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A REVIEW ON COATING OF NANO TITANIUM DIOXIDE WITH DIP-COATING METHOD

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***Abstract*— The Nanoparticles of titanium oxide, carbides, nitrides and carbonitrides can be used as coating material in order to enhance the surface properties of the substrate such as to obtain the required strength, hardness, corrosion and wear resistance. This paper reviews the applications of nanoparticle coating in Aerospace, Medical and Manufacturing field.**

***Keywords*— Nanoparticle, Sol-gel, Dip Coating, Tool Coating, Titanium Dioxide, Synthesis, Bio-medical implants, Coating method and nanoparticle coatings.**

I. INTRODUCTION

Nanoparticles or nanotechnology is an emerging field that allows enhancement of material properties, thus it is being used in many industries and has numerous applications. The extensive literature review on the subject of new technology has confirmed that nanoparticles exhibits number of special properties relative to bulk material [1]. In recent years so many developments on nanoparticle-based coating have been reviewed in various literature and conference proceedings. It is the difference in the behavior of nano sized particles and bulk particle of the same material that generate the interest in more frequent use of them.
Usually nanoparticles are particles having size in the range of 1 to 100 nm. As per the dimension of the nanoparticle is concerned, they can cover one or more size as shape. Nanoparticles can be characterized by particle-based system which is organic, inorganic and carbon-based particles. The nanoparticles exhibit improved material properties such as high surface energy, melting temperature, boiling temperature, wear resistance, corrosion resistance, reactivity, strength, surface area, sensitivity, stability, etc. due to the overall dimensional change i.e. reduction in the size. Recent development in this field has provided new methods for the deposition of lean films. It has provided the freedom in the plan and development of new resources with distinctive properties which are frequently not possible to achieve in mass materials. To select a particular synthesizing technique among various methods through which nanoparticles can be synthesized is based on the requirements for research and commercial use. The three main ways for synthesizing the nanoparticles are a physical, chemical and mechanical process which has seen a huge development in the past few decades.

II. SYNTHESIS OF NANOPARTICLE

The nanoparticles are synthesized by many different methods and all these methods can be categorized basically into bottom-up method or top-down method.

A. Top-Down Method

Top-down or destructive technique reduces the mass material or bulk particles to nanometric scale particles. Some of the most common methods classified under this synthesis technique are Mechanical milling, nanolithography, laser ablation, sputtering and thermal decomposition.

1) *Mechanical milling:* Most broadly used method to produce various nanoparticles is this method. In this powdered form of different material is poured in to a high-energy ball milling machine and are milled together. The factors like cold-welding, fracture and deformation plays important role [2]. Different factors have different rolls, deformation makes particle to change the shape, cold-welding increases the size and fracture results in decreasing the particle size. The end result of this process is a nano powder of an alloy.

2) *Nanolithography:* The term lithography has come from the combination of two Greek word ‘lithos’, which means stones, ‘graphy’, means to write. In modern terms we make structure, it may be in microns or in nano scale on substrate. Which is very well designed and it can has pattern also. It is a method of imprinting an essential pattern by removing he selected segment of coating on a substrate in the similar way it is applied. The most important advantages of nanolithography are to create a solo nanoparticle from a group with preferred shape and size. The disadvantages are the necessity of difficult equipment and the cost connected.

3) *Laser ablation:* Laser Ablation Synthesis in Solution (LASiS) is a general process for nanoparticle making from a variety of solvents. The laser beam strikes over a metal plate which is placed in a liquid solvent and it forms a plasma plum which gives generation of nano particles [3]. There is no need of different chemical compounds or stabilizing agents, which can be used as the liquid in which target metal plate is needed to be placed for constant production of nanoparticles. Hence it is a 'green' process.

4) *Sputtering:* In sputtering technique ions, energetic particles are bombarded over a target i.e. surface and due to the collision, deposition of nanoparticles takes place on exterior surface by ejecting particles from it [4]. In sputtering usually, a thin layer of nanoparticle is a deposited which is followed by annealing. The shape of the nanoparticle deposited is determined by the various parameters such as temperature, duration of annealing width of the layer, and, substrate type, etc. [5].

5) *Thermal decomposition:* In Thermal decomposition, as the name suggests is technique in which chemical reaction takes place and the compound is broken in to two or more substances and it is usually an endothermic chemical reaction which decomposes and breaks the element into chemical bonds in the compound [6]. The temperature at which element chemically decomposes is known as decomposition temperature. To explain the whole process in short, we can say the nanoparticles produced by chemical reaction at specific temperatures by decomposing the metal for producing secondary products.

B. Bottom-up Method

Bottom-up methods are those methods which involves constructive route for producing nanoparticle or we can say building up nanoparticles. Some the methods which fall under this categorization are bio-synthesis, chemical vapour deposition (CVD), Sol-gel, spinning and Pyrolisis.

1) *Spinning:* The nanoparticles are synthesized with help of a spinning disc reactor (SDR) in which spinning is carried out. The temperature in this reactor can be restricted. The reactor is packed with inert gases like argon, nitrogen to make sure there is no oxygen inside the chamber as to avoid chemical reactions [7]. The liquid which are precursor and water is injected into the chamber and disc is rotated at dissimilar speed, during this process the fusion of atoms or molecules occurs and precipitate is formed. This precipitate is then collected and dried [8]. The characteristic of nanoparticles synthesized from SDR is determined by the different working/input parameters which are the disc surface, disc turning speed, location of feed, liquid/precursor ratio, liquid flow rate, etc.

2) *Pyrolisis:* For large-scale production of nanoparticle the most commonly used process in industries is Pyrolysis. It this precursor is burned with flame. The precursor that is fed into the furnace is in liquid or vapour state. It is inserted into chamber at high force from a small outlet where it burns [9]. The burning or by-product gases after that is air classified to get the nanoparticles. To produce high temperature for easy evaporation a few of the furnaces make use of laser and plasma in the place of fire [10]. There are many advantages of paralysis process as it is very cost effective, simple, efficient and constant procedure with high yield.

3) *Biosynthesis:* Biosynthesis is green and environmental friendly method for the production of nanoparticles which are nontoxic and recyclable [11]. In Biosynthesis technique it uses microorganisms, plant extracts, fungi, etc. for bioreduction and capping purposes along with the precursors to produce nanoparticle besides of convention chemicals. The biosynthesized nanoparticles have distinctive and improved properties that find out its way in biomedical applications [12].

4) *Sol-Gel:* The sol-gel technique is of synthesizing nanoparticle is one of the handiest methods and it is classified under chemical method of synthesis, it is broadly used in the field of material science to produce protective coatings, optical coatings and ceramics. In this process a solution of metal alkoxide i.e. liquid precursor (sol) which undergoes chemical reaction at room temperature or at very low temperature to form "mers" these molecules form "polymers" by cross linking with each other and through this process it gradually produce a gel. The gel obtained after completion of the process is a one large matrix and continuous network of a solid polymer with another continuous network of liquid co-existing in the container. That is why it is bi-phase method that contains both a liquid phase (solvent) and a solid phase (integrated network, typically polymer network). It is a time taking process and it might take up to few days to transform into gel. As per the requirement of researcher further the phase reformation process can be accepted to improve the nanoparticles by different methods such as sedimentation, filtration and centrifugation. The moisture is then detached by drying which results in giving final solid state of the nanoparticles [13]. Sol-gel is the commonly chosen bottom-up method as it has many advantages over methods such as, high temperature ceramics can be synthesized at comparatively very low temperature. It provides you prices control over the purity of the compound formed and it also yields the highest specific surface area. In sol-gel method it is possible to combine an organic and inorganic material, which is not possible through any other process as for organic low temperature and inorganic very high temperature is required. The flexibility sol-gel process in producing numerous ceramics makes it extremely preferable method over other methods.

III. STRUCTURE OF COATING LAYERS

The coating structure of modern day advance coatings can be classified under four different types.

A. Single-layer or Monolayer Structure

As the name suggests, single layer of coating is called monolayer. A structure similar to tall columns comes into observation on looking at the coating structure under a microscope. This is easy to apply as it does not involve any complicated procedure, but it is also not very durable also and very prone to crack and damage. Therefore, it is always advisable to keep time to time check for any irregularity in the coating.

B. Multilayer Structure

The multilayer structure is the one in which many single layers are coated over one another. The layers of coatings can be of different materials. As in case of some particular applications it is very beneficial e.g. in case machining tool insert it requires to be tough, hard and heat dissipating, which is not possible solely by virtue of the properties of single material hence multilayer coating is done with different material to provide different properties. In most of the recent trend it is a multilayer coating of different nanomaterial.

C. Nanolayer Structure

The Nanolayer structure is that structure which has arrived due to the coating of a nanomaterial over a substrate. This is can be a single layer or a multilayer, according to the requirement.

D. Nano Composite Coating structure

Nanocomposite coating is coating of a composite nano material over a substrate to obtain the desired functional coating.

This phenomenon is because of increased reactivity, comparatively larger surface area to the volume or constancy in a chemical process and it has improved mechanical strength and other such properties. [14].

IV. PROPERTIES OF TITANIUM DIOXIDE DIP COATING TECHNIQUE

Titanium dioxide (TiO2, titania) is a broadly rich and low-cost material. Its melting temperature is 1843° C and boiling temperature is 2972 ° C. Once deposited as a thin film, its refractive index (n=2.4) and colour create it an outstanding reflective optical coating for dielectric mirrors. TiO2 is chemically and photo-chemically constant, non-toxic and insoluble under normal pH conditions. The corrosion resistance of titanium metal is due to the formation of a native oxide passivation layer. TiO2 occurs in three crystalline forms; brookite, anatase and rutile, the latter two being the more common. Rutile is the thermodynamically stable form. In the crystal lattice of TiO2 each Ti atom is bonded to six O atoms and each O atom is bonded to three Ti atoms to form a tetragonal crystal lattice. Anatase differs from rutile by the number of common edges of the TiO6 octahedra i.e., 4 for anatase and 2 for rutile. TiO2 is effectively an insulator at normal temperatures, however, the band gap (3.0 eV for rutile and 3.2 eV for anatase) is such that it will absorb ultra violet light at wavelengths just under 400 nm and it is referred to as a wide band gap semiconductor [15].

V. DIP COATING TECHNIQUE

Dip coating, as the name suggests is a method of achieving coating over substrate by immersing it in the coating material and withdrawing it back. The coating material is either in the liquid state or in the gel phase. By withdrawing the substrate at constant or stable speed coating is done. The evaporation leads the coating to dry and solidifies. Many nano material experts use this technique for research and industrial projects. The input parameters needed to be considered for better coating quality are, submersion time, functionality of the substrate surface, solution composition, withdrawal speed, withdrawal angle, concentration and temperature of solution and environmental conditions. The dip coating method can provide uniform, high quality films even on bulky, complex shapes [16].

The dip coating method is used to create thin films by self-assembly and with the sol-gel technique. The sol-gel method creates films of improved, precisely controlled thickness which are more often determined by the deposition speed and solution viscosity.

VI. APPLICATION

A. Currently a lot of research work is carried out in the field of bio-application, as to find out the most favourable conditions for bio-implant. Many researchers have suggested that nano-technology is one of the most useful tools available to obtain the desired surface conditions of implant. Titanium is most preferable bio-implant material as it has many favourable surface conditions. It was recently shown that titanium implants with rough surface topography and free energy increase osteoblast adhesion, maturation and subsequent bone formation. Some of the characteristics of titanium implants which influence the adhesion of different cell lines with the surface of titanium implants, spreading, growth and differentiation of mesenchymal stem cells are chemistry, charge distribution and topography. The titanium dioxide coating can be achieved over a metallic substrate through electrochemical anodisation method of the metallic substrate and other processes such as the hydrothermal or sol-gel template. TiO2 nanotubes in cell interactions is based on the fact that. TiO2 nanotube morphology is correlated with cell adhesion, which were shown to be maximally induced on smaller diameter nanotubes (15 nm) but hindered on larger diameter (100 nm) tubes, leading to cell death and apoptosis.

B. Another most important application of thin film coating is in Photoelectrochemical (PEC) cell, where it is required to have a thin TiO2 coating to minimize the adhesion of the evolved bubbles in the front window of PEC cells, thereby maximizing its transparency. Highly transparent, crack-free, and stable thin films of TiO2 were prepared by spin coating followed by sintering at 465°C for 45 min [17]. The thinner the film the better it is, so it opens a wide domain of research to achieve thin film of nano titanium oxide coating on glass substrate.

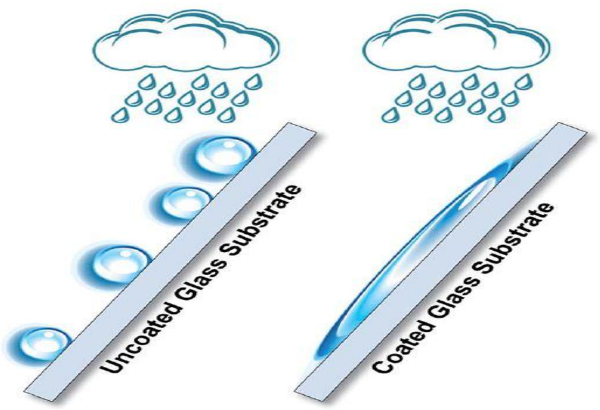

Fig. 1 Schematic representation of water droplets behaviour over (a) Uncoated glass substrates and (b) TiO2-coated glass substrates exhibiting the photoinduced superhydrophilicity state.

C. One of the most common domains where coating plays very important role is in the field of manufacturing, it is common practice to coat the cutting tool material with some other materials as the tool material must be at least 30 to 50% harder than the work piece material. The idea originated from the basic requirement to improve the properties of cutting tool (hot hardness, wear resistance. Thermal conductivity, abrasion resistance and other such properties) used in operations like turning, milling, drilling etc. Different cutting tool materials used for cutting operation in practice are high carbon steel, high speed steel, non-ferrous cast alloys, cemented carbides, ceramics and sintered oxides, ceramics, diamond, cubic boron nitride. As the machining operations require cutting tool to withstand high temperature ranging from 500°C to 1500°C we need material to retain its property at such temperature in order to perform the operation correctly [18]. But to craft the tool geometry of such materials is also a challenge because it involves high cost. So, it is advisable to coat the substrate material with a material which has desired properties and it is a common practice now in manufacturing industries. There are several materials available in the existing market which is used for coating tools. When cutting tools are properly coated and perform as designed, productivity increases as it has longer tool life and the possibility of dry machining. Coatings for hard milling, tapping and drilling all vary and are application-specific.

1) *Multilayer Nanoparticle Coating:* Nanoscale multilayer coatings consist of different materials alternately. It helps in enhancing the performance of single layered nanostructure. Each layer of different nano-material provides different ability to the coating structure. The feasibility of combination of different coating material is a matter of concern because factors such as crystal structure, type of material and their bonding ability plays vital role while selecting the materials [19]. The carefully designed multilayered nano-scale coating which involves taking care of feasibility of coating and the optimisation of number of coating results in the "super functionality" of the coating structure [20]. An investigation of multilayer film showed a much lower wear rate than its single layer [21]

VII. CONCLUSIONS

In tools, nanostructure coatings offer improved functionality over conventional coatings of tool inserts. By the virtue of advance coating structure tools gets ability to retain a crisp cutting edge. With help of such coatings the liquid lubricant use decreases and eventually it contributes to environmental friendly dry machining. . Nano material coating is multidisciplinary process of implementing coating on substrate, it consists synthesis of nanoparticle and its coating over substrate. There are several methods available for both synthesizing nanoparticle and coating it. In most of the cases they are co-related, as the coating technology somewhat depends upon synthesis process of nanoparticles. The present work focuses on the coating technique of synthesized titanium dioxide nanoparticle by Dip coating technique.

The superior mechanical and physical properties of nanostructure coatings make them well suited for extreme operating conditions such as aerospace applications.

The method which has gained considerable ground and credibility in recent years for synthesis of nanoparticle is Sol-Gel process. Films are prepared by spin, dip or spray coating on appropriate substrate.

The coated substrate is usually annealed to obtain a stable coating on the surface.

The sol-gel process has several advantages over other fabrication methods. It is simple, more economical, and easily achievable in laboratory and permits coating of complex geometries.

The layer thickness obtained in dip coating technique is usually 1-micron metre layers. Generally, the thinner the film the lower the internal stresses and number of defects.

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VIII. FUTURE SCOPE

The significant potential of nanostructure material combination is unexplored. There is a vast possibility in the field of surface engineering to design the multilayered nano structured coatings to increase the functionality of the substrate. It has application in bio-medical, aerospace, marine and manufacturing. The study has not been conducted to achieve nano TiO2 coating through Dip Coating Technique for any substrate.

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