Fundamental Aspects of Surface Engineering: A Review

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Abstract: ***Surface engineering refers to a comprehensive field of cost effective technologies that aim to design and modify the surface properties of components in order to reduce the deterioration over time. Surface engineering techniques are used to develop several functional mechanical and chemical properties. This is accomplished by making the surface robust to the environment in which it will be used. This paper covers several surface engineering techniques used to protect metal surfaces.***

Keywords: sputtering, laser cladding, ion beam deposition, plasma nitriding, cathodic arc deposition.

1. Introduction

Surface engineering operations have a significant role in tribology. All the methods used in this field aim at enhancing the surface properties of the component. (1)Surface engineering is an integrated field of technology dealing with adjusting the surface and bulk properties that cannot be obtained concurrently either by the coating material or by the surface material independently. (2)

Good coating criteria should include:
1. High temperature resistant
2. Good strength
3. Great thermal fatigue
4. Chemically inert
5. Low friction coefficient
6. Low cost----------------- (3)

Conventional surface engineering practices are diverse in methodology and scope of application. In general, surface engineering (both conventional and advanced) practices involve either microstructural modification or compositional changes or both. Figure1 presents a general classification of surface engineering practices used in metallurgical industries. (4)

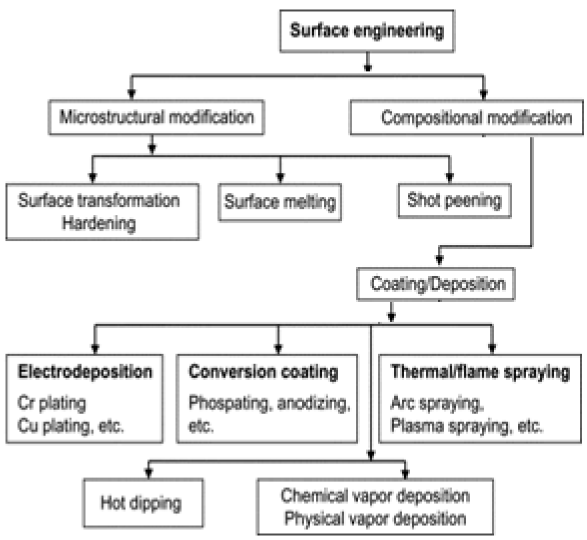

Figure 1: Classification of surface engineering techniques used in industries.

Examples of surface engineering techniques

1) Surface Treatments by Laser

The laser surface treatment involves local melting and evaporation, hence, surface texture consisting of micro/nano poles can be produced under the control environment. Using the assisting gas during laser processing results in chemical reactions taking place at the treated surface, which in turn causes chemical modification of the surface. Since laser surface treatment is associated with texturing at high cooling rates and chemical modifications, the treated surface has superior characteristics in terms of hardness, wear resistance, and hydrophobicity. (5) Laser surface treatment of materials are categorised as: A- Thermal processes during which no change of surface composition is done, like laser cutting, welding, tempering, annealing, melting, and transformation hardening.

Thermo-chemical processes during which changes in surface composition are done, like laser cladding, alloying, that leads to changes in the metallurgical structure. Furthermore, the advantages of these surface treatments include flexibility and the possibility of treating small areas leaving the other parts unaffected.

Laser surface hardening is an assuring practice for improving the surface properties of a component. It develops the tribological properties and the corrosion resistance of metal alloys and ceramics. Under laser irradiation the surface temperature is increased above the steel austenizing temperature and, by heat conduction to the bulk material, a thin steel layer is fast cooled down by a self-quenching process. The research on laser surface hardening includes the use of different high power lasers: CO_2, Nd:YAG or diode lasers.

Another way to improve the surface properties of the material is laser surface melting. Laser surface melting produces an increase in the hardness, toughness and wear resistance of the material surface in a short period of time. This process has been investigated by different authors using high power lasers. CO_2 or Nd:YAG lasers have been the most used. The crucial features of this operation are the rapid melting of the surface layer induced by irradiation with a laser beam and its rapid solidification at the cold substrate. This process produces a highly homogenous microstructure with very fine dendrites excluding the large typical carbides of tool steels.

The surface properties can also be improved by the deposition of a protective layer. Laser cladding process can produce a 0.3-1 mm thick coating onto a work piece, joining both materials by a fusion bond. A clad track is obtained by injecting powder particles into the molten pool produced by a moving laser beam. In order to cover areas considerably larger than the diameter of the laser beam, successive partially overlapping tracks are deposited. The powder injected can be either of the same material as the work piece, or a powder which could improve surface properties. When the powder material presents poor flow behaviour, it is preplaced on the component surface. This is the case of nanoparticles addition to the powders in order to obtain nanocomposites or nano-reinforced coatings. (6)

2) Physical Vapour Deposition (PVD):

The (PVD) describes a variety of vacuum deposition methods which can be used to produce thin films and coatings for a wide range of applications. The thickness of the deposits can vary from angstroms to millimeters. The basic (PVD) processes are classified into two general categories: sputtering and evaporation. (7)

a) Sputtering

Sputtering uses argon ions to dislodge atoms from the surface of a target material, then the atoms are electrically deposited to form a thin film on the component surface.

- **DC sputtering**

DC sputtering is a basic sputtering method using a constant (DC) voltage between the substrate (anode) and the target (cathode). Commonly argon (Ar) ions are used as the particles bombarding the target surface. Argon atoms are introduced into a vacuum chamber at very low pressure of about 1-10 m Torr. A DC voltage (0.5-5 kV) ionizes the argon atoms forming an ionized gas (plasma). The positively charged argon ions accelerate towards the cathode (target), bombard its surface and break the target atoms out. The atoms travel at various directions and settle on the substrate surface forming a deposited layer. DC sputtering is used for deposition of conductive materials (metals).The main disadvantage of the basic DC sputtering method is too low density of argon ions producing a low deposition rate (sputtering yield).

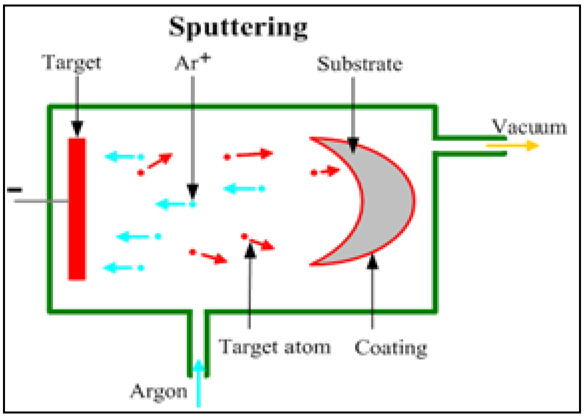

Figure 2: Schematic diagram of DC sputtering.

- **Magnetron sputtering**

Magnetron sputtering is the method of enhancing DC sputtering by crossed magnetic and electrical fields generating a high density plasma confined in the region adjacent to the cathode surface. The magnetic field is produced by permanent magnets installed just behind the target. The electrons in plasma travel along the magnetic field lines at a spiral trajectory. Along their way the electrons collide with argon atoms producing much more ions than in the basic DC sputtering method. Higher density plasma provides more frequent colliding with the target which results in a higher rate of deposition. Since the plasma is confined near the cathode, argon ions cannot reach the substrate therefore magnetron sputtering does not damage the substrate and provides lower heating of its surface. The deposition rate of magnetron sputtered hard coatings decreases with increase of N2 partial pressure. This reduction is caused by an increasing coverage of target by absorbed nitrogen or even nitridation of the target. This is called target poisoning. Conventional sputtering techniques were modified to improve ionization rates. High ionization magnetron sputtering techniques allow deposition of hard coating at a much higher ionization rate than conventional sputtering techniques. Sputtered coatings generally have a columnar structure and a smooth coating free of macro particles which is a typical problem of arc evaporation.

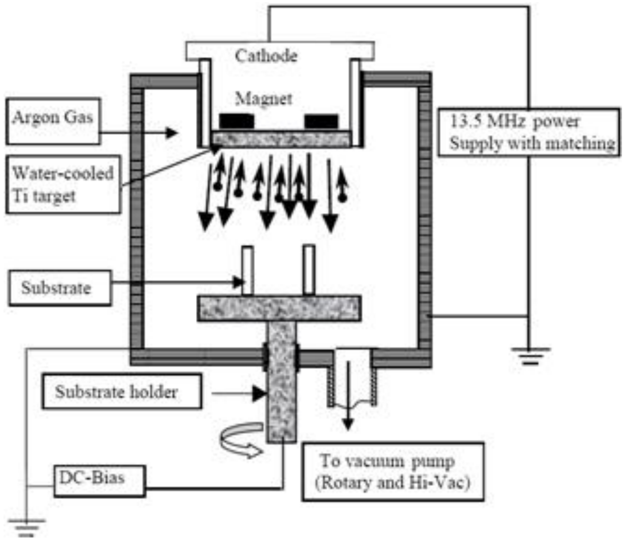

Figure 3: Schematic diagram of radio frequency planar magnetron

The potential of the target changes according to the voltage frequency. When it is positive the electrons of the plasma travel to the electrode, when the target turns negative the argon ions accelerate to its surface. Thus the target acts as the cathode during a part of each cycle, whereas the rest of the cycle acts as the anode. Since the mobility of the electrons and the ions are different due to the different masses (an ion is much heavier than an electron) the times are also different. The electrons reach the target surface much faster therefore the duration of the target as the anode is much shorter than the time when it is negative (the cathode). Thus the plasma acts as a rectifier producing a negative DC voltage (self-bias) at the target accelerating the argon ions to the target where they reposition its molecules. The molecules settle on the substrate surface and build the coating.

- **Reactive sputtering**

Reactive sputtering uses chemical reactions between the atoms on the substrate surface and the gas introduced into the vacuum chamber. Reactive sputtering is a combination of a conventional sputtering process with Chemical Vapour Deposition (CVD). Usually Oxygen or Nitrogen serves as the reactive gases. The target is metallic. The metal atoms reach the substrate surface where the reaction occurs. Oxide or nitride molecules deposit on the substrate surface forming the coating. There are two key points in this reactive sputtering process: Part of the reactive gas is going down the pumps, the rest is going into the growing thin film. Compounds tend to sputter more slowly than metals.

- **Plasma Sputtering**

The main principle is to build a vacuum chamber and fill it with Argon. By adding a high voltage, the argon will change to plasma state. The argon ion (Ar+) will move towards the cathode with a high speed and sputter the target material (use target as cathode). The target atom or molecular will hit substrate surface and condense as a film. Instead of heat melting in evaporation method, the plasma Ar+ ion hit and sputter the target is the main mechanism in plasma sputtering method. The target atom is knocked out by Ar+ ion, the knock force is so big that it can accelerate target atom a high speed. With such velocity, the target atom can hit and attach to substrate surface deeply. The film density is better than evaporation.

3) The EB-PVD Process

The electron beam-physical vapor deposition (EBPVD) process has overcome some of the difficulties associated with the CVD, PVD, and metal spray process. In the EB-PVD process, focused high-energy electron beams generated from electron guns are directed to melt and evaporate ingots, as well as to preheat the substrate inside the vacuum chamber (Figure 4).

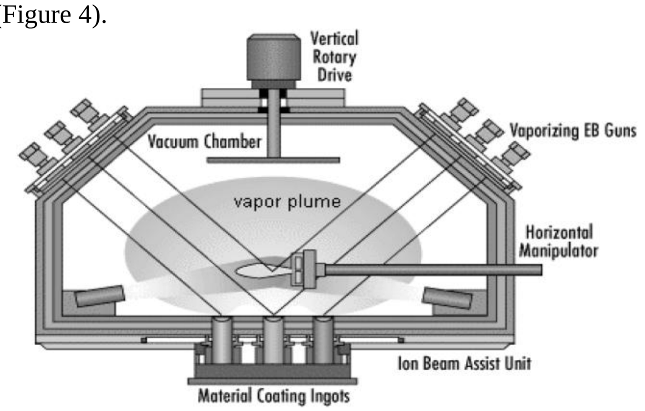

Figure 4: Schematic diagram of plasma sputtering

EB-PVD unit has six electron beam guns, four of which are used to evaporate the coating materials and two of which are used to preheat the substrate to facilitate coating adhesion. Each gun has a 45-kW capacity. The chamber will accommodate up to three ingots ranging in size from 49-68 mm in diameter and 450 mm long. The overall dimension of the production unit is about 1 cubic meter. The maximum diameter of the substrate (with vertical rotation) that can be accommodated is about 400mm; and can be rotated at a speed of 5.5 to 110 rpm with a maximum load of about 100-Kg.The unit also has a horizontal sample holder with a three axis part manipulator: two rotary axes of 0-14 rpm and a 0-4, 000 mm/min translation axis. It can carry samples weighing up to 20 kg. Since, EB-PVD is primarily a line-of sight process, therefore uniform coatings of complex parts (such as turbine blades)can be accomplished by continuously rotating the part during the coating process.

Advantages of the EB-PVD Process

The EB-PVD process offers many desirable characteristics such as relatively high deposition rates (up to 150 urn/minute with an evaporation rate of app. 10-15 Kg/hour), dense coatings, controlled composition control and microstructure, low contamination, and high thermal efficiency. Coatings produced by the EB-PVD process usually have a good surface finish and a uniform microstructure. Thus, multilayered ceramic/metallic coatings can be readily formed and various metallic and ceramic coatings (oxides, carbides, and nitrides) can be deposited at relatively low temperatures. Even elements with low vapor pressure such as molybdenum, tungsten, and carbon are readily evaporated by this process. The state of the internal stresses can be changed (i.e., from tensile to compressive) by the forcible injection of high-energy ion (100-1, 000 eV).

4) Cathodic Arc Deposition

PVD coating processes generally take place between temperatures of 200°C to 500°C to minimize stresses associated with thermal expansion mismatch as compared to the high temperatures (1000°C) of CVD. In the cathodic arc deposition process, a pulsed or continuous high current-density, low voltage electric current is passed between two separate electrodes (cathode and anode) under low pressure vacuum, vaporizing the cathode material while simultaneously ionizing the vapor, forming plasma. The high current density (usually 104-106A/cm2) causes arc erosion by vaporization and melting while ejecting molten solid particles from the cathode surface, with a high percentage of the vaporized species being ionized with elevated energy (50-150eV) and some multiply charged.

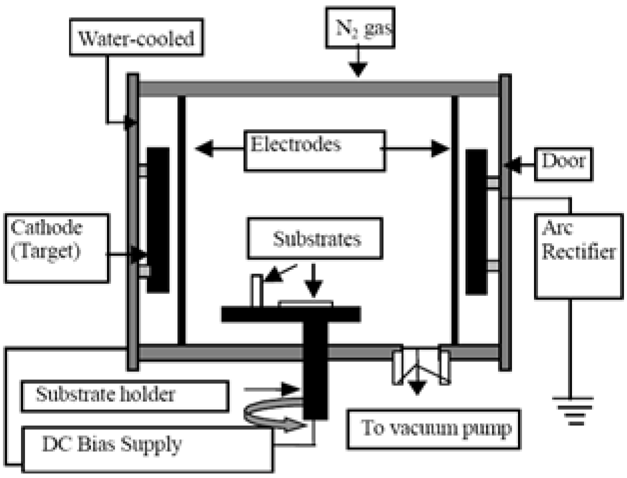

Figure 5: Schematic diagram of the Cathodic Arc Evaporation (CAE) PVD Technique

For example, in the case of TiN, as the vaporized titanium (cathode target) passes through the arc, it becomes ionized forming plasma. The kinetic energy of the depositing species in cathodic arc, are much greater than those of other PVD processes with energies between 50-150 eV. Therefore, the plasma becomes highly reactive as a greater percentage of the vapor is ionized. As a result of the high kinetic energy, an intermixed layer of the substrate and coating or between layers of a multilayer coating (10-300 Å thick) can be formed that increases the degree of coating adhesion while minimizing residual stresses. Advantages of cathodic arc processes are: High level of atom ionization in the plasma. Better adhesion can be achieved as a result of the intermixed reaction zone. Low-processing temperatures allow the coating of heat-sensitive substrates components. Multilayered coatings and functionally graded compositions can easily be produced. (8)

2. Ion Beam Deposition

Ion beam modification of materials may be achieved by ion implantation or ion irradiation. These are unique approaches to altering the near surface region of a wide range of solid materials in a manner that is independent of many of the constraints associated with conventional processing methods. (9)In comparison with alternative surface modification techniques, ion implantation has a number of advantages: 1)the process is inherently low temperature and thermal distortion of components is not a problem, 2) since ion implantation is not a coating process, there is no interface that may become susceptible to decohesion due to mechanical stress or corrosion, 3) dimensional changes are negligible on an engineering tolerance scale, being on the order of a few tens of nanometers, 4) surface polish is improved due to preferential sputter erosion of asperities, 5) the implanted atoms are dispersed on a microscopic (and sometimes on an atomic) level producing the most efficient and beneficial effect of the additive, and 6) significant compressive surface stresses are produced which will partially compensate externally imposed tensile stresses and lengthen component life against creep or fatigue by surface initiated cracking. (10)

The methods presented in this paper are:

2.1 Ion Beam Mixing (IBM) Ion beam mixing involves the use of energetic ion beams for driving and thereby "intermixing" the pre-deposited thin film atoms into substrates, via the dynamic collision cascades produced by the penetrating ions. The process is schematically shown in Fig. 6. Aside from the influence of sputter depth profiling, there were some indications that the ion induced reactions could be used for material modification. From the technological point of view Ion beam Mixings offers a unique possibility to form almost any alloy of any composition and highly metastable, often amorphous, structure.

2.2 Ion Beam Assisted Deposition (IB AD)

IB AD consists of simultaneously depositing the desired material using some evaporating technique and bombarding by energetic ion beams. Aschematic diagram of the process is shown in Fig. 6. This technique has been studied by a number of researchers for the purpose of understanding the role of energetic ions in the conventional physical vapour deposition (PVD) processes. It has been recognized that the presence of energetic ions has a synergistic effect on thin film growth. There are several aspects of film growth that have been beneficially influenced by ion bombardment during thin film deposition including: a) film nucleation growth, b) adhesion, c) internal stress, d) surface morphology, e) density and f) composition..This technique combines the advantages of a vacuum coating method, electron beam evaporation and ion implantation. In contrast to plasma-based physical vapour deposition (PVD) techniques, the actual coating process is decoupled from the energy-input process. This makes the technique highly versatile and flexible. It has a large number of parameters, which are independent from each other and can be varied over a wide range. Additionally, it is highly reproducible.

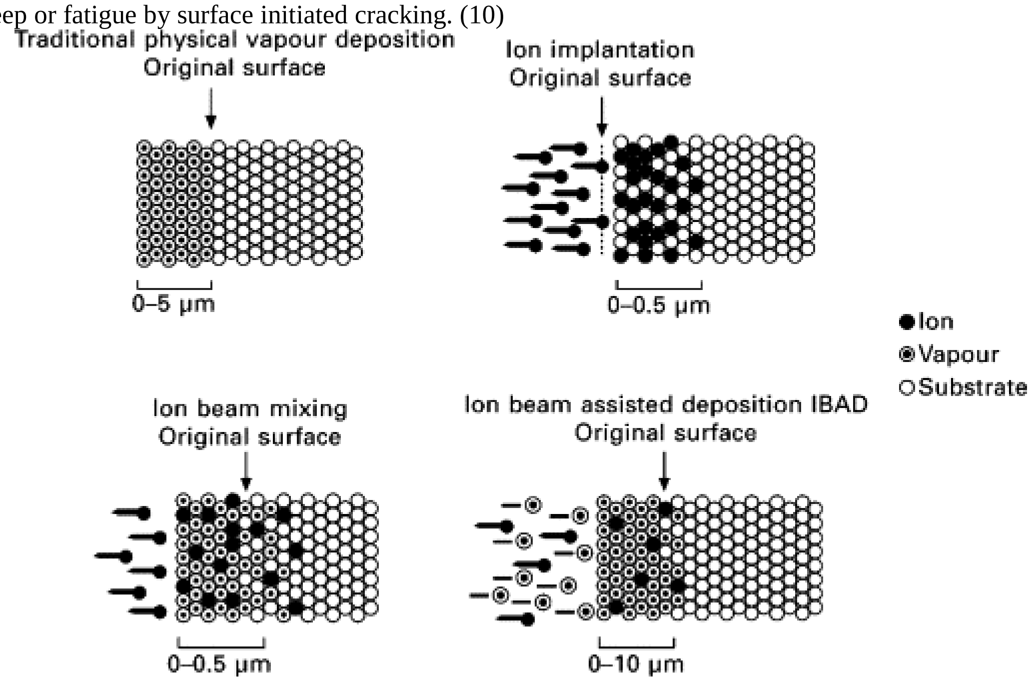

Figure 6: Schematic diagrams of thin films produced by different surface engineering processes. (12)

2.3 Plasma Arc

Plasma arc spray (APS) depositions are being used to provide ceramic or metal alloy surface on steel and other substrates for many types of process equipment. The plasma arc spray process belongs to that family of processes that are used to produce "thermal sprayed coatings". The process consists of injecting a powdered material into a highly turbulent, high temperature ionized gas stream. The powder melts and is accelerated towards a target substrate. Upon impact, molten droplets are essentially splat cooled which gives rise to the rapid solidification rate characteristic of the microstructure of the deposit. Powders ranging from a few microns to several hundred microns in diameter are injected at rates from <250 g/hr to >10 kg/hr to form deposits or spray-cast structure that ranges from 1 ^m-5 |im thickness. The process is so versatile that virtually any material that exhibits molten condition can be stoichiometrically deposited.

2.4 Metal Vapour Vacuum Arc (MEVVA)

The metal vapour vacuum arc source was invented in the mid 1980s at Lawrence Berkeley Laboratory for application in high-energy physics, and is now extending its application field to surface modifications of materials. MEVVA has, in principle, great advantage in the production of high ion current density of various metals (including C), which has been difficult to obtain by using conventional ion implanter. It can produce pulsed intense metal ion current, and is easy to operate. The energy of ion is between 20 keV and 200 keV, and the average ion current is between 1 mA and 10 mA. Vacuum during the process is maintained at -10" torr.

2.5 Plasma Nitriding of advantages: 1) the process is inherently low

Plasma Nitriding has been successfully employed to modify the surface of various engineering materials to improve their metallurgical and mechanical properties. The plasma nitriding process makes use of an abnormal glow discharge, which is associated with high current and charge densities. The components to be nitrided are electrically isolated and placed in a vacuum furnace, which is evacuated and back-filled with the treatment gas. A dc voltage is then applied between the component (cathode) and furnace walls (anode) and the potential difference ionizes the treatment gas producing the glow discharge. Positive ions in the treatment gas are accelerated towards the negatively biased substrates and hit the surface with high kinetic energy giving rise to sputtering of the surface, and heating of the components. In the plasma nitriding of titanium alloys, nitrogen ions impinge on the surface and react to form a nitrogen rich film, which results in both the formation of a compound nitride layer on the surface and the diffusion of nitrogen in the substrate. Plasma nitriding gives high surface hardness, large production rate and gradual transition to structure of substrate material. (11)s Plasma nitriding is carried out in nitrogen- hydrogen atmosphere at 400-600°C and a pressure of approx. 50-500 Pa. Because nitrogen and hydrogen are brought into the vacuum chamber as individual gases, the ratio of nitrogen to hydrogen can be controlled allowing variations of thickness and composition of the compound layer, consequently. (13) (s)

3. Summary

As mentioned above surface engineering is a broad range of industrial processes that involves altering the properties of the surface of parts to enhance the mechanical performance of the surface.

This paper reviews a number of surface engineering processes that modify the surface without changing its composition and other processes that modify the surface with accompanied compositional change.

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