing process that can be carried out in both batch and continuous type furnaces. Literatures indicate that it has become by far the most popular method for mass production of carburized parts, particularly when thin cases and large quantity of parts are required (Davis, 2002; Higgins, 1997; Ruchuan, 2005). The workpiece is heated at about 900ºC for three to four hours in an atmosphere containing gases which will deposit carbon atoms by decomposition at the workpiece surfaces (Wadhwa and Akhai, 2014). This atmosphere is generally based on the hydrocarbons methane (natural gas) CH_4; and propane, C_3H_8 which are either partially burnt in the furnace or are diluted with a carrier gas in order to produce an atmosphere giving the required carbon potential at the work surface. The carbon content of the case can be controlled more accurately and easily than in either solid or liquid carburizing. Carburization of 310 stainless steel exposed at 800ºC – 1100ºC in 2% CH_4/ H_2 carburizing gas mixture for 50 hours duration conducted by Ruchuan (2005) revealed that 1000ºC is an appropriate boundary temperature, below which the environment result in mixed oxidizing / carburizing behavior, while above the temperature reducing / carburizing behavior occurs. The findings from the experimental investigation agreed well with the thermodynamic analysis of the carburization process. Below 1000ºC, 310 stainless steel suffered external carburization, oxidation, and internal carburization. In excess of 1000ºC, extensive external carburization occurred and internal chromium carbide disappeared. Gas carburization permits accurate control of surface carbon content and case depth resulting in a more uniform case depth than obtainable in the other two carburization processes. It is a cleaner, safer process which takes shorter time compared to the other processes. However, the process equipment such as furnace, gas generators, trays are quite expensive. The process equally requires reasonable level of operating skill unlike either pack or liquid carburizing. There is also difficulty in handling fire hazards arising from the use of toxic gases (Higgins, 1997).

The vacuum carburizing process involves carburizing in a low pressure environment that is oxygen-free. The atmosphere is significantly simplified although the furnace enclosure is difficult (Kosur, 2011). A single component environment containing uncomplicated gaseous hydrocarbon like methane is used. Since the environment used for heating is oxygen free, the carburizing temperatures can be considerably increased without surface oxidation. The higher temperatures increase the carbon solubility and the diffusion rate. Thus, the time necessary for case depth is minimized. One of the most important advantages of this process is high carbon availability, ensuring extremely homogenous carburizing even for complex geometries and very high load densities (Totten and Howes, 1997). The soot and tar formation which is one of limitation of this process has been eliminated by Acetylene vacuum carburization (AvaC) process which involves alternate injection of acetylene (boost) and a neutral gas like nitrogen for diffusion. During boost injection, acetylene will only dissociate in contact with all-metal surfaces, thus allowing for uniform carburizing. At the same time, it almost totally eliminates the soot and tar formation problem known to occur from propane. Others disadvantages are higher initial capital equipment cost, part cleanliness is more critical in order to achieve desired result, and empirical process control which requires processing loads to determine optimum settings (Herring *et al*.,2002)

3.1.2 Nitriding

Nitriding is a highly specialized surface hardening treatment that produces a thin but high hardness case on a wide variety of steels. The significant advantage of nitriding over other surface hardening processes is that the case hardness is developed without quenching and the attendant distortion problems (Amadi and Anaele, 2015). Finishing operations can be eliminated or held to a minimum. Nitriding is a thermo-chemical process generates pronounced improvements in the mechanical and chemical properties, as well as the fatigue endurance and the corrosion resistance of steels (Mohseni *et al*., 2014; Puntambekar, 2013). The process basically consists of nitrogen incorporation through the surface and its subsequent diffusion into the material bulk (Puntambekar, 2013; Zagonel *et al.*, 2009). The principle involves the introduction of nitrogen in the form of ions or atoms to the surface of the work piece in order to form a hardened case without distorting the bulk structure of the material (Zagonel *et al*., 2012). In commercial applications, the typical modified zone is up to 200-300 μm thick, rarely exceeding 600 μm (ASM International, 2001). Its impact on surface hardness distribution, in terms of the maximum value and penetration depth, as compared with other heat and thermochemical treatments, is shown in Figure 5. The graph illustrates that some nitrided steels have a higher surface hardness than carburized steels but a lower overall total case-depth. The higher hardness comes from combining nitrogen and alloying elements in the steel.

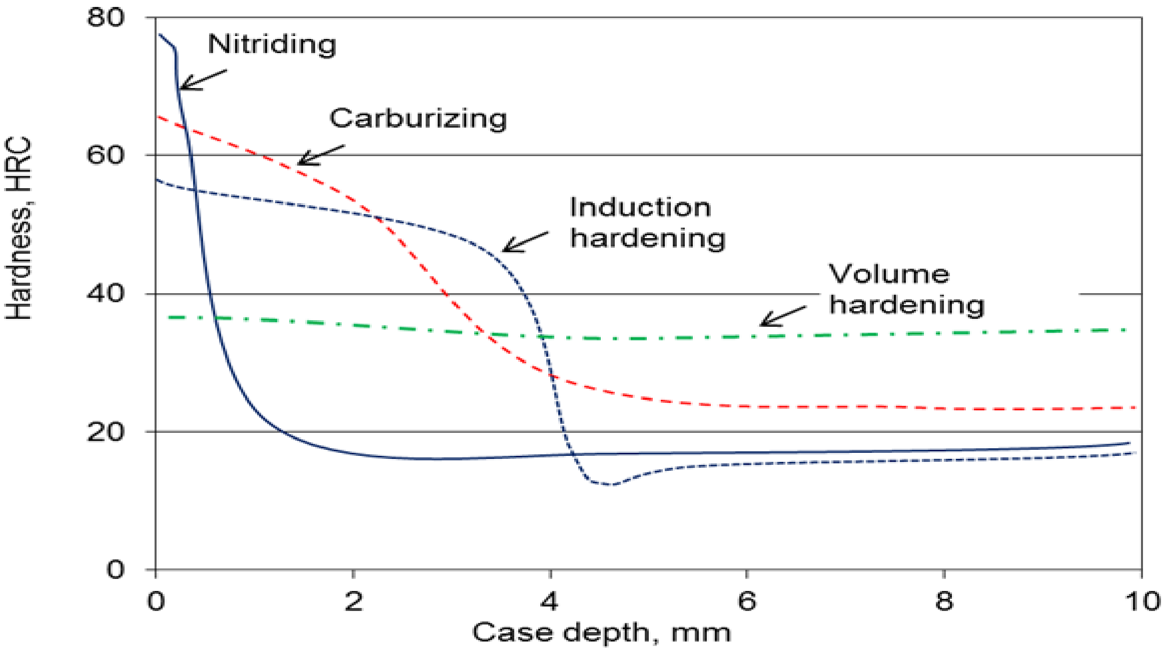
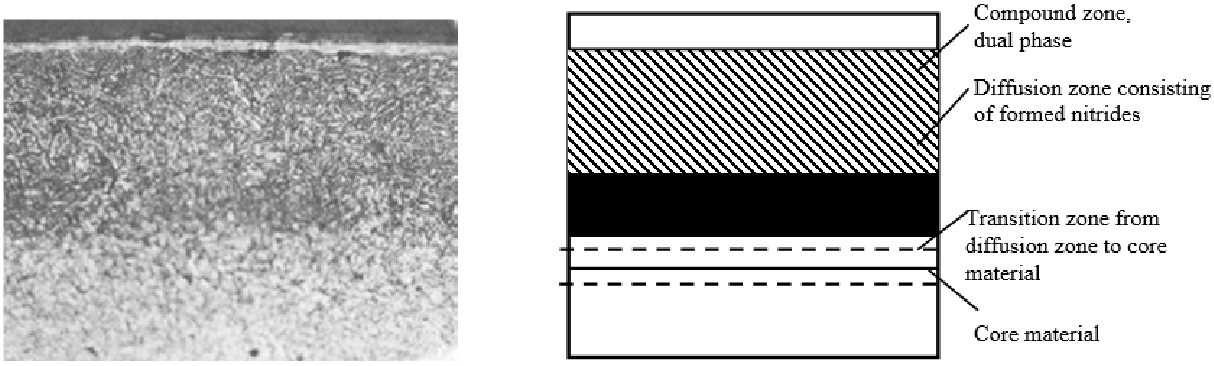


Figure 5. Hardness depth profiles for selected thermal and thermochemical treatments, emphasizing differences in the maximum hardness and penetration depth (Czerwinski, 2012)

Even though nitriding processes are widely used in industrial applications, many fundamental aspects of the process are still not fully understood (Zagonel *et al*., 2009). Some of these fundamental aspects are the influence of N concentration at the materials surface and treatment time, the nitride precipitation kinetics of iron and alloying elements such as Cr, Mo and V, which profoundly influence nitriding (Zagonel *et al.*, 2009). The N concentration in the solid at the surface is determined by the chemical potential of N in the nitriding atmosphere provided local equilibrium exists at the surface. The surface of the material after implantation consists of two layers: the compound zone, consisting of the ε-$Fe_{2\text{-}3}N$ and γ-Fe4N phases, and right underneath the compound zone is the diffusion layer. Figure 6 (a) and (b) are profile of a typical nitrided case structure (ASM International, 2003; Biro, 2013). This region is made up of stable nitrides formed by reaction with elements such as Cr, V, Mo, W and Al. (Sourmail, 2001). The diffusion layer is also called the case depth, and its thickness is determined by the microstructure of the work piece, the gas composition and the temperature of the system (Zagonel *et al.*, 2012; Wang and Liu, 2013).



(a) (b)

Figure 6. Schematic profile and microstructure of nitride layer: (a) sectional microstructure of nitrided layer(Biro, 2013) and (b) differential zones in nitrided layer (ASM International, 2003)

The figure shows the compound zone whose composition of either ε- or γ- phase is determined by the amount of nitrogen diffusion that has taken place and the temperature of the system. When the nitrogen content is between 5.7 to 6.1 weight percent at 450ºC, ε-phase nitride is formed. However, when temperature was furthered increased to 490ºC - 680ºC, γ-Fe_4N was formed. Table 2 provides the range of nitriding steel composition, typical mechanical properties and applications for nitrided steels. There are many presentations of the nitriding process depending on the medium for injecting the nitrogen; and these are gas nitriding, plasma nitriding, pack nitriding, and salt bath nitriding.

Gas nitriding can be condcuted in the gaseous phase, in which ammonia is the source of nitrogen decomposes into nitrogen and hydrogen as represented in Equation (1) (Biro, 2013) .

$$2NH_3 \rightarrow 2N + 3H_2 \tag{1}$$

Gas nitriding is an important thermochemical surface treatment that is used to improve the wear and corrosion resistance as well as the fatigue endurance of steel parts (Yang, 2012). In gas nitriding, nitrogen is introduced into a steel surface from a controlled atmosphere by holding the metal at a suitable temperature in contact with a nitrogenous gas, usually ammonia, NH_3. The process represents one of the most efficient among the various methods of improving the surface properties of engineering components, especially the parts with complicated shapes requiring homogeneous hardening of the surface (Krastev, 2012).

Plasma ion nitriding is a low temperature glow discharge technique, whereby the nitrogen is produced in the form of ions. The plasma process involves the bombardment of the nitrogen source (ammonia) with electrons, which ionize the nitrogen atoms (Yagita and Ohki, 2010). However, one limitation of the plasma ion process is the lack of a uniform distribution of heat across the work piece during heating (Zagonel *et al.*, 2012). Plasma nitriding uses plasma-discharge technology at lower temperature to introduce nascent nitrogen onto the steel surface. It is equally referred to as ion nitriding; and it is widely applied in the hardening of ferrous materials (Zagonel *et al.*, 2012; Yagita and Ohki, 2010). Plasma is formed by high-voltage electrical energy in vacuum. Nitrogen ions are then accelerated to impinge on the workpiece which is connected as a cathode. The ion bombardment heats the work piece, cleans the surface and provides the nascent nitrogen for diffusion into the steel material (Davis, 2002).

Table 2. Nitriding steel composition, typical mechanical properties, characteristics and uses (Higgins 1997).

Composition %					**Typical mechanical properties**		**Characteristics and Application**
C	Cr	Mo	V	Al	Tensile strength (Nmm-2	Vickers pyramid hardness (VPN)	
0.5	1.5	0.2	-	1.1	1200	1075	Maximum surface hardness, coupled with high core- strength. where is this needed? Provide specific examples.
0.2	1.5	0.2	-	1.1	600	1075	Maximum surface hardness, combined with ease of machining before hardening
0.4	3.0	1.0	0.2	-	1400	875	Provide characteristics Ball races, etc., where high core-strength is necessary
0.3	3.0	0.4	-	-	1000	875	Provide characteristics; Aero crankshafts, air-screw shaft, aero cylinder, crank- pins and journals

Pack nitriding uses nitrogen-bearing organic compounds as a source of nitrogen The steels are packed in glass, ceramic or aluminum containers together with the nitriding compound which is often dispersed in an inert packing media. Upon heating, the organic compounds used in the process form reaction products that are relatively stable at temperatures up to 570ºC. The reaction products are decomposed at the nitriding temperature and they provide a source of nitrogen. The process time can range from 2 hours to 16 hours (Yang, 2012).

Salt bath nitriding is a nitriding process in which hardening is carried out by heating the workpiece to the austenitizing temperature in a molten salt bath, containing cyanide and cyanate compounds. It can be applied to carbon steels, low-alloy steels, tool steels, stainless steels and cast iron. The case hardening medium is a nitrogen-bearing salt bath containing cyanides or cyanates. During the process, the dimensional stability of the workpiece can be preserved, thus processing of finished parts is possible. This implies that it can be used to complement engineering properties developed during carburizing and carbonitriding.

In general, nitriding is applicable to a wide variety of carbon steels, low alloy steels, tool steels, stainless steels and cast irons. Optimum properties after nitriding are promoted by the presence of strong nitride-forming elements such as Al, Cr, Mn, Mo, and V in the base alloy. There is a limitation on carbon content which should not exceed 0.5%, as most nitride-forming elements also form stable carbides which limit binding of nitrogen (ASM International, 2001). When the differences in hardness depth profiles for carbon and alloyed steels are essential (Figure 7a), there are corresponding substantial differences between individual grades, designed for nitriding (Figure 7b). While exceptional high surface hardening is achieved with steels containing Al, forming AlN nitrides; the additions of Al, typically in the range of 1%, cause steel brittleness. The nickel nitriding steels containing aluminum develop higher core strengths than do nickel-free nitriding grades. Nickel also increases the toughness of the nitrided case (ASM International, 2003). The base steel properties are of importance to provide the support for nitrided case, especially in applications where components carry high compressive and bending stresses. The various compositions and the associated properties of nitriding steels are presented in Table 2.

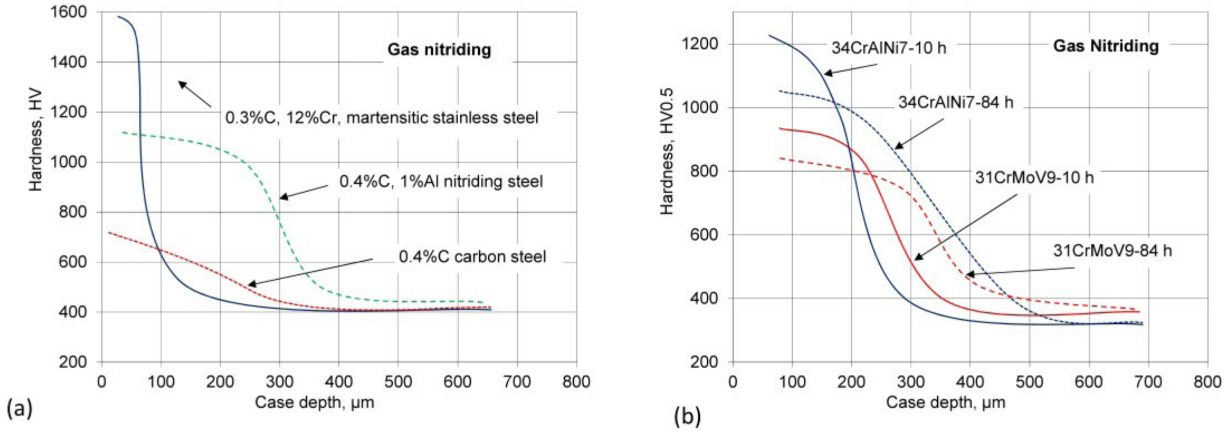


Figure 7. Effect of the steel composition on hardness depth profiles after nitriding: (a) comparison between carbon and alloyed grades; (b) comparison between two nitriding grades (with permission from Schmolz + Bickenbach) cited from Czerwinski, 2012)

3.1.3 Carbonitriding

The process of carbonitriding involves the simultaneous infusion of carbon and nitrogen into the surface of a metal. Nitrogen is inserted in the system through the introduction of ammonia, while carbon is added by the use of a hydrocarbon such as propane (Herring, 2011). It is often conducted in the temperature range of 850-880ºC and results in direct hardening at the saturation temperature. It is a modification of the carburizing process, with the advantage of reaching higher hardness values over the conventional carburizing process (ASM International, 2002). Figure 8 revealed hardness values of carbonitriding and some selected diffusion processes.

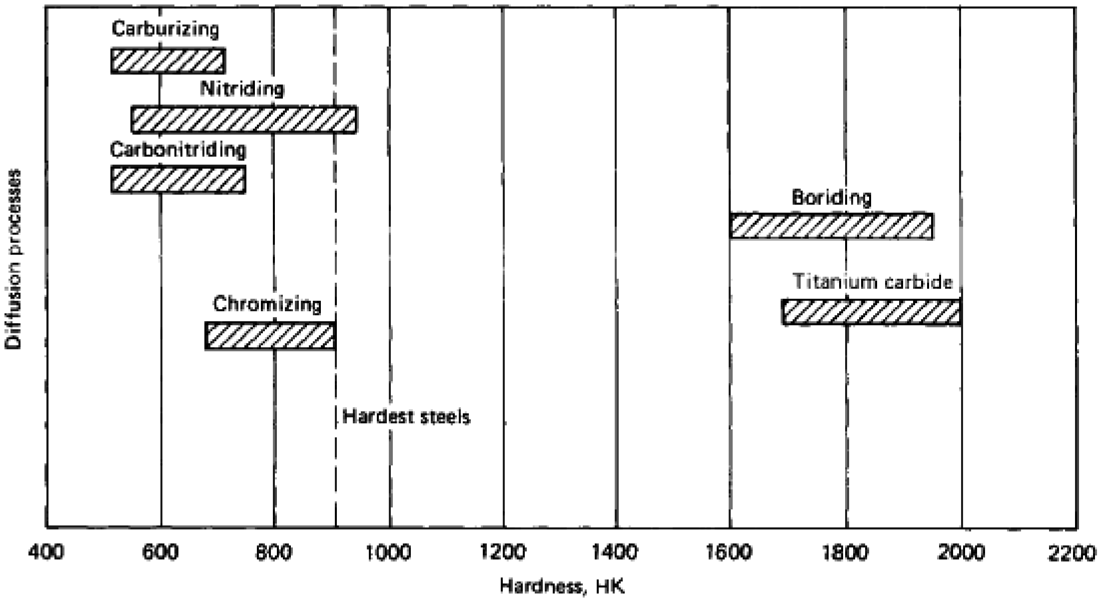


Figure 8. Spectrum of hardness obtainable with selected diffusion processes of steel (Schneider, 2013)

At carbonitriding temperatures, which are substantially higher than those used during nitriding or nitrocarburizing, steel is in the austenitic state, having high solubility of carbon. After carbonitriding, quenching is followed by the second step of low-temperature tempering or stress relieving to improve toughness. At the processing stage, nitrogen inhibits diffusion of carbon, resulting in thinner case, improves hardenability and forms nitrides. After treatment, the presence of nitrogen in carburized steel increases hardness, wear resistance and delays tempering. The latter is of importance for elevated temperature applications. Carbonitriding is widely accepted for surface improvement of plain carbon steels, having low hardenability. According to the comparative study of both processes, carbonitriding and nitrocarburizing develop compressive stress and are associated with the size and shape distortion (Campagna *et al.*, 2011). However, nitrocarburizing causes lower compressive stress and size/shape distortion, as is the case for SAE 1010 steel (Czerwinski, 2012).

Since carbon and nitrogen form hard carbides and nitrides with titanium, carbonitriding is applicable to titanium and its alloys. In the case of laser gas assisted carbonitriding of Ti-6Al-4V alloy, 55 μm thick layer composed of TiCxN1-x, TiN and TiC phases developed (Czerwinski, 2012). In that of pure titanium, a surface modified layer consisting of near-surface layer of carbonitrides and thick layer of α-stabilized solid solution of titanium with nitrogen and oxygen is formed by carbonitriding at 850ºC for 5h (Liu, 2005). As the partial nitrogen pressure changes from 105 Pa to 100 Pa and to 10 Pa the surface hardness decreases and composition alters to $TiC_{0.25}N_{0.75}$ to $TiC_{0.50}N_{0.50}$ and $TiC_{0.52}N_{0.48}$, respectively (Czerwinski, 2012). The characteristics of carbonitriding process, its uses along with other surface hardening processes are summarised in Table 3.

Table 3. Surface hardening processes (Higgins, 1997).

Process	**Category of workpiece**	**Characteristics**
Casehardening (solid and gas)	Gears,king-pins, ball- and roller bearings, rocker-arms-gauges	A wide variety of low- carbon and low- alloy steels can be treated. Local soft surfaces are easily retained. Gas carburizing is a rapid process.
Casehardening (liquid cyanide)	Used mainly for light cases	The case tends to be of poorer quality. But thin cases can be produced quickly
Nitriding	Crankshaft, cam-shafts, gears requiring high core-strength	A very high surface hardness, combined with a high core- strength when required. Surface will withstand tempering influences up to 500Oc. Less suitable than other methods if surface has to withstand very high pressure, e.g. gear- teeth
Carbonitriding	Particularly useful for treating small components	Safe, clean, and easy to operate, applicable to mass- production methods
Ion nitriding	Crankshafts; many other components in various industries	A high degree of control and uniformity is possible
Flame and induction hardening	Tappets, cam-shafts, gears where high core- strength is required	Particularly useful where high core- strength is necessary, since a high-carbon steel can be used and heat treated accordingly. Rapid output possible, but equipment often needs to be designed for a particular job;hence suitable mainly for long runs

The carbonitriding treatment explores simultaneous carbonitriding at the coating gas interface and carburizing at the coating-substrate interface. At carbonitriding temperatures, the substrate also acts as a source of carbon and, in fact, during these processes, the flux of the element causing hardening (C,N) is moving from two interfaces the substrate/coating and gas/coating (Mittemeijer, 2013). The resulting microstructure from a typical nitrocarburizing process is shown in Figure 9 with the delineation of three distinct layers.

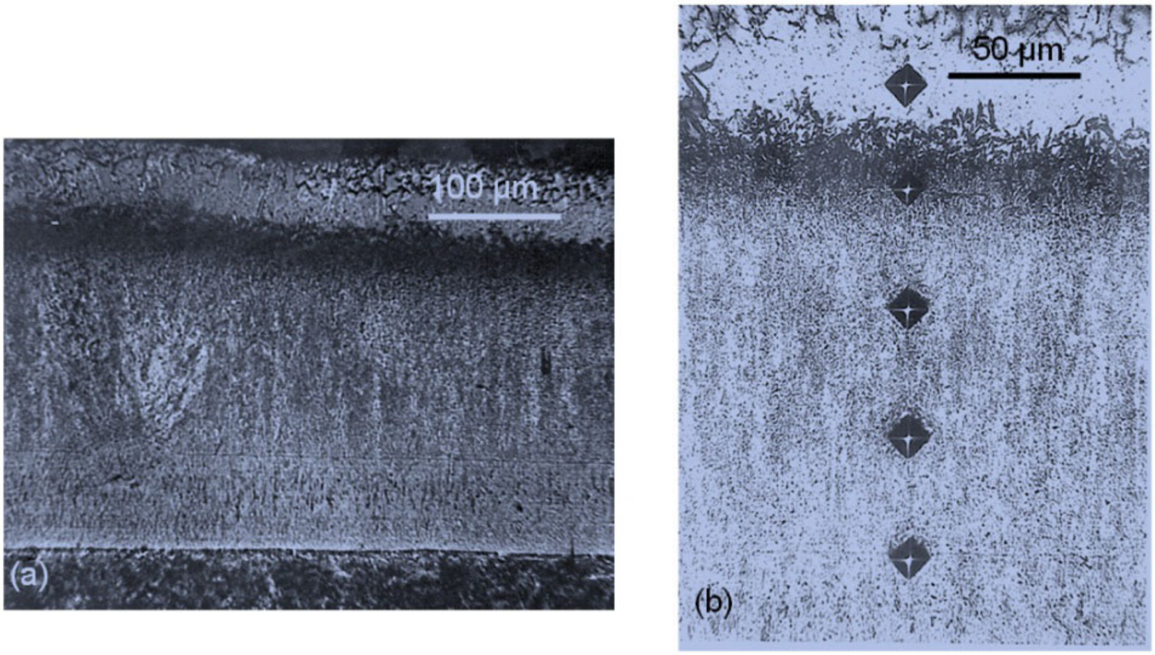


Figure 9. Microstructure of Fe-10%Ni coating after nitrocarburizing at 670 ºC for 1.5 h in solid medium (with permission from Springer Verlag) cited from Czerwinski, 2012.

The microhardness profile across the coating maximum subsurface region is shown in Figure 10. A comparison with the corresponding microstructure indicates that the hardness peak is caused by a layer of carbonitrides, typically situated in the near-surface region. It should be emphasized that during carbonitriding, the microstructural changes in the coating are accompanied by changes in the substrate. The extent of those changes is essentially the same as that described previously for diffusion annealing.

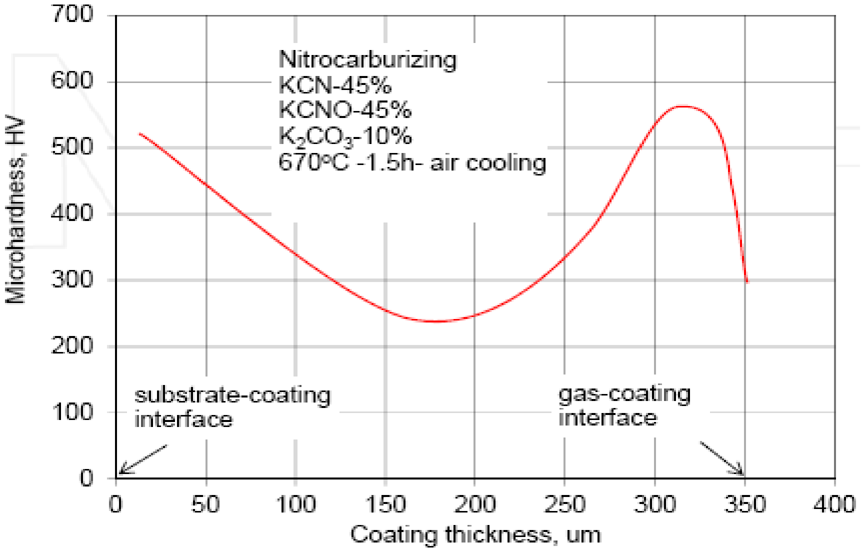


Figure 10. Hardness depth profile within Fe-10%Ni coating on steel substrate after nitrocarburizing (with permission from Springer Verlag) cited from Czerwinski, 2012)

3.1.4 Flame Hardening

In this process, unlike carburizing, there is no change in elemental composition of the alloying species. The affected surface is heated to a temperature above its critical temperature, by means of a travelling oxyacetylene torch, and is immediately quenched by a jet of water issuing from a supply built into the torch assembly in order to achieve a hard martensitic surface and a ductile interior (Rajab, 2009) as shown in Figure 11. It can generate temperature up to 3000ºC (Talapatra *et al*., 2013). Metals treated in this way are usually steels of at least 0.4% carbon and higher. Alloy steels containing up to 4.0% nickel and 1.0% chromium respond well to such treatment. There is a little scaling, decarburization or distortion in flame hardening. Since the heating and cooling are very fast, the core remain unaffected (Rajan *et al*.,2011). The process is simple, mass distortion is absent and any shape can be flame hardened. Furthermore, the equipment cost/investment is cheaper than induction hardening (Table 1). Also, selectively hardened and wider depth of hardened layer can be obtained. It is however difficult to control the temperature which may lead to overheating of the surface. It is also a challenge adjusting the case depth. Also, the cost per piece on a mass scale production is higher than in induction hardening. The application of flame hardening to different grades of steel and the resulting case characteristics are presented Table 4. The characteristics of fuel gases used for flame hardening are equally shown in Table 5.

Table 4. Common steel applied for flame hardening, case depth obtained and typical applications (Raja, 2009)

Steel Grade	**Hardening Temperature/ ºC**	**Maximum Surface**	**Case Depth/mm**	**Typical Applications**
AISI1045	860- 900	50- 60	3.2	Gears, spindles, pinions, guide ways, cam shafts, gudgeon pins
AISI1055	835- 865	55- 62	3.2	Lathe spindles, guide ways, tail stock sleeves, gudgeon pins, worm shafts, gear shafts
AISI1060	820- 850	58- 65	3.2	Tools for machining industry
AISI4140	860-890	50- 55	4.8	Highly stressed components like pinions, crank shafts, gear shafts
AISI5140	860- 890	50- 55	4.8	Highly stressed components like shafts, crank shafts, and parts for machining shafts
AISI6150	860- 890	55- 60	4.8	Components subjected to heavy loads with oscillating or impact loads such as gears, drilling rods, dredger pins
AISI8640	850- 880	50- 55	4.8	Very highly stressed components like gear shafts, gears, pinions

Table 5. Characteristics of fuel gases used for flame hardening (Gronegress, 2013)

Gas	**Heating Value/ MJ/m^3**	**Flame Temperature/ ^{o}C**	
		With Oxygen	**With Air**
Acetylene	53.4	3105	2325
City gas	11.2 – 33.5	2540	1985
Natural gas (Methane)	37.3	2705	1875
Propane	93.9	2635	1925

Lee *et al.* (2004) reported that the control of surface hardness, hardness depth and residual stresses are dependent on conditions such as surface temperature, cooling rate and exposed height from the water surface in flame hardening of low carbon 12Cr steel. For instance, increasing cooling rate generates greater depth and increased hardness. Lee *et al.* (2006) further reported that treatment temperatures between 870^{o}C and 860^{o}C minimized residual stress without substantially compromising the hardness of the treated case. Stress corrosion cracking, brittle fracture, fatigue failures are main associated failures while carrying out the flame hardening (Rossino *et al.*,2014) due to improper selection and control of thermal process parameters. Grum *et al.* (2001) focused on increasing the hardness by mechanized flame hardening procedure though, the optimal process parameters were not considered. Jeyaraj *et al.* (2015) investigated the effect of process parameters such as surface temperature of specimen, stand-off distance (SOD) and quenching time using L9 orthogonal array Taguchi`s approach. The schematic diagram of experimental set up of typical flame hardening process used for the experimentation is shown in Figure 11. The work showed that the microhardness of all specimens increased after flame hardening process. The highest hardness value is about 773.5 HV obtained at temperature 950°C, SOD 30 mm and quenching time of 25 seconds and the least value is about 329 HV obtained at 750°C, SOD 20 mm and quenching time of 50 seconds. Also, it was established that the microhardness value depend on the process parameters with the rank order of quenching time, temperature and SOD respectively.

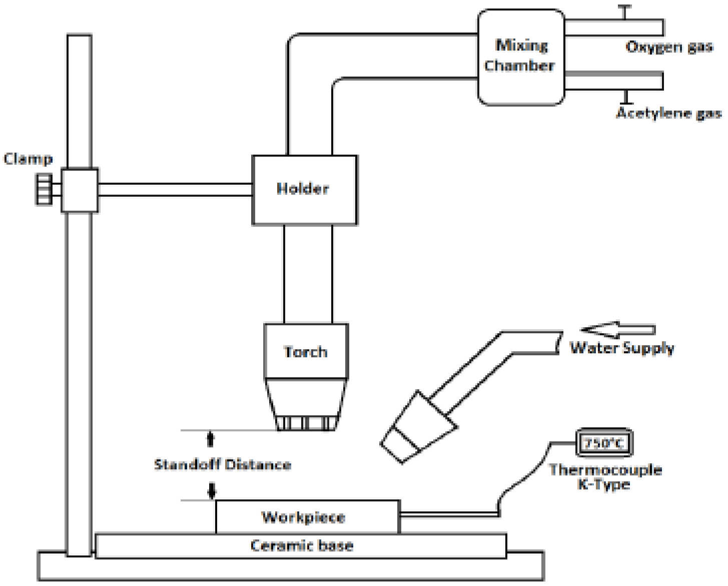
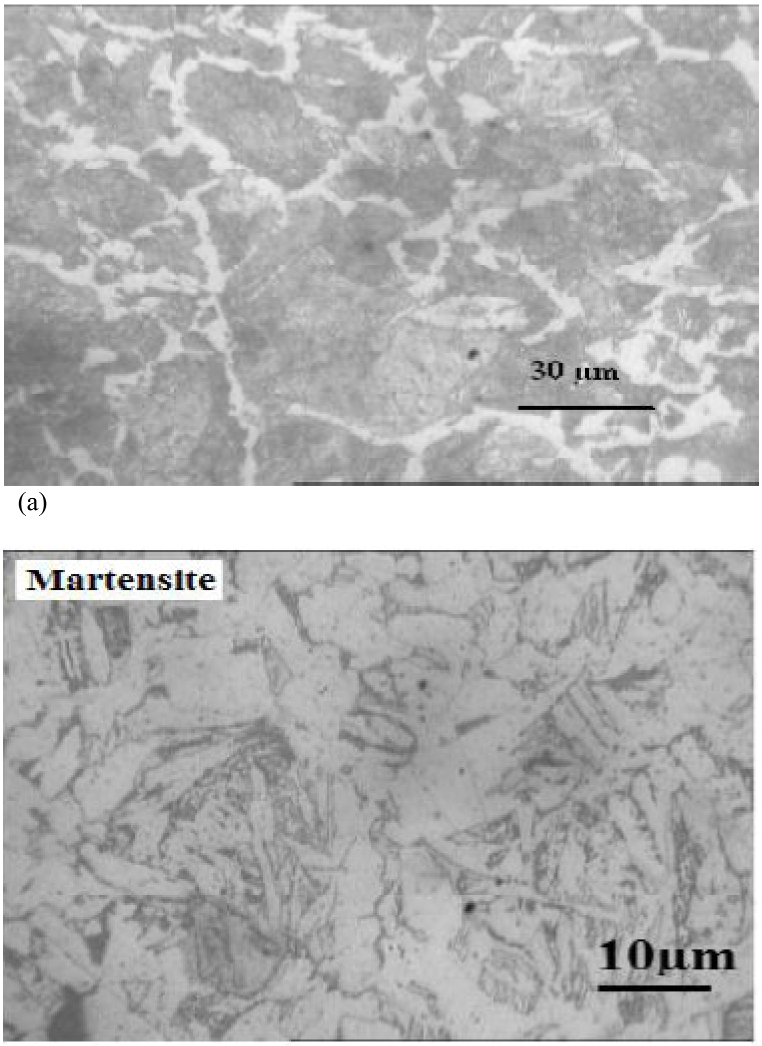


Figure 11. **S**chematic diagram of experimental set up of typical flame hardening process (Jeyaraj *et al.*, 2015)

The work of Jeyaraj *et al.* (2015) also showed that after flame hardening, wholesome formation of martensite in the microstructure was apparent as shown in Figure 12 (a) and (b).



(a)

(b)

Figure 12. Microstructure of medium carbon steel: (a) before flame hardening and (b) after flame hardening (Jeyaraj *et al*., 2015)

3.1.5 Induction Hardening

Induction hardening is a process whereby a material surface is heated and subsequently quenched in order to improve its mechanical properties and wear resistance (Slatter, *et al.*, 2011). The workpiece usually cylindrical is held stationary while the induction coil is wound round it for heating (Brill and Schibisch, 2015). The apparatus involved in this operation include an AC power source, an induction coil, a rectifier circuit, an inverter circuit and a suitable quenching system (Dappen and Amiri, 2015). Alternating current from the power source is converted to direct current by the rectifier circuit, and the AC signal from the rectifier is in turn transformed to DC signal by the inverter circuit and this passes through the coil. The induction coil heats up the workpiece by stimulating eddy currents which raise its temperature, and the metal gets heated rapidly (Rudnev and Totten, 2015). Figure 13 shows the principle of induction hardening process.

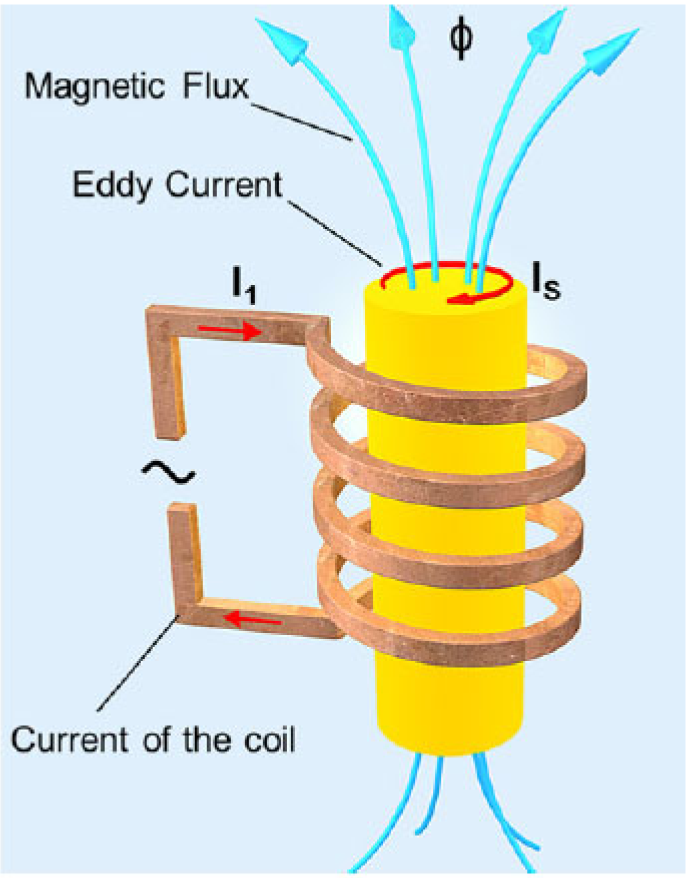


Figure 13. Principle of induction hardening process (Brill and Schibisch, 2015)

The depth of heating produced by induction is related to the frequency of the alternating current, power input, time, part coupling and quench delay (Schneider, 2013). The higher the frequency, the thinner or more shallow the heating. Therefore, deeper case depths and even through hardening are produced by using lower frequencies (Schneider, 2013). The process can be incorporated in production line, case depth can be easily controlled, the operation cost per part is cheap, higher fatigue strength is obtainable, and only slight deformation occurs. Its application is limited to ferrous metal with carbon content not less than 0.4% and with cylindrical shape (Brill and Schibisch, 2015).

The process sequence during hardening consists essentially of heating, holding, quenching and possibly a subsequent tempering process, and is thus significantly shorter than the process sequence for convectional case hardening (Brill and Schibisch, 2015). The process is monitored by an appropriate control system so that the hardening results are reliably reproduced. The microstructure properties can be set to the required depth in carbon based materials by varying the frequency employed, the energy input, the quenching method and the constant coupling distance between and inductor. The hardening process is tailored specifically to the hardening requirement (Brill and Schibisch, 2015).

The work of Suzuki *et al*. (2009) on development of induction surface hardening process for small diameter carbon steel specimens revealed that the result of heat treatment for 6 mm diameter specimens produced a hardened zone depth of about 0.4 mm and hardness value of about 600HV near the surface. Also, the specimens with deep hardened zone exhibited a compressive residual stress about 500MPa whereas those with shallow zones had compressive residual stress of about 200MPa. In the hoop direction, it turned out that residual stress was not formed by induction hardening in the study. The distortion of large hardened zone specimen was similar to full quenched specimen, and the distortion of shallow hardened zone specimens showed similar tendency of annealed or as-received specimen. The best result of heat treatment was on 3 mm diameter specimen which produced a hardened zone of about 0.09 mm and hardness value was about 600 HV.

3.1.6 Boronizing

Boron atoms are diffused into the surface of a workpiece to form complex boride with the base material (Yorulmaz, 2007). It is a metallurgical surface modification method by which metal is heated within a boron-rich environment in order to increase wear resistance (Krastev, 2012). It has been found to be an effective method for significantly increasing the surface hardness and the wear resistance of metals (Krastev, 2012; Yilmaz, 2007). In the case of St41 low carbon steel boronized using boronizing powder that consist of 5% B_4C, 5% KBF_4 and 90%

SiC at 900°C for 2-8 hours, the maximum microhardness reached 1750 and 123HVfor borided layer and substrate respectively. The thickness of borided layer on the St41 steel depended on the treatment time, the longer the treatment time, the thicker the borided layer. The depth of the borided layer which also depended on the pressure, treatment time, and temperature, ranged from 126 to 186 µm. The longer boronizing treatment time gave rise to thicker boride layer (Sutrisno and Hikam, 2013).

Boron atoms, owing to their relatively small size and high mobility at process temperature can diffuse into ferrous metals, resulting in the formation of ferroboron phases Fe_2B and FeB which are very hard, high wear strengths, and low friction coefficients intermetallics (Sutrisno and Hikam, 2013). Figure 14 showed a sawtooth configuration of the boride layer exhibited for low carbon /unalloyed steel while Figure 15 shows a high carbon/alloy steel with a more suppressed configuration of the high carbon boride layer. The work of Sutrisno and Hikam, (2013) on St41 low carbon steel also confirmed the sawtooth morphology exhibited by low carbon steel as shown in Figure 16. This process is similar in its physical and chemical characteristics to other surface hardening treatments, such as carburization and nitriding (Gissler and Jehn, 1992). It has been successfully applied to all ferrous materials, nickel alloys, titanium alloys, and sintered carbides (Sesen and Ozgen, 2014). The most frequently utilized method is pack boronizing which is a process similar to pack carburizing process (Dong et al., 2009). Especially, powder-pack boronizing has the advantage of simplicity and cost-effectiveness in comparison with other boronizing processes (Dong *et al.*, 2009). The thickness and proportion of each boride depend on chemical composition of workpiece, boronizing medium, process temperature and duration of treatment (Sutrisno and Hikam, 2013; Dong *et al.*, 2009; Gunes, 2014; Gunes *et al.*, 2012). Hardness of boride layer produced on carbon steels is much greater than that produced by any other conventional surface hardening treatments. It exceeds that of the hardened tool steel and is equivalent to that of tungsten carbide (Davis 2002). Hardness of the boride layer can be retained at higher temperatures than the nitride layer (Davis 2002). The typical surface hardness of borided steels compared with other treatments and hard materials are given in Table 6.

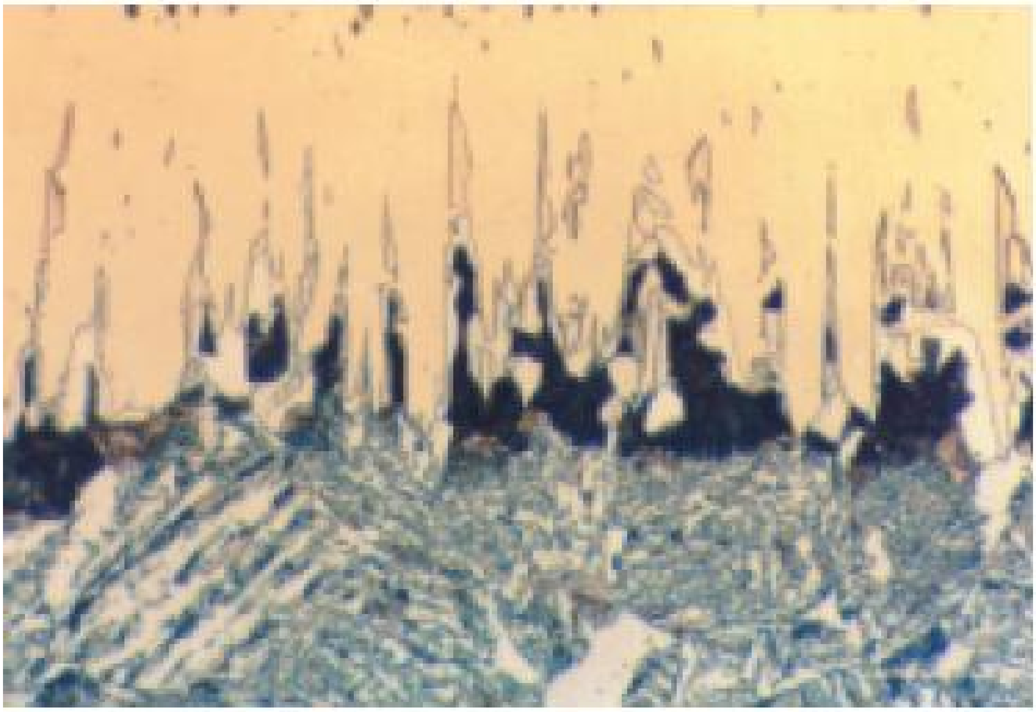


Figure 14. Low carbon/unalloyed steels exhibit a sawtooth configuration of the boride layer (https://www.bodycote.com/en/heat-treatment-plant)

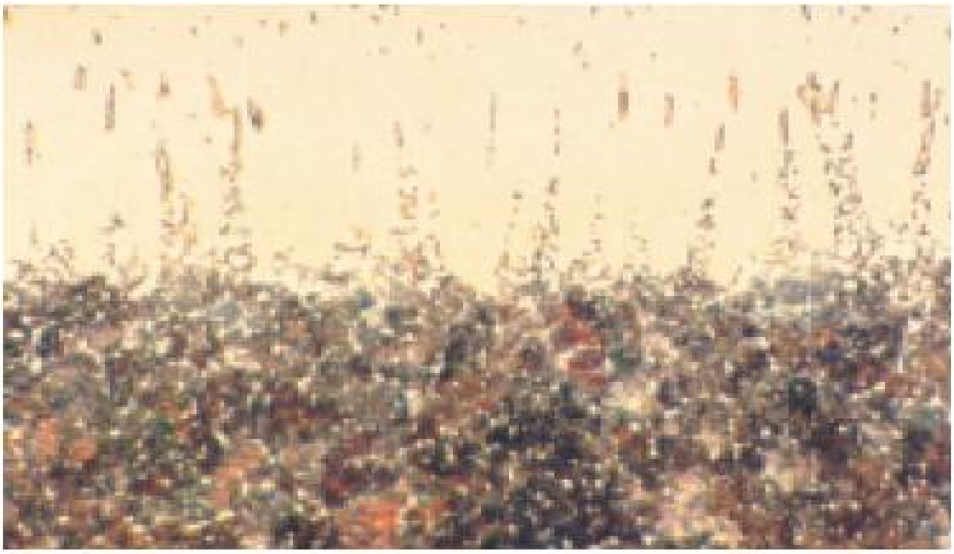


Figure 15. High Carbon/Alloy Steels Have a More Suppressed Configuration of the High Carbon Boride Layer (52100 Steel Pictured. (https://www.bodycote.com/en/heat-treatment-plant)

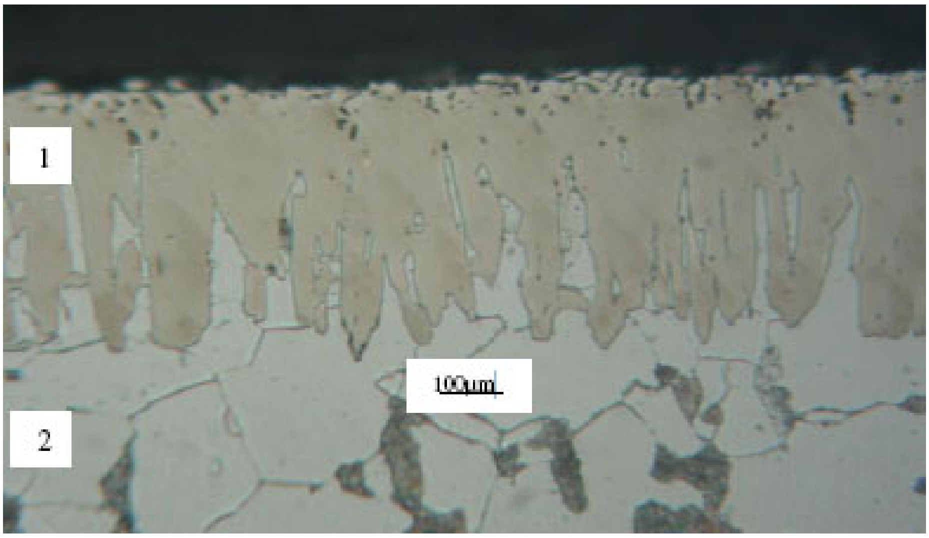


Figure 16. Sawtooth morphology of borided St41 low carbon steel (Sutrisno and Hikam, 2013)

Table 6: Typical Surface Hardness of Borided Steels Compared with other Treatment and Hard Materials (Sinha, 1991 cited from Kamaludin, 2015)

Materials	Microhardness (HV)
Borided Steel	1400 – 2100
Quenched Steel	900
Hardened and Tempered H13 Die Steel	540 – 600
Hardened and Tempered A2 Die Steel	630 – 700
High Speed Steel (BM – 42)	900 – 910
Nitrided Steels	650 – 1100
Carburized Low – Alloy Steel	650 – 950
Hard Chromium Plating	800 – 1100
Cemented Carbide, WC + Co	1160 – 1820
TiN	2000
TiC	3500
SiC	4000
B_4C	5000
Diamond	>10000

The benefits of boronizing includes: (1) increased tool and mold life; (2) good resistance to abrasive, sliding and adhesive wear; (3) reduced use of lubrication; (4) can be polished to a high finish; (5) reduced tendency to cold weld; (6) low coefficient of friction (Yilmaz, 2007).

Generally, a boron compound layer develops on the surface of boronized ferrous alloys. This compound layer (or boride layer) is normally composed of two sublayers; the outermost rich in FeB and the innermost rich in Fe_2B (Yilmaz *et al.*, 2016; Bejar and Moreno, 2006). Underneath the compound layer, the diffusion zone hardly exists because the solubility of boron in Fe is very small (Bejar and Moreno, 2006). Since the FeB phase is more brittle and harder, and has a higher coefficient of thermal expansion than the Fe_2B, cracking of the double-phase boride layer is often observed (Bejar and Moreno, 2006; Arun *et al.*, 2013).

Different types of pre or post boronizing treatments are conducted on materials in order to minimize cracking due to the brittleness of the double-phase boride layer. Some of those that have been attempted and reported in literature are: carburizing, laser treatment, quenching, ions implantation and gas nitriding (Kamaludin, 2015). By boronizing a carburized steel, a reduction of the microhardness gradient across the case is obtained. In laser treatment, the coarse and columnar structure of the boride layer can be changed into a fine grain structure. In quenching, the hardness gradient between the boride layer and substrate can be reduced. In N ions implantation, part of FeB and Fe_2B is discomposed and *c*-BN, FeN and Fe_2–3N compounds could be formed. In gas nitriding, the outermost sublayer (FeB) can be transformed into the ductile Fe_4N phase, whereas the innermost sublayer (Fe_2B) can be transformed into the Fe_4N and $B_{25}N$ phases. Gopalakrishnan *et al.*(2002) showed that boronizing with cyclical interruption of the process produces a change in the morphology of the typical boride needles resulting in an improvement in some mechanical properties (toughness and ductility). On the other hand, it has been shown that in a ferrous alloy, the content of some elements, such as C, Cr and Ni, has a great influence on the boride layer. With the increase of the C content, the thickness of this layer decreases and its hardness either increases (Bejar and Monero, 2006), or first decreases (up to 0.5% C) and then increases (Bejar and Monero, 2006). As carbon does not dissolve significantly in FeB and Fe_2B, C is driven ahead of the boronized layer, forming a poly-phase zone rich in carbides and borocarbides (Fe_3C, $Cr_{23}C6$, Fe_7C_3 and $Fe_3(B,C)$) between the Fe_2B sub-layer and the matrix (Bejar and Monero, 2006). This explains why the boride layer on high carbon steel is very brittle and poorly bonded to the base metal (Bejar and Monero, 2006; Yilmaz *et al.*, 2016). One effect of Cr is to increase the amount of the FeB phase in the boride layer (Bejar and Monero, 2006). Other effects are to increase the hardness and the brittleness of the surface layer and to produce a layer that is not very compact on the outside (Bejar and Monero, 2006). In the case of Ni, by increasing its percentage the compound layer becomes more regular and thinner (Bejar and Monero, 2006). In most of the studies under reference, B_4C was the boronizing agent (other agents were BCl_3 and ferroboron alloy). Due to the problems associated with the cracking of the boride layer, it seems advisable to study the possibility of using another boronizing agent that generates a low boronizing potential (Bejar and Monero, 2006), in order to form a surface layer of Fe_2B boride only. The work of Bejar and Moreno (2006) on successful boronizing of 1020, 1045, 4140 and 4340 steals in a mixture of borax and SiC at 1273 K produced a boride layer that is a Fe_2B single phase.

3.2 Metal and Conversion Coating

There are quite a number of processes for the deposition or formation of coatings on substrate materials, as well as a nearly unlimited number of coating materials. The choice of the appropriate combination of coating process and material for the respective application requires extensive understanding of the dynamics of coating process. Table 7 lists principal coating processes, common coating materials, typical attainable coating thickness, and sample applications. Some processes are not suitable for certain coating materials; also, the necessary coating thicknesses are not attainable with all methods. Beyond that, the equipment necessary for some processes can be quite complex and, therefore, costly. The use of cost analysis can determine whether a coating is a practical solution, or otherwise. Today's regulations require that ecological criteria of the respective coating processes must also be examined, as not all methods are environmentally subtle (Regenstein, 1998).

Table 7: Principal coating processes and characteristics (Sulzer Metco, 2014)

Coating Process	Typical Coating Thickness	Coating Material	Characteristics	Examples
PVD	1 – 5 µm	Ti(C,N)	Wear resistance	Machine tools
CVD	1 – 50 µm.	SiC	Wear resistance	Fiber coatings
Baked Polymers	1 – 10 µm	Polymers	Corrosion resistance, Aesthetics	Automobile
Thermal Spray	0.04 – 3 mm	Ceramic and metallic alloys	Wear resistance, corrosion resistance	Bearings
Hard Chromium Plate	10 – 100 µm	Chrome	Wear resistance	Rolls
Weld Hardfacing/Overlay	0.5 – 5 mm	Steel, Stellite	Wear resistance	Valves
Galvanize	1 – 5 µm	Zinc	Corrosion resistance	Steel sheet
Braze Overlay	10 – 100 µm	Ni-Cr-B-Si alloys	Very hard, dense surface	Shafts

3.2.1 Galvanizing

Galvanizing is a process of coating iron or steel with zinc (Zn) in order to provide greater protection against corrosion for the iron or steel base. The process of galvanizing sheet iron was developed simultaneously in France and England in 1837. The methods employed a "hot dipping" process to coat sheet iron with Zn (Coni, *et al.*, 2009). Like tinplate, early galvanized metals were hand dipped. Today almost all galvanized iron and steel is electroplated. Galvanneal is a commercial hot-dipped Zn coating on sheet steel (Long *et al.*, 2004; Gayle,*et al.*, 1998). After the initial coating, the metal is heat treated to alloy the Zn to the iron base. The resultant surface layer is a complex zinc-iron alloy, where more than one specific phase exist (Mei, *et al.*, 2015). Like conventional galvanizing, "galvannealing," also protects the sheet steel from corrosion. Further, the rough, porous surface of the galvanneal coating assists paint to adhere to the steel and improves the spot welding performance of the steel sheet (Mei *et al.*, 2015). The automotive industry is the largest customer for Galvanneal products. Typical automotive applications include various stamped body components, doors, inner panels, brackets, and some structural components. Compared to other steel coated products produced by electro-processes, Galvanneal is inexpensive (Long *et al.*, 2004).

Among the variety of coating types, Zn coating is widely used as a protective coating on steel and one of the very important problems in galvanizing is the need for improvement in the protective and functional properties of Zn coatings (Bejat *et al.*, 2004). According to literature (Bejat *et al.*,2004; Pandey, 2013), Zn alloys can provide improved corrosion resistance compared to pure Zn in the protection of ferrous- based metals. Pandey (2013) and Bejat *et al.* (2004) both reported that this is easily achieved by alloying Zn with more noble metals, mostly with metals of the iron group (Ni, Co and Fe). Among these class of alloys, zinc–iron alloys have been quite extensively considered as coating materials, since they showed excellent corrosion resistance (due to the nature of the zinc–iron phase), good paintability, formability and weldability and ease of formation of the coating (Pandey, 2013). The co-deposition of iron group metals with zinc has several unique features (Abou-Krisha *et al.*, 2016). Alloy electrodeposition is widely used in the production of new materials that require mechanical, chemical, and physical properties (Karahan, 2008). The electrodeposition method is suitable for producing reproducible electrodeposited films at the same conditions. Zn coatings have been applied as the first protection layer on steel, mainly in automobile industry (Karahan, 2008; Pandey, 2013). In particular, Fe- Zn crystalline electrodeposits are promising alternative to pure Zn and galvannealed steel, due to their improved mechanical properties and corrosion resistance (Pandey, 2013). Iron - Zinc alloy coatings have been widely used by the automotive industry because of some advantages which zinc coatings cannot provide. Park and Szpunar (2000); Pandey (2013) and Abou-Krisha *et al.*(2016) reported that zinc-iron coatings not only provide excellent corrosion resistance but also exhibit improved mechanical properties compared to Zn coatings. Hot-dip Galvanizing is the most common methods for applying protective coatings of zinc to iron and steel. It involves the immersion of iron or steel in molten zinc, after the surface of the base metal has been properly cleaned. This process gives a relatively thick coating of zinc that freezes into a crystalline surface pattern known as spangles. During the process, a multiple layered structure of iron- or steel-zinc alloys is formed between the inner surface of the zinc coating and the iron or steel. These middle layers tend to be hard and brittle and may peel or flake if the iron or steel element is bent. This process involves the application of zinc onto a "fabricated" shape. This means the steel is shaped into the final product; a structural beam, a large diameter pipe, or a small fastener, and then dipped into molten zinc to apply the zinc coating. These items are coated either one at a time or, in the case of small parts, as a number of parts contained in a "basket". Hence, the terms "batch" or "after fabrication" are used to describe this process (Trpcevska *et al.*, 2010). In many ways the general or batch process is the same as the continuous process in that the objective is to apply an unbroken coating of corrosion resistant zinc onto the surface of steel.

A major limitation in hot-dip galvanizing is that the process requires keeping the temperature of the bath above the temperature of molten zinc which consume large volume of fuel resulting in a considerable loss of zinc. Additionally, increased inspection and rework due to zinc drips may be required on complicated shapes such as grooved couplings and fittings. These limitations prompted researchers in finding alternative to the process. Radzik (2002) worked on the use of thermal spray zinc as an alternative to the hot dipped galvanizing process. The work conducted in accordance with ASTMB 117 using independent laboratory testing established that thermal sprayed zinc exhibited superior corrosion resistance to that of hot dipped galvanizing for ductile iron piping products when tested. The work also confirmed ease of application to complex shapes, ability to control the coating thickness and adhesion of the zinc to the iron substrate as being superior in thermal sprayed zinc relative to hot dipped galvanizing.

3.2.2 Aluminizing

Aluminizing is a proprietary process in which steel components are packed into a retort and exposed to aluminium vapour at a temperature above about 925^{o}C. The aluminium diffuses into the steel, and this forms a true metallurgical alloy containing over 50% aluminium at the surface (Garverick, 1994). Hot-dip aluminizing is an effective and inexpensive coating process to protect steels from oxidation (Huilgol *et al.*, 2013). The quality of coating depends on the properties of the intermetallics layer forming at the interface. A brittle intermetallic layer may peel off from surface during forming operations which generally follows aluminizing treatment (Huilgol *et al.*, 2013; Dybkov, 1994). Therefore, it becomes necessary to study the formation of intermetallics layer under different conditions (Huilgol *et al.*, 2013). Gebhardt and Obrowski (1953) observed that when steel comes in contact with the molten aluminum, the major intermetallic layer formed is Fe_2Al_5. Bouché *et al.* (1998) reported the formation of two intermetallic layers, namely, Fe_2Al_5 and $FeAl_3$, when solid iron is dipped in liquid aluminum over the temperature range 700°C to 900°C. They reported that the growth behaviour is initially non parabolic which later transited to parabolic trend. Kinetic studies done by Bouayad *et al.* (2003) for medium dipping times (<45 min) showed that the growth of Fe_2Al_5 layer is diffusion controlled and $FeAl_3$ layer growth is linear with time. Many researchers tried to explain the observed tongue-like morphology of the intermetallic layers (Huilgol *et al.*, 2013; Bouché *et al.*, 1998; Dybkov, 1994) that the anisotropic diffusion is responsible for this growth. Springer *et al.*(2011) investigated inter diffusion between low carbon steel and pure Al (99.99%) and Al alloy (Al-5%Si) between temperatures 600°C and 675°C and showed that growth rate of -layer (Fe_2Al_5) is diffusion controlled and it governs overall intermetallic layer growth. Cheng and Wang (2011) observed that as the silicon content in the molten bath increases, the thickness of intermetallic layer decreases; the interface between intermetallic layer and steel substrate becomes flat. Cheng and Wang (2012) investigated the effect of nickel preplating on the formation of intermetallic layer in mild steel dipped in pure Al. Li *et al.*, (2003) investigated the phase constituents within the intermetallic layer formed during hot-dip aluminizing. Bhat *et al.*, (2013) discussed the effect of $ZnCl_2$ + NH_4Cl flux on the microstructural formation during dip aluminizing of steel with aluminum. It is also reported that Si and Cu are the alloying elements in the aluminizing bath which are effective in restraining the growth of intermetallic layer (Huilgol *et al.*, 2013). Addition of Cu has an additional effect that promotes formation of cubic variant for Al_7Fe_2Si (Huilgol *et al.*, 2013). Cubic variants are better than hexagonal variants because of improved ductility (Huilgol et al., 2013). Thus, this revealing attributes of Al, Si and Cu elements in controlling growth of intermetallics was the basis of using Al-Si-Cu alloy as filler materials during dissimilar tungsten inert gas (TIG) welding of aluminum alloys to stainless steels (Song *et al.*, 2010; Lin *et al.*, 2010).

Huigol *et al.* (2013) conducted hot-dip aluminizing of low carbon steel in molten Al-7Si-2Cu bath at 690°C for dipping time ranging from 300 to 2400 seconds; and identified four intermetallic phases, Al_7Fe_2Si, -$FeAl_3$, -Fe_2Al_5, and $Al_2Fe_3Si_3$ in the reaction layer. Al_7Fe_2Si phase was observed adjacent to aluminum-silicon topcoat, $FeAl_3$ between and Fe_2Al_5, Fe_2Al_5 adjacent to base materials, and -$Al_2Fe_3Si_3$ precipitates within Fe_2Al_5 layer. Figure 17 shows the inter-metallic phases of aluminum. The findings also noted that the average thickness of Fe_2Al_5 layer increased linearly with square root of dipping time, while for the rest of the layers such relationship was not observed. The tongue-like morphology of Fe_2Al_5 layer was more pronounced at higher dipping time. Overall intermetallic layer thickness followed parabolic relationship with dipping time. Aluminizing or aluminum diffusion alloying is an economical process for inhibiting corrosion by protecting the surface of steels, stainless steels and nickel alloys operating in severe high-temperature environments. Similar to the galvanizing process, aluminum is metallurgically bonded to the steel surface, providing excellent heat reflectivity and corrosion protection. Aluminizing or diffusion of aluminum into the surface of the steel or alloy helps slow down or stop corrosion by protecting the surface in corrosive and/or high temperature environments. It is also very effective in combating the effects of sulphidation, oxidation, and carburization.

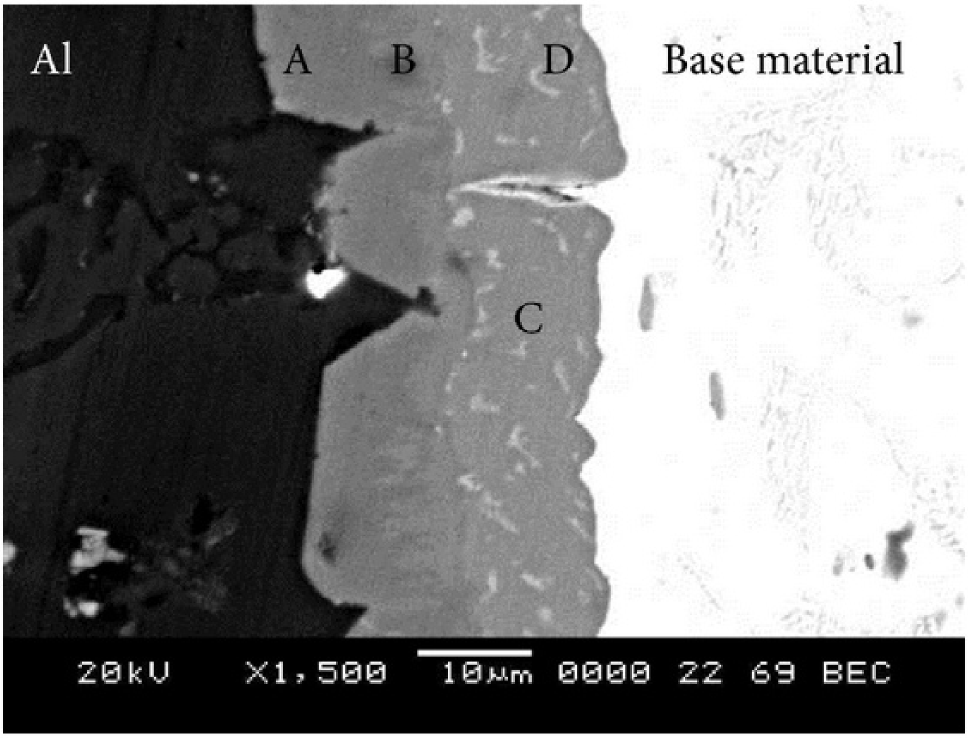


Figure 17. Intermetallic phases of aluminum (Huilgol *et al.*, 2013)

3.2.3 Electroplating

Electroplating is an electrodeposition process for producing a dense, uniform, and adherent coating, usually of metal or alloys, upon a surface by the act of electric current (Lou and Huang, 2006). The coating produced is usually for decorative and or protective purposes, or enhancing specific properties of the surface (Jadid and Pourjafar, 2014). The surface can be conductors, such as metal, or nonconductors, such as plastics. Electroplating products are widely used for many industries, such as automobile, ship, air space, machinery, electronics, jewelry, defense, and toy industries. The core part of the electroplating process is the electrolytic cell (electroplating unit). In the electrolytic cell (electroplating unit) a current is passed through a bath containing electrolyte, the anode, and the cathode as shown in Figure 18. In industrial production, pre treatment and post treatment steps are usually needed as well (Lou and Huang, 2006). The workpiece to be plated is the cathode (negative terminal). The anode, however, can be one of the two types: sacrificial anode (dissolvable anode) and permanent anode (inert anode). The sacrificial anodes are made of the metal that is to be deposited. The permanent anodes can only complete the electrical circuit, but cannot provide a source of fresh metal to replace what has been removed from the solution by deposition at the cathode. Platinum and carbon are usually used as inert anodes (Lou and Huang, 2006). Electrolyte is the electrical conductor in which current is carried by ions rather than by free electrons (as in a metal).

The metallic ions of the salt in the electrolyte carry a positive charge and are thus attracted to the cathode. When they reach the negatively charged workpiece, it provides electrons to reduce those positively charged ions to metallic form, and then the metal atoms will be deposited onto the surface of the negatively charged workpiece. The electroplating industry has been experiencing continuous innovations and also facing significant challenges from economic and environmental perspectives. The purpose of electroplating is to produce a qualified coating with the desirable attributes. Based on the specifications of the coating and the substrate, one may select a specific electroplating process for a given application.

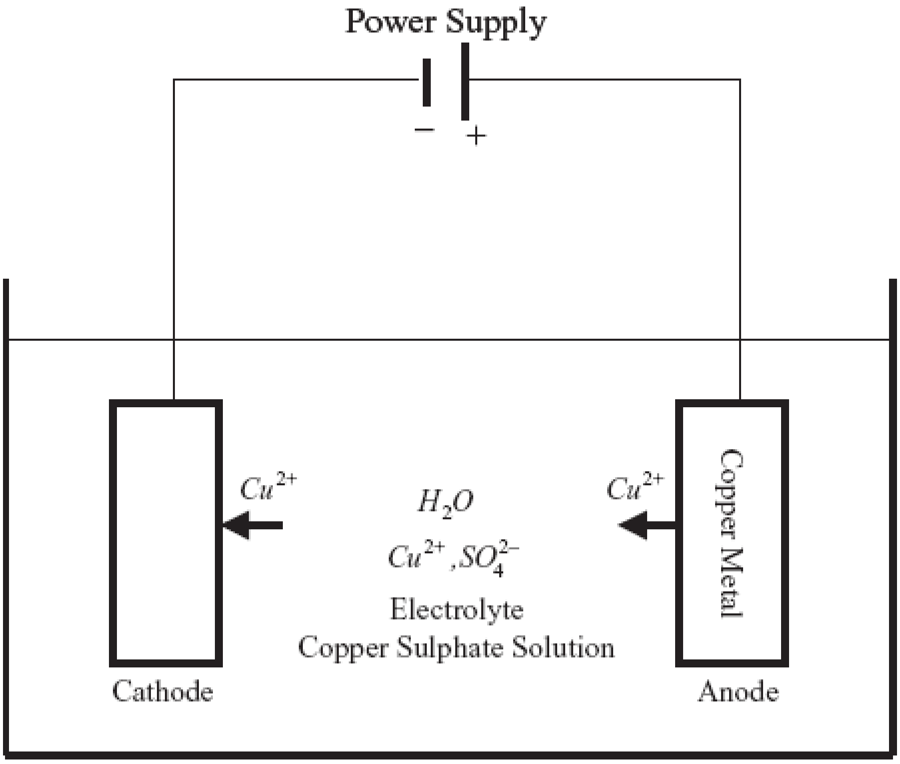


Figure 18. Principle of electroplating process (Lou, 2006)

Applications of electroplating are numerous because it is an inexpensive and simple method; it is used in all aspects of electronics, optics, and the automobile industry where, for example, chrome plating is used to enhance the corrosion resistance of metal parts. Other applications of electroplating are listed in Table 8.

Table 8. Electroplating characteristics and applications (Balseal, 2003)

Metal Coating	Characteristics	Typical Applications
Zinc	Excellent corrosion protection for steel; economic and safe	Connecting elements, auto and construction industry, plant engineering
Alloys- Zinc, Copper, and Precious metal	Excellent corrosion protection, decorative finish, wear resistant	Extreme corrosion resistance combined with high thermal stress e.g., car exhausts, engine elements, and electronics parts
Copper, Nickel, Chrome	Excellent corrosion protection, decorative finish	Motor vehicles, plumbing fittings, steel furniture, shop fittings
Hard Chrome	Extreme hardness, resistance to wear, corrosion protection, improved lubricating properties	Hydraulics, mold making, vehicles, shafts, and bearing
Silver, Silver alloys	Good conductivity for heat and electricity, antibacterial, decorative finish with enhanced value	Jewelry, electrical and electronic parts, household goods
Gold	Flexible, non reactive with other elements, good electrical conductivity, resistance to corrosion, enhanced value	Jewelry, electrical and electronic parts, household goods
Bronze	Resistance to wear and corrosion, flexible	Bearing shells
Tin	Softness, flexible, solderable	Household appliances, electronics, printed circuits, food industry

Abdel Gawad *et al.* (2006) investigated the influence of plating parameters such as current density and plating time on the coating thickness of chromium deposited layer. It was found that the coating thickness increases with increasing current density and plating time. The results showed that 1 to 2 µm thickness of chromium coating on carbon fibers can be achieved at 0.27 A/cm^2 and 15 min. The effect of time on the transformation of chromium layer to chromium carbide was equally studied. The results indicated that suitable time for complete transformation of the most stable carbide phase Cr_3C_2 was achieved by heating the chromium coated fiber for 6 h in vacuum at 900 °C.

Wahab *et al.* (2013) also studied the separating between the electrodes and duration of electroplating process variables. Their effect on the thickness and uniformity of coating was analyzed and quantified using design of experiment. The nickel deposition was conducted by electroplating in a standard Watt's solution keeping other plating parameters (current: 0.1 Amp, electric potential: 1.0 V, and pH: 3.5) constant. The separating distance between anode and cathode was varied at 5, 10, and 15 mm, while the plating times were 10, 20, and 30 minutes. Coating thickness was found to be proportional to the plating time and inversely proportional to the electrode separating distance, while the uniformity tends to improve at a large electrode separating distance.

Popoola and Fayomi (2011) investigated the effect of some process variables such as depth of immersion, distance between the anode and cathode, voltage and plating time on the thickness of zinc coating deposited on low carbon steel substrates. In this work, low carbon steel substrate immersed in solution zinc electroplating bath at 0.5 – 1.0V provided best plating properties when plated at 0.8V for 20 minutes. It was equally established that coating mass increases with increasing voltage, plating time, depth of immersion and shorter distance of the object (cathode) from the anode. . The scanning electron microscope (SEM) and optical photographic microscope (OM) of the coating showed fine grained deposit of deposited zinc and inclusion of additional agent.

Literature in this aspect recorded tremendous achievement on deposition of metals by electroplating. Amuda *et al.* (2010) also established that optimum deposition of zinc was achieved at plating temperature of 30°C, plating bath PH of 4.4, current density of 40mA/cm^2 and plating time of 30 minutes for 8.7 mg of zinc deposition. Beyond, this combination of process parameters, the profile of the Zn coating decreased. Also, Popoola *et al.* (2012) developed Zn-Al film which was used to electroplate mild steel. The result of the work indicated significant alteration in chemical and mechanical properties of mild steel through introduction of Al into the coating. The micro-hardness value increased by 92%; wear rate decreased by 90% and a significant increase in the corrosion resistance was achieved.

3.2.4 Electrophoretic deposition

Electrophoretic deposition (EPD) is a coating technique whereby particles (of a material) in a colloidal suspension are transferred to the surface of the substrate, which is usually an electrode of an opposite charge from that of the particles (Besra and Liu, 2007). EPD is one of the colloidal processes in ceramic production and has advantages of short formation time, simple apparatus, little restriction of the shape of substrate, no requirement for binder burnout as the green coating contains few or no organics. Compared to other advanced shaping techniques, the EPD process is very versatile since it can be modified easily for a specific application (Velez *et al.*, 2014). For example, deposition can be made on flat, cylindrical or any other shaped substrate with only minor change in electrode design and positioning. In particular, despite being a wet process, EPD offers easy control of the thickness and morphology of a deposited film through simple adjustment of the deposition time and applied potential. Table 9 presents the distinction between electrophoretic deposition and electroplating processes (Besra, 2007). The basic difference between an electrophoretic deposition process (EPD) and an electrolytic deposition process (ELD) is that the former is based on the suspension of particles in a solvent whereas the later is based on solution of salts, i.e., ionic species (Besra, 2007).

Table 9. Distinction between electrophoretic deposition and electroplating processes (Besra, 2007)

Property	**Electroplating**	**Electrophoretic deposition**
Moving species	Ions	Solid particles
Charge transfer on deposition	Ion reduction	None
Required conductance of liquid medium	High	Low
Preferred liquid	Water	Organic

EPD is divided into two processes, namely electrophoresis, which is the migration of particle from the suspension to the surface of the electrode by the potential difference between the anode and cathode; and deposition of a film of charged particles on the substrate as shown in Figure 19. Once the particles are deposited on the substrate, they lose their charge. The particles after setting down on the metal are not usually compacted together on deposition, but require an extra step of densification such as sintering or curing in order to produce a compacted coating.

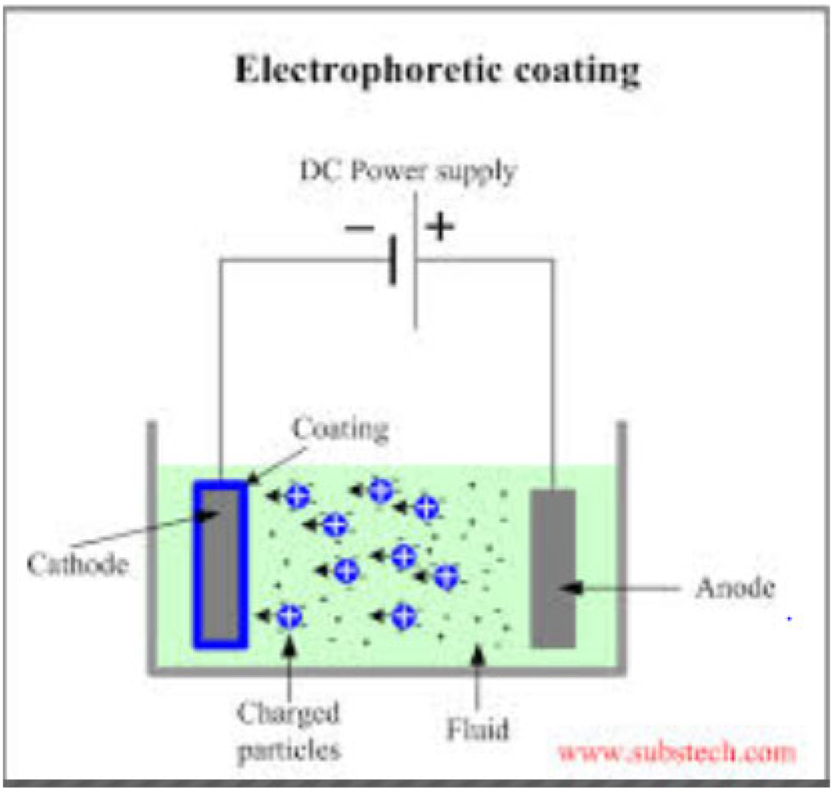


Figure 19. Electrophoretic Deposition Process (www.substech.com)

This densification is performed to close up gaps within the coating which may develop into microstructural flaws, in order to prevent failure during service (van Tassel and Randall, 2006). The type of electrolyte or suspension used influences the quality of deposition obtained. Suspensions containing water (aqueous electrolytes) are not preferred because of the electrolysis of water (production of H_2 and O_2) which occurs during their use, and this causes reduction of coating adherence (Besra, 2007). EPD takes two forms: anodic deposition and cathodic deposition. In the anodic deposition, the substrate acts as the positive electrode, attracting negatively charged particles; while in the cathodic, the substrate is the negative electrode as shown in Figure 20. Occasionally, deposition of ceramic particles involve the addition of an electrolyte to the suspension, which gets adsorbed to the surface of the particles creating charged particles and facilitating uniformly deposited films (Besra, 2007).

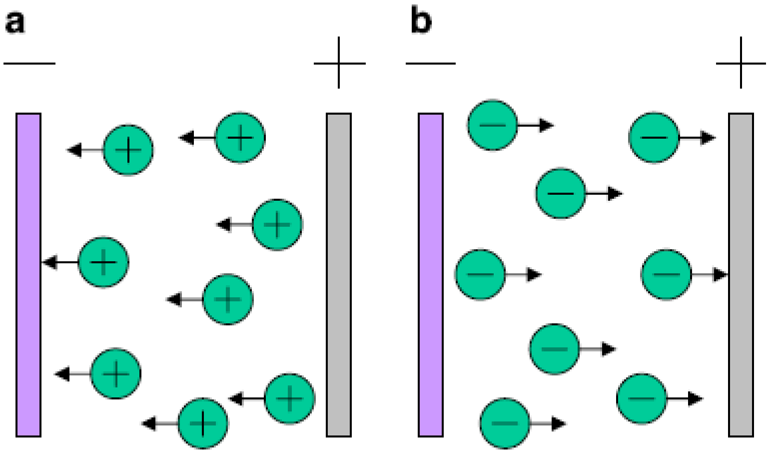


Figure 20. Schematic illustration of electrophoretic deposition process (a) catholic EPD (b) anodic EPD (Besra, 2007)

This process is industrially used for applying coatings to metal fabricated products. It has been widely used to coat automobile bodies and parts, tractors and heavy equipment, electrical switch gear, appliances, metal furniture, beverage containers, fasteners, and many other industrial products (De Riccardis, 2012). EPD process has merits for production of uniform coating thickness without porosity, complex shape fabricated objects can easily be coated, both inside cavities as well as on the outside surfaces; the speed of coating is high, the purity of coating is high and it is applicable to wide range of materials (metals, ceramics, polymers,). It is easy to control the coating composition, the process is normally automated and requires less human labour than other coating processes. Its highly efficient utilization of the coating materials results in lower costs relative to other processes. The aqueous process which is commonly used has less risk of fire relative to the solvent-borne coatings that they have replaced, and modern electrophoretic paint products are significantly more environmentally friendly than many other painting technologies.

According to Sarkar and Nicholson (1996), particle/electrode reactions are not involved in EPD, and ceramic particles do not lose their charge on being deposited which can be shown from the observation that reversal of the electric field will strip off the deposited layer . Therefore, it is important to use similarly charged particles and similar solvent–binder–dispersant systems for gaining better control of layer thickness. The principal driving force for EPD is the charge on the particle and the electrophoretic mobility of the particles in the solvent under the influence of an applied electric field. The EPD technique has been used successfully for thick film of silica (Sarkar and Nicholson, 1996; Besra, 2007), nanosize zeolite membrane (Shan *et al*., 2004), hydroxyapatite coating on metal substrate for biomedical applications (Zykova *et al.*, 2015), luminescent materials (Meng, 2013), high-temperature superconducting (HT_C or HTS) films (Chen *et al*., 2011), gas diffusion electrodes and sensors (Bodansky and Latner, 1972), multi-layer composites (Boccaccini *et al.*, 2010), glass and ceramic matrix composites by infiltration of ceramic particles onto fibre fabrics (Boccaccini and Trusty, 1998), oxide nanorods (Cao, 2004), carbon nanotube film (Chen *et al.*, 2012), functionally graded ceramics (Sarkar and Nicholson, 1996), layered ceramics (Yang *et al.*, 2011), superconductors, piezoelectric materials (Besra, 2007), etc. Indeed, the only intrinsic disadvantages of EPD, compared with other colloidal processes (e.g. dip and slurry coating), is that it cannot use water as the liquid medium, because the application of a voltage to water causes the evolution of hydrogen and oxygen gases at the electrodes which could adversely affect the quality of the deposits formed (Mohanty *et al.*, 2008). However, given the numerous non-aqueous solvents that are available, this can readily be avoided.

3.2.5 Anodization

Anodization is used in industry as a surface treatment technique to render materials with resistance against uncontrolled oxidation, abrasion, and corrosion (Lin *et al.*, 2015). Although this technique was developed long time ago, it was not until 1990s that researchers discovered the usefulness of the technique that highly ordered nanoporous structures can be achieved by properly tuning anodization conditions including electrolyte composition and concentration, temperature, as well as anodization voltage ((Lin *et al.*, 2015). Among all valued metals that can be anodized, aluminum (Al) and titanium (Ti), particularly Al, can be anodized into nanoporous structures with well-controlled diameter, pitch, and depth ((Lin *et al.*, 2015). Membranes consisting of these nanostructures, i.e., anodic titanium oxide (ATO) and anodic aluminum oxide (AAO), have wide nano-engineering applications that have attracted enormous attention (Poinern *et al.*, 2011; Lin *et al.*, 2015). For example, AAO membranes have been used as templates to directly assemble semiconductor nanowires and nanorods for photodetection and solar energy conversion (Fan *et al*., 2006; Lin *et al.*, 2015).

The effect of anodization parameters, e.g. anodizing voltage, anodizing current, duration time, electrolyte temperature, electrolyte type and concentration, on the volume expansion of anodized Al, Al-1wt%Si and Al-1%Cu thin films was studied by Abd-Elnaiemi *et al.* (2013). The volume expansion factor of anodic porous alumina was found to vary from 1.32 to 2.08, depending on the anodizing voltage, anodizing current density and electrolyte type. The electrolyte temperature and impurity type have slight effect on the volume expansion factor. The relation between the pore density of porous alumina and the anodizing voltage is found to follow the relation *NP=9.4×1010exp(-0.042V)*. In addition, the current efficiency during the anodization was determined to be about 83%. Lin *et al.* (2015) investigated the effect of highly controllable electrochemical anodization process to fabricate porous AAO membranes; and reported a linear correlation between the integrated electric charge flow in the circuit and the growth thickness of AAO.

Advantages of anodizing process include its durability in terms of its resistant to wear and corrosion. It is easy to maintain. The process creates aesthetically pleasing finish. It is easy to fabricate and has colour sustainability. It is limited to colour selection. Anodizing especially, aluminum anodizing has a variety of commercial uses and diverse consumer applications across a wide range of industries. This strong and resistant finish are beneficial in the parts used in aircraft and automotive products. Architectural and construction projects often incorporate these strengthened materials into their external structures, as they are capable of withstanding all types of weather. Many components used in both day-to-day and industrial electronics are also improved through this valuable process (Jamaati *et al.*, 2010).

3.3 Vapour Deposition Technique

Vapour deposition involves the formation of coatings or deposits on a substrate from a material in the vapour state through condensation, chemical reaction or conversion resulting in structural and compositional change in the substrate (Glynn and O'Dwyer, 2017). Such structural changes may alter the mechanical, corrosion, thermal, electrical, optical and wear characteristics of the substrate. There are two variants of the vapor deposition process;

and these are chemical vapour deposition and physical vapour deposition.

3.3.1 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a versatile and economic means of producing thick or thin films of high purity at moderately low temperatures. CVD is a widely used materials-processing technology. The majority of its applications involve applying solid thin-film coatings to surfaces, but it is also used to produce high-purity bulk materials and powders, as well as fabricating composite materials via infiltration techniques. It has been used to deposit a very wide range of materials (Creighton and Ho, 2001). It involves chemical reactions in heated plasma of gas phase leading to the formation of solid particles near the substrate. The reacting elements or compounds get dissociated or combined in the gaseous phase, while they are deposited in the solid state as particles as shown in Figure 21. This heterogeneous reaction (involving change of state) could occur either close to or on the substrate's surface (Jones and Hitchman, 2009).

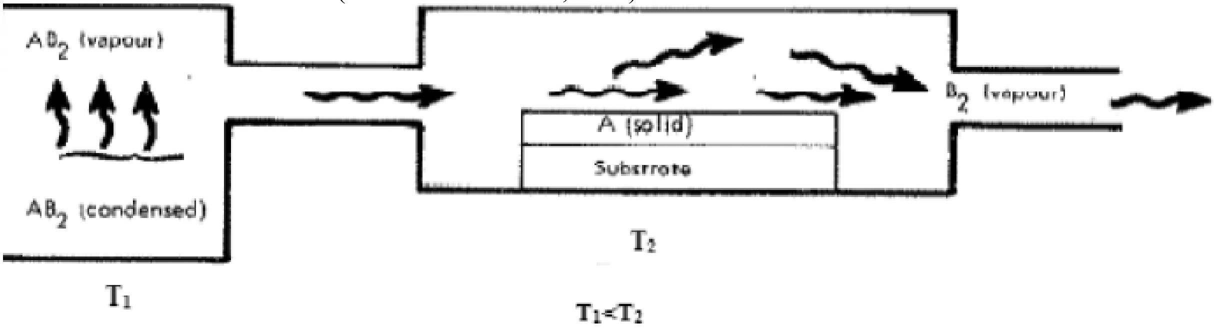


Figure 21. Schematic illustration of chemical vapour deposition (CVD) process (Rashidi *et al.*, 2015)

CVD has a number of advantages as a method for depositing thin films. One of the primary advantages is that CVD films are generally quite conformal, i.e., that the film thickness on the sidewalls of features is comparable to the thickness on the top. This means that the films can be applied to elaborately shaped pieces, including the insides and undersides of features, and that high-aspect ratio holes and other features can be completely filled. In contrast, physical vapor deposition (PVD) techniques, such as sputtering or evaporation, generally require a line-of-sight between the surface to be coated and the source. Another advantage of CVD is that, in addition to the wide variety of materials that can be deposited, they can be deposited with very high purity. This results from the relative ease with which impurities are removed from gaseous precursors using distillation techniques. Other advantages include relatively high deposition rates, and the fact that CVD often does not require as high a vacuum as PVD processes (Creighton and Ho, 2001).

The reactions in a CVD system usually involve the production of solid particles and the emission of gaseous by- product from the transformation of reactants in the gaseous phase. CVD is a complex process of depositing thin coatings on a substrate surface via chemical reactions of gaseous materials. It is a useful process to produce materials of high purity, density and strength. It has emerged as a novel manufacturing technique in industrial sectors such as semiconductor and ceramic industries (Rashidi *et al.*, 2015). The process is extensively used in the production of high purity thin coating. The deposition of the films can be performed at considerably lower temperature by applying different types of catalysts (Rashidi *et al.*, 2015). Catalyst enhanced chemical vapour deposition (CECVD) has emerged as a new enhancement technique. It is particularly suitable for the deposition of metallic films on thermally sensitive substrates. Materials with different properties can be produced by changing the substrate temperature, composition of the reaction gas mixture, total pressure gas flow, and experimental conditions, etc. (Moarrefzadeh, 2012).

Rashidi *et al.* (2015) reviewed catalyst role in CVD where the significant role of catalyst in the deposition of various materials on different substrates surface was investigated. The work revealed that the use of catalyst enhanced CVD process particularly in the synthesis of nanomaterials on thermally sensitive substrates.. The work further established that the use of catalysts not only ensure that the deposition is conducted at considerably low temperature but also produce films of high purity. The work also provided data about nanomaterials synthesis by CECVD process. Catalytic chemical vapor deposition (CCVD) is another efficient and low-cost method for the mass production of highly pure carbon nanotubes (CNTs). In this process, CNTs are produced by the catalytic decomposition of hydrocarbon vapours. Cobalt, Iron, Nickel and their alloys are the most widely used catalysts in CNTs production through CVD process. By the application of suitable nano-catalysts, the CVD temperature can be brought down to room temperature in CNTs growth. Transition metals have been reported to be appropriate catalyst in this process as they are capable of decomposing the hydrocarbons used for CNTs growth. Alloys of these metals have proved to be better catalysts and produce CNTs of high quality (Rashidi *et al.*, 2015).

Also, the work of Klaus and George (2000) on SiO_2 CVD at room temperature using $SiCl_4$ and H_2O with an NH_3 catalyst revealed that deposition of Silicon dioxide (SiO_2) films at room temperature using a catalyzed CVD reaction could be accomplished as in Equation 2.

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \text{ …………………(2)}$$

catalyzed with ammonia (NH_3). The NH_3 catalyst lowered the required temperature for SiO_2 CVD from >627°C to 40 - 60 °C. The NH_3 also reduced the $SiCl_4$ and H_2O pressures required for efficient SiO_2 CVD from several torr to <500 mTorr (several MPa to < 6.7 X 10^{-6}MPa).

There are various methods for conducting CVD in creating the vapour phase that facilitates chemical reactions; and these are:

Thermally activated chemical vapour deposition (TCVD) involves the use of a heated resistive filament to dissociate the gas molecules in order to produce precursors which would participate in further reactions to produce the film of coatings (Jones and Hitchman, 2009). Single and multiple layers of ceramic materials such as alumina (Al_2O_3) can be deposited using this method at temperatures between 900°C and 1100°C (Kumar and Ando, 2010).

Plasma enhanced chemical vapor deposition (PECVD) involves the decomposition of the precursor molecules by charged gas particles (plasma), the contact with plasma could occur either at the layer above the substrate, or the precursor reactants could be absorbed to the substrate and consequently decomposed to form the coating film (Hamedani *et al*., 2016). Mathur and Kuhn (2006) after depositing titanium oxide coatings on steel substrates, via thermically activated CVD at 450 -500^{0}C and plasma assisted CVD at 200^{0}C observed that the PECVD produced a better structured, homogenous, smoother and denser coating than TCVD. They ascribed this difference in result to the increase in nucleation sites on the surface of the coated substrate caused by its bombardment with ions produced by the plasma. Nucleation in these locations brought about the formation of finely- structured grains of coating.

Laser assisted chemical vapor deposition involves the dissociation of precursors with the use of a focused energy light beam otherwise known as a laser. It offers advantage of precision of film grown, since the laser beam could be directed to the exact area of desired film deposition and growth (Bondi *et al.*, 2006).

Certain parameters influence the quality of coatings and films deposited on a substrate by CVD process on surface strengthening. They determine the uniformity and thickness of the coating obtained (Gupta *et al*., 1991). Some of these include:

i. Reaction kinetics: low temperature and pressure of the boundary layer facilitates quick deposition of the particles on the surface (Pedersen and Elliott, 2014). Thus, the rate of particle deposition is high. On the other hand, high temperature and pressure speed up reaction resulting in low deposition rate. The boundary layer is also thicker in this case.
ii. Presence of catalyst: Klaus and George (2000), while depositing SiO_2 films by chemical deposition through the mixing of $SiCl_4$ and H_2O, observed an unusual increase in the deposition thickness at low temperature and pressure on addition of ammonia as a catalyst

3.1.2 Physical Vapour Deposition

Physical vapour deposition (PVD) involves the use of energy to liberate atoms from the surface of a material, usually called the target (Rigsbee, 1989). These atoms then condense and bond with the surface of the substance, forming a thin layer. The use of hard and wear resistant PVD coatings on cutting tools is now widespread in global manufacturing for reducing production cost and improving productivity, all of which are essential for the industry to remain economically competitive (Mubarak *et al*., 2005).

Mubarak *et al*. (2005) reviewed the status of deposition of hard coatings using different PVD techniques and compare their properties which include a summary of target/cathode materials and various synthesis techniques. Pure metal cathodes/targets or alloy cathodes/target made either by casting or by powder metallurgy were used in PVD processes. The review includes the drawbacks of cathodic arc evaporation (CAE) and conventional magnetron sputtering processes as well as their improvements. The work showed that deposition parameters are different for cathodic arc deposition and magnetron sputtering. From the study, It was noted that Arc Bond Sputter (ABS) Technique for PVD hard coating is the best technique but at the same time the most expensive.

The merits of PVD include deposition of harder and more corrosion resistant coating than coatings applied by the electroplating process. Most of its coatings have high temperature and good impact strength, excellent abrasion resistance and are so durable that protective topcoats are almost never necessary. It has the ability to utilize virtually any type of inorganic and some organic coating materials on an equally diverse group of substrates and surfaces using a wide variety of finishes. It is more environmentally friendly than traditional coating processes such as electroplating and painting. More than one technique can be used to deposit a given film (Mattox, 2014).

The limitations of PVD process include constraints imposed by specific technologies. For example, line-of-sight transfer is typical of most PVD coating techniques, however there are methods that allow full coverage of complex geometries. Some PVD technologies typically operate at very high temperatures and vacuums, requiring special attention by operating personnel (Senthilkumar *et al.*, 2016). PVD process requires a cooling water system to dissipate large heat loads.

The application of PVD coatings are generally used to improve hardness, wear resistance and oxidation resistance. Thus, such coatings are used in a wide range of applications such as: aerospace, automotive, surgical/medical, dies and moulds for all manner of material processing, cutting tools, firearms, optics, watches, and thin films (window tint, food packaging, etc.)

PVD can be accomplished through any of the following highlighted process routes:

i. Resistive Heating: The target is heated to a certain level at which metal atoms begin to evaporate from its surface and condense into the surface of the substrate. The evaporated atoms carry energy between 0.04 and 0.3eV, which is relatively low, compared to other methods of evaporation. This low energy is incapable of damaging the structure of the deposited layer of the substrate, and underlying ones.

ii. Pulsed Laser Deposition: Evaporation is achieved when a high energy laser beam is focused on the target. The metallic atoms are produced in form of plasma. The atoms arrive at the high energy, between 10 and 100eV. This is capable of modifying the surface of the metals. The advantage of the high energy beam is that evaporation can be induced even in metal oxides of low vapour pressure.

iii. Sputter Deposition: The target is bombarded by high energy ions usually produced by plasma above the target or by an ion gun. Atoms and ions are released into the gaseous phase at high energy (between 1 and 20eV) by the target. These ions are then deposited on the surface of the metal. Also electrons are released from the target, trapped in a magnetic field above it. On colliding with the sputter gas, these electrons produce ions which help sustain the plasma. In this way, the evaporation can occur even at low pressures. Although ions are characteristically used to bombard the target, the electrical charge of the incident particle is of little significance to the quality of coatings deposited, as charged species (ions) are neutralized on arrival at the target. Also, the energy emitted by sputter deposition is greater than that of resistive heating, which therefore translates to the production of highly adherent coatings, which form good bonds with the substrate (Pranevicius, 2006).

iv. Ion beam sputtering is a type of sputter deposition process whereby the sputtered species (charged particles) are liberated by the bombardment of the source target with an electron beam. The sputtered atoms are vaporized, ionized and accelerated by a plasma region between the target and the substrate; and condense upon the substrate to form a thin film of ions, atoms and molecules (Colligon, 2003).

The outcome of a physical deposition process, the quality and properties of the coatings deposited are influenced by some process parameters and these include:

i. Temperature during service: Lou (2011) observed that the friction coefficient (μ) occurring between a system of sputter deposited TiAlN/VN coating and an aluminum steel ball surface increased with temperature. This increase in μ was accompanied by an increase in the rate of delamination and spalling. A steep increase in coefficient of friction was observed between 100 and 200^{o} C, and from 400 to 500^{o}C. Decrease in μ was obtained between 600 and 700^{o}C, despite the fact that the wear rate worsened with the occurrence of a massive oxidation during this phase. This unexpected trend was attributed to the resistance to shear by an oxide layer (V_2O_5) formed above the coating. At these elevated temperatures, wear had transformed from being a mere mechanic phenomenon to being oxidation-driven. Oxidation began at about 200^{o}C when ambient water vapour was absorbed by the surface, and gradually, the H-O bond of water was broken down. The oxygen reacted with the vanadium within the coating, forming V_2O_5, which formed a lubricant layer above the coating, reducing friction. Fateh *et al.* (2007), after conducting similar test between an alumina (Al_2O_3) ball and a separate sample of TiN and VN coatings, reported that though both coatings were oxidized during temperature increase (about 300 and 400^{o}C respectively), only V_2O_5 – the product of VN oxidation – brought about a significant change in the friction coefficient, melting into lubricant film to douse the effect of surface contact between both surfaces. It was further observed that the V_2O_5 film reacted with the alumina counter-surface, forming AlO_4, detected at 400^{o}C and predominant at about 700^{o}C. They concluded that VN exhibited better tribological behaviour at elevated temperatures than TiN coatings.

ii. Substrate temperature: The microstructure, toughness and wear resistance of deposited layers improved with an increase in the temperature of substrate during deposition. For instance, Zhang and Li (2003) reported that an increase in the temperature of the substrate resulted in a finer microstructure containing fewer voids. There was equally a decrease in the coefficient of friction. In similar vein, Mednikarov *et al.* (2005) observed a slight increase in hardness and a decrease in grain size with an increase in substrate temperature when depositing AlN on a silicon substrate through magnetron sputter deposition. Wohlmuth and Adesida (2005) also observed a transition of the deposited film from a monocrystalline state to a polycrystalline state when the substrate was at elevated temperature (200^{o}C to 300^{o}C) during the deposition of indium-tin-oxide and cadmium-tin-oxide via radio frequency (R.F) magnetron sputtering. Similar trend was observed during the deposition of TiN particles on high speed steel (HSS) substrate in which an increase in the surface roughness and coefficient of friction occurred causing wear and tear (Caliskan *et al.*,2013). However, Li *et al.* (2000) observed that the substrates at high temperature demonstrated a greater hardness compared to those coated at lower temperature (200°C) during the deposition of aluminium oxide particles using pulsed DC magnetron sputtering. Although, when a magnetic field was employed to restrict the movement of charge species just above the substrate and substrate bias voltage was increased, a crystalline (instead of amorphous) film structure was developed which had greater hardness value even at low temperature.

iii. Hardness of mating surfaces: Singh et al. (2012), observed a progressive increase in the coefficient of friction, wear track width and extent of wear with magnetron-sputtered100Cr6 steel, Al_2O_3 and Si_3N_4 surfaces respectively, regardless of the substrate temperature. This was attributed to the differences in hardness value of 3, 23 and 29GPa for the steel, Alumina and Si_3N_4 respectively. Rodriguez *et al.* (2004), whilst testing the influence of various properties on the wear resistance of multi-layered tungsten carbide PVD coated high speed steel 1.3343 samples, noted that although the material's hardness helps in improving its wear resistance, it does not have much effect on the wear behaviour as the roughness and surface morphology of the material surface and the partial pressure of the carrier gas. Martini and Ceschini (2011) reported similar characteristics when evaluating the tribological properties of PVD deposited WC/C, CrN/NbN coatings on Ti6A14V substrate. The WC/C sputter-deposited coating, demonstrated superior wear and friction properties under sliding contact with an SAE52100-EN100Cr6 steel counter face. The good wear behaviour of the WC/C coating was attributed to the formation of alternating layers of amorphous carbon-based tribo-film (lubricant) which adheres to the WC film to reduce friction.

iv. Gas pressure and flow rate: Yang and Hu (2010) observed that high pressure of the Ar/N_2 carrier gas caused low hardness and film thickness because deposition was hindered by increased particle collision in the plasma phase above the substrate. Increased flow rate also caused excess Nitrogen to react with the target (CrAl), thereby decreasing its porosity and hindering deposition. The optimum Ar/N_2 ratio was found to be 1:1.

v. Voltage bias: Wang *et al.* (2012) tested the dependence of microstructure, hardness and fracture toughness on increase in voltage bias in silicon wafer substrate coated with CrAlN via magnetron sputtering. The result showed improved hardness and fracture toughness as a result of smaller grains and a denser microstructure. The increase in voltage bias also caused a buildup of residual stresses as atoms collide and are distorted in the lattice system. This distortion occurred until a voltage of 260V was reached. Devia et al. (2010) deposited TiAlN on AISI O1steel via triode magnetron sputtering (using a polarized grid) with increasing voltage bias, observed an increase in grain size and surface roughness as a result of high energy ions which impinged the film surface, causing an elevation in temperature. At this high temperature, the substrate‘s structure is prone to distortion or damage. Lugscheider et al. (1995) postulated that this challenge can be prevented by increasing the stand-off-distance (SOD), that is, the distance between the target material and the substrate.

3.4 Sputtering

Sputtering is a mechanism by which atoms are dislodged from the surface of a material as a result of collision with high-energy particles (Srivastava, 2014). Sputtering is a momentum transfer process in which atoms from a cathode/target are driven off by bombarding ions. Sputtered atoms travel until they strike a substrate, where they deposit to form the desired layer (Mattox, 1995) as shown in Figure 22. Thus, PVD by Sputtering is a term used to refer to a technique wherein atoms or molecules are ejected from a target material by high-energy particle bombardment so that the ejected atoms or molecules can condense on a substrate as a thin film. Sputtering has become one of the most widely used techniques for depositing various metallic films on wafers, including aluminum, aluminum alloys, platinum, gold, TiW, and tungsten (Fangfang, 2008). Sputtering deposition technique may be described as a sequence of these steps: (1) ions are generated and directed at a target material; (2) the ions sputter atoms from the target; (3) the sputtered atoms get transported to the substrate through a region of reduced pressure; and 4) the sputtered atoms condense on the substrate, forming a thin film.

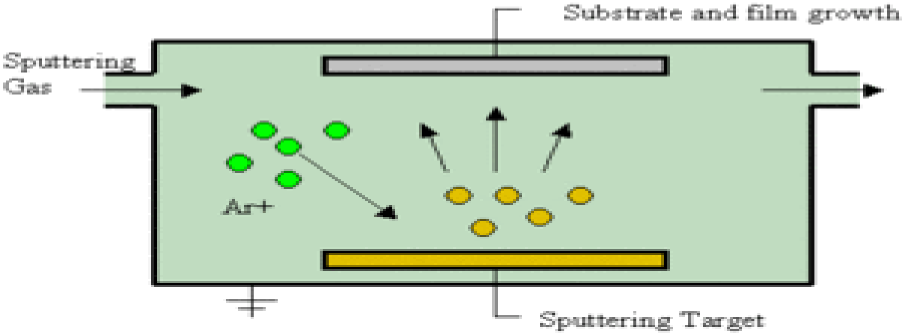


Figure 22. Schematic illustration of Sputtering Deposition Process (Hivatec.ca/consulting-design/thin-film-deposition)

Highly transparent and conductive thin films of ZnO doped with a rare-earth element, Sc or Y, prepared by D.C. magnetron sputtering using a powder target was investigated by Minami et al (2000). The resistivity of the ZnO/Sc thin films was always lower than that of the ZnO/Y thin films. In this work, a resistivity in the order of 10^{-4} Ω cm was obtained in these films. The resistivity of the ZnO/Sc thin films decreased as the Sc_2O_3 content increased up to about 2 wt.%; any further increase of the Sc_2O_3 content caused the resistivity to increase. A resistivity of 3.1 Å×10^{-4} Ω cm was obtained in ZnO/Sc thin films prepared on a glass substrate at a temperature of 200°C with a Sc_2O_3 content of 2 wt.%. An average transmittance of above 85% in the visible range was obtained for doped ZnO thin films. The electrical and optical properties, as well as the thermal stability of resistivity of the ZnO/Sc thin films were comparable to those of ZnO/Al.

Assuncao *et al.* (2003) investigated the effect of highly transparent and conductive rare earth-doped ZnO thin films prepared by magnetron sputtering. They deposited highly conducting and transparent gallium doped ZnO thin films on inexpensive soda lime glass substrates via R.F. magnetron sputtering at room temperature. The argon sputtering pressure was varied between 0.15 and 2.1 Pa. The lowest resistivity of 2.6×10^{-4} Ω cm (sheet resistance ≈6 Ω/sq was obtained at argon sputtering pressure of 0.15 Pa and a R.F. power of 175 W for a thickness ≈600 nm). The films presented an overall transmittance in the visible spectra of approximately 90%. The increase in the resistivity for higher sputtering pressures is due to a decrease in both mobility and carrier concentration, and this is associated with a change on the surface morphology. The low resistivity, accomplished with a high growth rate (290 Å/min) at room temperature deposition, enables these films deposition onto polymeric substrates for flexible optoelectronic devices.

An important advantage of sputter deposition is that even materials with very high melting points are easily sputtered. But the evaporation of these materials in a resistance evaporator or Knudsen cell is problematic or impossible (Murri, 2013). Sputter deposited films have a composition close to that of the source material. The difference is due to different elements spreading differently because of their different mass (light elements are deflected more easily by the gas) but this difference is constant. Sputtered films typically have a better adhesion on the substrate than evaporated films. A target contains a large amount of material and it is maintenance free making the technique suited for ultrahigh vacuum applications. Sputtering sources contain no hot parts (to avoid heating they are typically water cooled) and are compatible with reactive gases such as oxygen. Sputtering can be performed top-down while evaporation must be performed bottom-up. Advanced processes such as epitaxial growth are possible.

Some downsides of sputtering process are that: (1) the process is more difficult to combine with a lift-off for structuring the film, (2) active control of layer-by-layer growth is difficult compared to pulsed laser deposition and (3) inert sputtering gases are built into the growing film as impurities. These challenges are due to the diffuse transport characteristic of sputtering which makes a full shadow impossible. Thus, it is difficult to fully restrict where the movement of the atoms treads which can lead to contamination problems (Murri, 2013).

Sputtering is used extensively in the semiconductor industry to deposit thin films of various materials in integrated circuit processing. Thin antireflection coatings on glass for optical applications are also deposited by sputtering. Because of the low substrate temperatures used, sputtering is an ideal method to deposit contact metals for thin-film transistors. Perhaps the most familiar products of sputtering are low-emissivity coatings on glass, used in double-pane window assemblies. The coating is a multilayer containing silver and metal oxides such as zinc oxide, tin oxide, or titanium dioxide. A large industry has developed around tool bit coating using sputtered nitrides, such as titanium nitride, creating the familiar gold colored hard coat. Sputtering is also used as the process to deposit the metal (e.g. aluminum) layer during the fabrication of CDs and DVDs (Murri, 2013).

3.5 Ion implantation

Ion implantation is a materials engineering process by which ions of a material can be implanted into another solid, thereby changing the physical propertiesof the solid (Sattler, 2010). This process is used to change the

physical, chemical, or electrical properties of the solid. Ion implantation is used in semiconductor device fabrication and in metal finishing, as well as various applications in materials science research (Caruta, 2005).
Ion implantation equipment typically consists of an ion source, where ions of the desired element are produced, an accelerator, where the ions are electrostatically accelerated to a high energy, and a target chamber, where the ions impinge on a target, which is the material to be implanted. Figure 23 shows a schematic illustration of ion implantation process. Thus ion implantation is a special case of particle radiation. Each ion is typically a single atom or molecule, and thus the actual amount of material implanted in the target is the integral over time of the ion current. This amount is called the dose. The currents supplied by implanters are typically small (microamperes), and thus the dose which can be implanted in a reasonable amount of time is small. Therefore, ion implantation finds application in cases where the amount of chemical change required is small. It has direct application in metal finishing process such as: tool steel toughening, surface finishing and ion beam mixing (Manova, 2010). The limitations of the process are crystallographic damage, damage recovery and amorphization (Kelly et al., 2015).

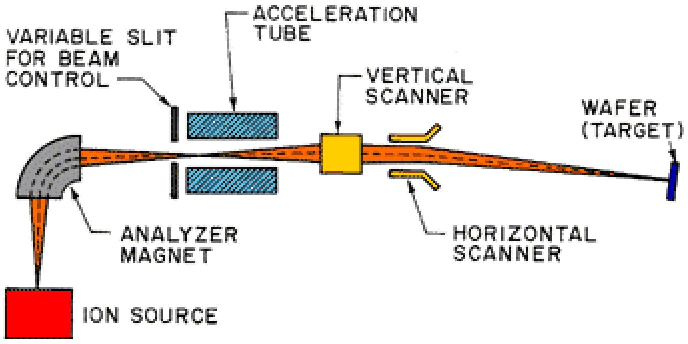


Figure 23. Schematic illustration of ion implantation process (https://matenggroup/wordpress.com)

Wang and Chiu (2002) investigated the characterization of TiN coatings post- treated by metal-plasma ion implantation process to further extend the tribological performance of TiN layers. The metal-plasma ion implantation (MPII) process was used as an effective tool for surface enhancement of TiN coatings. The study reported that the wear resistance of TiN coatings was improved by ion implantation of Al by MPII treatment. Analysis of the chemical state by X- ray Photoelectron Spectroscopy XPS and the calculation of residual stress by X-ray Diffraction (XRD) suggested that the implanted Al substitutes Ti in the TiN lattice sites, and forms binary AlN or ternary TiAlN compounds. The as-deposited TiN film showed a compressive stress of approximately 12.55 GPa, which was relaxed by the MPII treatment. The formation of AlN/TiAlN improves the wear resistance of TiN film by the reduction of residual stress in the coating. Al implantation enhances the oxidation resistance of TiN at the initial stage of oxidation. Weight gain as a result of the formation of TiO_2 occurred during oxidation. The initial oxidation kinetics follows parabolic behavior with k_p=4.12 g^2 cm^{-4} s^{-1}, higher than that of Al-implanted TiN. Ghicov *et al.* (2006) investigated the effect of ion implantation and annealing for an efficient N-doping of TiO_2 nanotubes. Self-organized anodic titania nanotube layers were doped with nitrogen successfully using ion implantation. Photo-electrochemical measurements combined with XRD measurements show that the damage created by ion bombardment (that leads to a drastic decrease of the photo-conversion efficiency) can be “annealed out” by an adequate heat treatment. This results in an N-doped crystalline anatase nanotube structure with strongly enhanced photocurrent response in both the UV and the visible range as shown in Figure 24. Also, Wang and Weng (2002) investigated the microstructure characteristics of CrN coating synthesized by a hybrid PVD and MPII process. In the study, enhancement of the surface properties of CrN, such as the density and wetting characteristics were accomplished with energetic ion implantation treatment. At the initial coating stage, low dosage of MPII ions flux helps in surface activation and ion mixing. Subsequently, surface treatments of the as-deposited CrN coating with implantation of metal and/or carbon ions result in densification and phase transformation at a near-surface regime. The wear resistance, corrosion resistance, fatigue strength and mold-releasing mechanism are significantly improved.

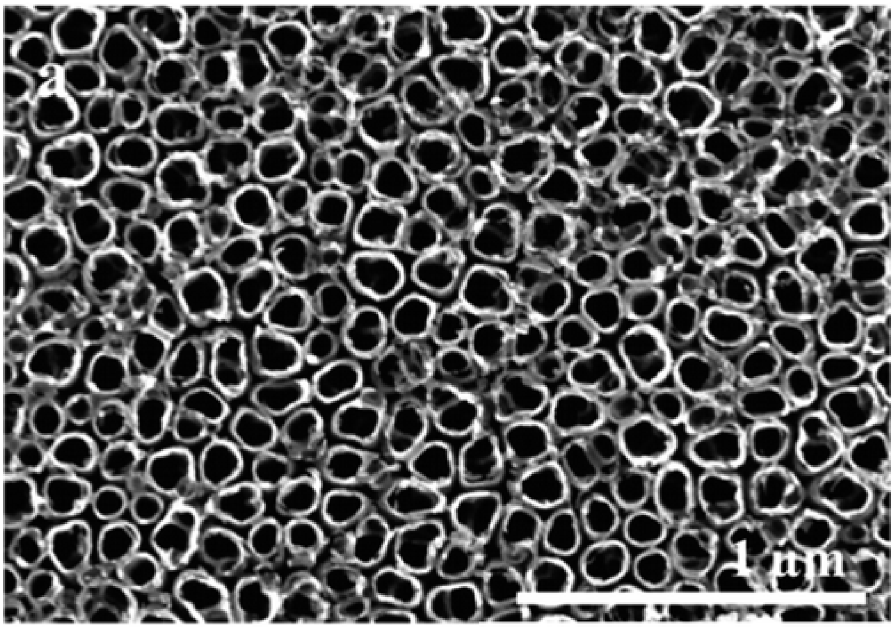


Figure 24. N-doped crystalline anatase nanotube structure (Ghicov *et al.*, 2006)

3.6 Sol-Gel Deposition

A sol is a dispersion of the solid particles (~ 0.1-1 µm) in a liquid where only the Brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The sol-gel coating process usually consists of four (4) steps: (1) The desired colloidal particles dispersed in a liquid to form a sol. (2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning. (3) The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network. (4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating (Gaishun *et al.*, 2008). The basic sol-gel reaction, shown in Figure 25, consists of two chemical reactions that produce a thin film when the sol is applied to a substrate. The first is a hydrolysis reaction and the second is a condensation reaction. The hydrolysis reaction produces the sol, and then, in the condensation reaction, a macroscopic gel is formed on the substrate producing a thin film.

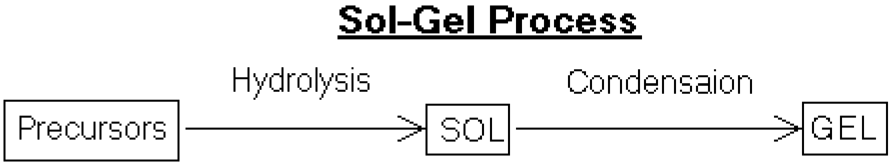


Figure 25. The basic sol-gel reaction (Viana *et al.*, 2006)

According to Viana *et al.* (2006) as represented in Equation 3, the basic sol-gel reaction starts when the metal alkoxide $Si(OCH_2CH_3)_4$ (tetraethoxysilane, or TEOS) is mixed with water (H_2O) and a hydrolysis reaction occurs. TEOS is used because along with other metal alkoxides, it reacts readily with water. Ethanol is used as a solvent because water and alkoxides are immiscible. The hydrolysis reaction is completed when all (OCH_2CH_3) groups are replaced by (OH) except there is absence of a catalyst as well as insufficient water. :

$$Si(OCH_2CH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4CH_3CH_2OH \text{ ....(3)}$$

producing a sol consisting of $Si(OH)_4$ (silicic acid) and CH_3CH_2OH (ethanol). Two partially hydrolyzed molecules can link together in a condensation reaction that liberates water as represented in Equation (4):

$$2Si(OH)_4 \rightarrow (OH)_3Si—O—Si(OH)_3 + H_2O \text{ ....(4)}$$

As the reaction proceeds, the number of Si—O—Si bonds increases in a process called Poly- merization, which produces a macroscopic gel (Mellor, 2001). When producing thin films, this gel is formed by rapid evaporation of the solvent. Though not required, the addition of HCl as a catalyst greatly increases the normally slow reaction rate. Acidic conditions will make it likely that an alkoxide group will be protonated. This will withdraw electron density from the silicon atom, which will make it more electrophilic and it will therefore react more readily with water (Brinker, 1988).

The deposition of thin films on glass, ceramics, and metal substrates is one of the most important applications of the solgel process. Single and multi-component oxide coatings can be obtained by spray, spin or dip-coating process in large scale at a cost lower than those of other methods (Viana *et.al*., 2006). The colloidal solution used as a precursor must have appropriated physical-chemical properties to produce transparent, adherent and homogeneous films with a large variation in their characteristics. This process facilitates the monitoring of the precursor solution parameters in such way that the obtained films have a good control on the chemical composition, thickness, morphology and texture (Viana *et.al*., 2006). The dry films obtained by this process can be amorphous or crystalline, porous or dense, depending on the thermal treatment, and can be deposited onto various kinds of substrates as illustrated in Figure 26. Titanium oxide (TiO_2) film is a very important material due to its multifunctional application in photocatalysis, hydrophobic material, photovoltaic cells, photochromic and electrochromic devices, gas sensor, biosensor, corrosion protection, bactericide, optical device, among others (Onah *et al*.,2012; Viana *et al*., 2006). TiO_2 can occur in a number of crystalline forms, the most important of which are anatase, rutile and brokite. Nowadays, it is one of the most extensively studied metal oxide, both as particulate and thin film form. Their properties depend on the crystalline phase, roughness, porosity, and particle size and distribution. When the particle size is sufficiently small it is possible to observe quantum size effects. Viana *et al*., (2006) studied a colloidal solution with titanium alkoxide dissolved in its equivalent alcohol to prepare transparent, homogeneous, adherent and crystalline titanium oxide films. The films deposited in glass plates, Pyrex and quartz, were thermally treated and orphologically, optically, structurally, and texturally characterized. The titanium oxide thin films obtained were pure, crystalline, adherent, transparent, homogeneous, and free of microcracks. Films thermally treated between 100 and 400°C presented low crystallinity when compared with TiO_2 nanoparticles also prepared by sol-gel process. The crystallinity increased and the porosity decreased with the increasing in the thermal treatment temperature. The thicker and denser films presented more hydrophobicity than the porous ones. Pylnev (2012) proposed the shaking of the sol stabilized by polymer prior to deposition as a new parameter for polymer assisted sol- gel deposition method. It was shown that if the stabilized polymer sol was shaken, the ratio of $CeO_2(111)$ grains to $CeO_2(001)$ grains obtained on $SrTiO_3(001)$ substrate decreases significantly. In addition, it changes the surface of the CeO_2 films making grains much less delineated.

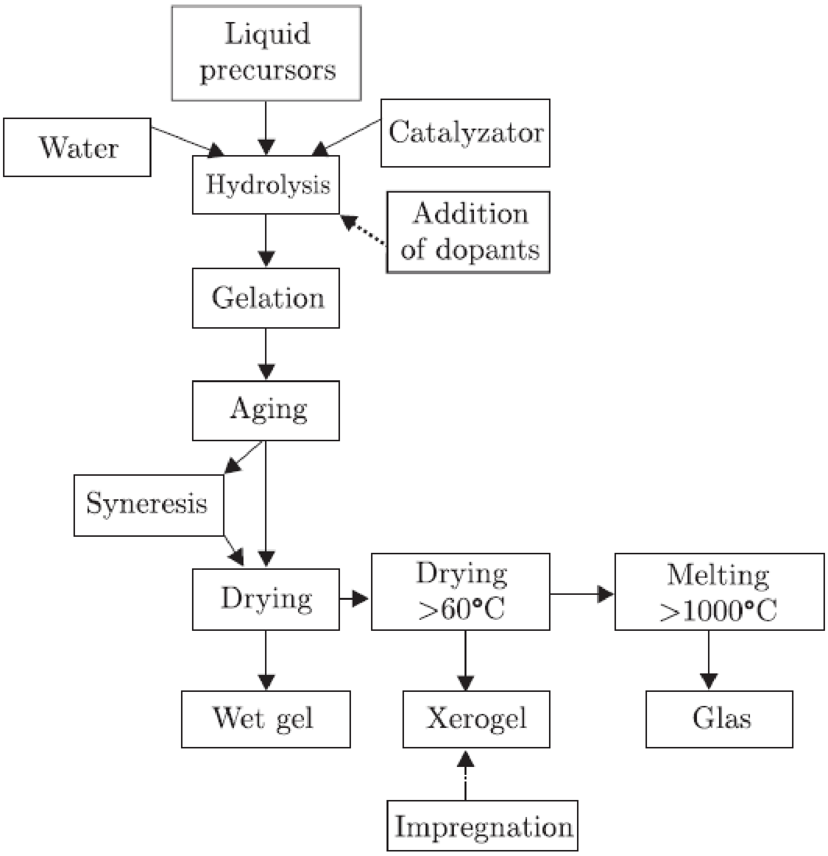


Figure26. Schematic representation of the solgel production process (Podbielaska and Jazra, 2005)

Sol- Gel deposition has the advantages of producing thin bond-coating which provide excellent adhesion between the metallic substrate and the top coat. This produces thick coating which enhances corrosion protection performance; and also permits ease in shaping materials into complex geometries in a gel state. Sol gel deposition produces, high purity products allowing the organo-metallic precursor of the desired ceramic oxides to be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel. Other positive attributes of sol gel deposition process are, flexible composition, capacity for low temperature sintering (200-600^{o}C), simple and economical for the production of high quality coatings. Despite its advantages, sol-gel technique never arrives at its full industrial potential. This was due to some limitations such as weak bonding, low wear-resistance, high permeability, and difficulty in controlling porosity. In particular, the limit of the maximum coating thickness is 0.5 μm when a crack-free property is an indispensable requirement (Khadher *et. al*., 2016). The trapped organics with the thick coating often result in failure during thermal process. The present sol-gel technique is very substrate-dependent, and the thermal expansion mismatch limits the wide application of sol-gel technique.

Some substrates, such as mild steel are prone to corrosion during aqueous chemically bonded composite sol-gel (CB-CSG) processing, which typically proceeds in acidic environment of pH 2- 4. A conventional method to address this matter is to phosphate the substrate, e.g. using zinc or iron phosphate (Narayanan, 2005). However, these thin (less than a few microns) and micro-porous phosphate films are unstable at the elevated process temperature of chemical bonding of 300°C which may lead to additional interfacial porosity. This may further provide access of corrosive species to steel surface. Such coating system will not provide long-term corrosion protection to the steel surface. In order to overcome some of the limitations of traditional CB-CSG coatings, a non-porous and thermally stable “bond-coat” alumina reinforced siloxane matrix composite (ASMC) film is deposited on mild steel surface. This protects the surface during the CB-CSG processing and also provides a non-permeable membrane for corrosion protection in storage and service (Sani, 2009). Thus, the "topcoat" of CB-CSG protects the siloxane bond coat (and the metallic substrate) from the wear damage. The siloxane bond coat provides a fluid impermeable function and relaxes the thermal stresses.

3.7 Plasma Treatment

Plasma is a partially ionized gas comprised of ions, radicals, metastables, and neutral molecules (Levy, 2012). It can also be described as a bombardment of ions on the processed material surface. As such plasma treatment results in three effects: (1) heating of the material, (2) surface cleaning (i.e. oxide removal, de-lubrication) and (3) surface polishing (i.e., increased micro-roughness, decreased macro-roughness). This makes Plasma Annealer particularly suitable for applications that require high quality of surface finish. Plasma cleaning works by exposing the target surface to a controlled, low temperature, plasma that is produced by introducing reactive gas molecules to an electric field (Bogaerts *et al*., 2002). Excitation of the reactive gas molecules results in a partially ionized medium comprising a variety of energetic particles (plasma). These energetic particles then react with the substrate surface; removing organic contaminants and low molecular weight material (LMWM) from the surface, and b) leaving behind, or “grafts,” functional groups on the material surface with which to bond. This has the effect of increasing metal nucleation sites on the film surface, which further results in enhanced barrier properties.

In plasma coatings, a nano-scale polymer layer is formed over the entire surface area of an object placed in the plasma. The plasma coating process takes just a few minutes. The coating produced is typically less than 1/100th thickness of a human hair, colourless, odourless and does not affect the look or feel of the material in any way. It is equally a permanent coating being bound to the material surface on an atomic scale (Chu *et al*., 2002). The plasma spraying process involves the generation of a plasma jet, the injection and treatment of particles within the plasma jet and finally the formation of the coating as shown in Figure 27. To generate the plasma jet, a working gas such as an argon/ hydrogen mixture is passed through a powerful electric arc discharge formed in the gap between a cathode and anode. The energy released rapidly heats up the gas mixture, converting it to high- temperature plasma at about 14 000 K. Rapid expansion occurs, lifting the speed of the jet and giving it a very high nozzle speed of up to 800 m/s. The coating material, in a fine powder form (within the range 20–90 mm), is then injected into the plasma jet. Molten droplets form, which are propelled at high speed towards the substrate to be coated (Xie *et al*., 2004).

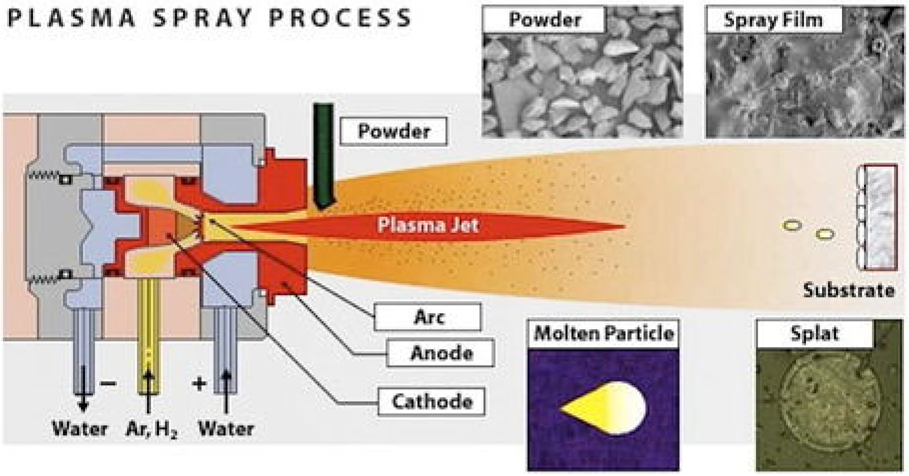


Figure 27. Image of Plasma spray process (https://www.sciencelearn.com.org.nz)

Wu (2004) investigated the surface modification of poly (1,4-phenylene-*cis*-benzobisoxazole) (PBO) fiber by oxygen plasma treatments. The corresponding changes in the surface free energy components were carefully evaluated using a Cahn dynamic contact angle analysis system. The result showed that the total surface free energy (γ) of PBO fiber increased from 43.3 to 61.1 mJ m^{-2} (by 41%) using 70 W oxygen plasma treatment for 5 min. The polar component of the surface free energy increased much more readily than the dispersive component. In addition, the untreated PBO fiber had a tensile strength of 5.72 GPa while the treated PBO fiber had an average of 5.55 GPa. This represented a small reduction of only 3%. The effect of oxygen plasma treatment on the composite's interfacial adhesion property was conducted using microbond fiber pull-out test. The interfacial shear strength increased from 34.7 MPa for the untreated PBO fiber system to 44.7 MPa, after the oxygen plasma treatment for 5 min. This suggested that oxygen plasma is an effective process for rigid-rod PBO fiber. Also, Lin *et al.* (1997) investigated the effect of plasma treatment of automotive steel for corrosion protection using a dry energetic process for coatings. The study revealed that the plasma treated coating system outperformed the current phosphated galvanized steel system in scab corrosion tests.

The key advantages of plasma treatment compared to traditional processes are: surface cleaning without surface erosion, good surface finish (micro-roughness), energy efficiency, low processing and maintenance costs, accuracy of mechanical properties, and processing speed and operational flexibility (Samardi, 2013).

There are numerous applications in almost any industry where some form of plasma treatment can be of benefit. Samardi (2013) reported that almost all major automotive manufacturers have used plasma treatments for bonding headlight housings, seats, and even windshields since 1995. Modern aircraft construction even utilizes plasma treatment before any paint is applied to ensure it is of the highest quality. Heimann (2008) reported that all instrument displays have a plasma coating to prevent reflection. In the packaging industry, plasma treatments should homogenous and consistent in every way imaginable for defect free coating.

Plasma facilitates a method of surface treatment so advanced that it does not matter whether the process is to print on a glass bottle, a plastic grocery bag, or the side of an airplane. Plasma technology has enabled the creation of an optimum surface anywhere (Cha and Park, 2014). Plasma coatings are one of the most exciting areas of plasma technology, offering enormous potential to enhance a material's function and value over a wide range of applications.

4.0 Modeling and Computational Simulation of Surface Modification Process

Modeling and computational simulation of surface modification process are emerging for more understanding of the process mechanism and applications. Researchers had critically compared the theoretical values and experimentation values of some techniques in this area to develop model for industrial applications. Modeling and simulations have been widely used to investigate the importance of various relative parameters that influence surface coating, minimizes the experimental cost and gives insight into the physical processes using either analytical or numerical methods. Analytical methods provide an effective study of materials source effect whereas numerical solutions focus on the effect of material properties. This has actually assisted researchers in the field to predict experimental values through theoretical approach which has shown close convergence with experimental characterisation. The application of this has been widely used in industries for modifying materials surface using modeling and computational simulation approach to achieve the same result as experimentation methods.

Israr (2013) developed a combination of Cellular Automata (CA) and Boundary Element Method (BEM) to simulate pitting corrosion growth under certain environment. It was assumed according to him that pitting corrosion can be simplified to electrochemical corrosion cell and the distribution of potential around this corrosion cell can then be simulated by BEM. The result shows certain shapes tend to grow at certain type environment and these pits are comparable to commonly observed pit shapes. In addition, stress analysis was carried out to investigate the severity of corrosion pits of varying shapes and sizes. The result also show that certain pits induced highly varying stress concentration as it grows which was in conformity with experimentation.

Li (2012) introduces an effective and feasible computer–aided modelling/simulation methodology to study and analyse the anti-corrosion performance in regular and nano coatings. The nano coating technology applies the non-chromate, effective slip-resistant, scratch-resistant, and anti-abrasion coatings to improve material performance. According to his work, the effective lifecycle of nanocoating is significantly longer than regular surface coatings, and the anti-corrosion performance of nanocoating is more durable and reliable than regular coatings with no contamination to the environment. The computer-aided modeling, computational simulation, and prototype testing methodology introduced in his work helps to understand the anti-corrosion mechanism and superior performance of nanocoating in rust prevention. Both computational and prototype testing in this research show close results in anti-corrosion performance which validates the credibility and feasibility of this research methodology.

5.0 Trends and Direction in Surface Modification of Metallic Materials

Surface modification over the years has progressed from the conventional thermochemical and conversion coating processes to advanced deposition techniques of high beam energy deposition and sol-gel techniques. The process has been extended to a wide range of materials specification with substantial improvement in surface characteristics. Yet there is a continuous demand for better quality surface features particularly at the nanoscale as obtained in the electronic industries and biomedical application. Therefore, there are continuous incentives for researchers to further explore ways in expanding the horizon of the various surface modification techniques while addressing the inherent challenges associated with each of the process options of surface modification although depending on the application. Arising from these are new research frontiers in surface modification most especially in liquid phase surface melting processes typically represented by electron beam and laser surface modification processes. While thermochemical processes still find application in several industries, high energy beam process such as electron beam and laser surface melting appears to be fast becoming the standard in the metal industries. Therefore, emerging research efforts in surface modification for metallic materials are majorly being focused on understanding wholesomely the mechanisms underpinning the process dynamics. Some of these emerging research trends include interface structure and morphology in high beam surface modification, development of amorphous coating, optimization of process parameters and integration of other techniques to high beam surface modification such as laser assisted cold spray process. New research frontiers are equally emerging from modeling and simulation of surface modification process for greater insight into the mechanism of surface modification.

Furthermore, high energy beam processes are capital intensive and requires great expertise and competence; and thus, the widespread application of the processes are limited by skill and economics particularly in low income economies. Therefore, researchers are also interested in evaluating the adoption of cheap low energy process such as oxy-acetylene flame torch for surface modification. Research questions in this process include providing answers to what type of flame is required for what type of materials? What is the stand-off distance (SOD) for defect free oxy-acetylene coating on materials? What is the nature of shielding for protection of the surface and what is the means of delivering the shielding gas and in what ratio? For instance, optimization parameters for the surface modification of mild steel via oxy-acetylene flame torch are currently being evaluated by the authors. Preliminary results show that the fuel-air ratio is a significant parameter in initiating the liquid phase melting of the preplaced powder at a higher ratio than the fuel but significant contamination do occur. This suggests there is need for shielding to protect the molten region from contamination which otherwise results in defective coatings.

6.0 Conclusion

The extensive spectrum of the processes for the altering of the surface chemistry, crystal/microstructure and topography of metallic materials for improved surface functionalities has been presented. The progression of surface modification from the basic thermochemical treatment through conversion coating to vapour deposition techniques have been reviewed. The detailed treatment of these processes has exposed the complexity of the processes in terms of process dynamics, materials application and limitation of each of the processes. The application areas have equally been presented. It emerged from this review that because of the peculiarity of each process and materials susceptibility, these processes cannot be applied across the complete materials spectrum. Each process appears fit for specific class of materials. Therefore, further development in the surface modification industry should be focused on addressing the challenges associated with the reviewed processes such as formation of sustained adherent coating devoid of porosity, incidence of cracks and optimisation of process parameters.

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