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# Review on Intermetallic and Ceramic Nanoparticle Coatings for Application in High Temperatures

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**Abstract:- As compared to material with ordinary grain size, Nano Materials have special properties. The Idea is to study the properties and coating techniques for ceramic and intermetallic nanostructure which could be deposited as a protective layer. Some methods include Inert gas condensation, PVD, CVD, Sol-gel, Electrochemical deposition, thermal spray, and pulsed electro-spark deposition. The composition of the material and microstructure can be controlled using different electrodes, and adjusting the parameters of the setup. Nano Material coatings on surface can modify chemical, mechanical and electronic properties. It can also improve high-temperature corrosion and corrosive wear resistance. These modification techniques can have various applications in turbine blades, engine parts for petrochemical, aerospace and electronic device industries.**

***Keywords**:- Nanoparticles, Synthesis of nanoparticles, Nano ceramics, Intermetallic, Deposition, Coating.*

## I. INTRODUCTION

The paper is all about a review on application of nanomaterial in high temperatures. General aspects of nanomaterial as compared to bulk materials is discussed. Various methods for synthesis of nanomaterial, Intermetallic Nano materials and Nano ceramics. Coating methods for Nano materials and application in materials which are exposed to high temperatures.

## II. PROPERTIES OF NANOMATERIALS

### *A. Surface to Volume ratio*

The surface to the volume ratio is quite large in case of nanoparticles .That is if 1cm of cube is broken in cubes of 10nm edge than surface area is increased by 106 times. While in crystalline particles smaller than 10nm, the amount of atoms at the surface becomes more significant. The size of the particle is inversely proportional to the surface volume ratio. In 10nm particle 10% of atoms participate in surface atoms while in 1nm particle more than half of atoms are surface atoms.

### *B. Change in surface structure*

Each atom in volume of nanoparticles is surrounded by a specific number of atoms called coordination number. Thus decrease in coordination number of surface atom leads to weaker cohesive energy which could lead to reduction in melting temperature.

### *C. Electronic property*

Valance electrons occupy the energy bands in crystalline solids. The occupancy, width and separation of these bands decide the electrical, optical and magnetic properties. As the particle is reduced in size these energy bands get thin and sharp. For Nano sized particles the electrons get scattered on the surface and resistivity increases.

### *D. Optical property*

When the size of a crystal becomes smaller and comparable to wavelength of visible light, nanoparticles partially transmit the light which results in change of color. For example Au nanoparticle of size between 30 - 500nm appears blue to red in color from larger to smaller size.

### *E. Magnetic Property*

The total magnetic moment is the property which depends upon number of atoms; it depends upon the size of the cluster. It enhances orbital and spin moments on the surface of tiny nanoparticle. As the cluster size is increased at few nanometers the spin moment decreases because the presence of atoms with low coordination number on the surface.

### *F. Catalytic Property*

Surface atoms are the active centers for the catalytic process. As compared common grain size material Nano material have more number of atoms on the surface. Due to which the Nano materials are highly reactive catalyst. [1]

## III. SYNTHESIS OF NANOPARTICLES

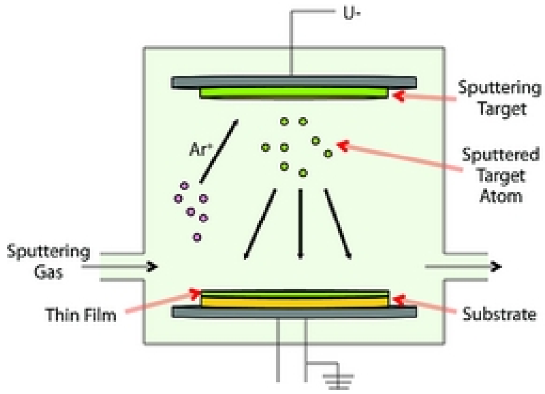
### *A. Physical Vapor Deposition (PVD)*

PVD is a thin film deposition process in which the material is heated to form vapors in high vacuum environment. These Vapors are deposited on a conductive surface as a pure metal or alloy coating. Now since the material is coated from atom to atom or molecule to molecule, this process has highly pure and high performance coatings as compared to electroplating. PVD coating process is a clean and environment friendly process, as it does not releases any harmful gases or toxins as compared to conventional coating process.

PVD process is widely used in solar industry as well as in surgical implants, as it gives highest purity coatings. Coatings produced by PVD are high wear and tear resistant and have good hardness. Science these coatings reduce friction they find wide application in high performance moving parts like automobile and tool industry. PVD coatings are resistant to corrosion, scratches and crapes, the have high finish and they do not fade. They find various application in decorative items, household fixtures, watches and tinting of glass.

In PVD process the material to be deposited is kept inside a high vacuum chamber with pressure approximately 10 to 2 mbar. The material is vaporized to form plasma of atoms or molecules and deposited on a substrate. There can wide range of substrates depending upon the coating material. The substrate is heated and cleaned thoroughly before clamping in deposition chamber. The pressure and temperature are then adjusted depending upon coating material and substrate. The process usually takes place between 150 to 500 Deg C.

These processes can be applied to various kinds of ceramic, polymers, alloys and composites etc.

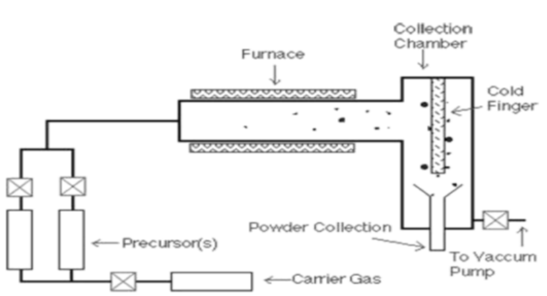



*B. Chemical Vapour Deposition and Chemical Vapour Condensation:*

In CVD process, the vaporized precursor is absorbed on a substance which is maintained at a high temperature. The adsorbed molecules react with other molecules or get decompose to produce crystals. There are three main steps in CVD process.

- Reactants are transported on growth surface by a boundary layer.
- Chemical reactions take place on growth surface.
- By products formed by the gas-phase reaction have to be removed from the surface.

CVC technique involves pyrolysis of vapor form of metal organic precursors in a reduced pressure environment. A metal organic precursor is introduced in the hot zone of the reactor. The reactor allows synthesis of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of reactor and coated nanoparticles by supplying a second precursor in a second stage of reactor.




*C. Sol-gel Technique*

Other than the techniques mentioned above, the sol-gel processing technique is also extensively used. Colloidal particles are much larger than normal molecules or nanoparticles. Although, upon mixing with liquid colloid particles appear bulky whereas Nanoparticles always look clear. The Process involves the evolution of networks through the formation of colloidal suspension abbreviated as “sol” and gelatin to form a network in continuous liquid phase abbreviated as “gel”. Thus called Sol-gel formation. It occurs in four stages.

- Hydrolysis
- Condensation
- Growth of particles
- Agglomeration of particles

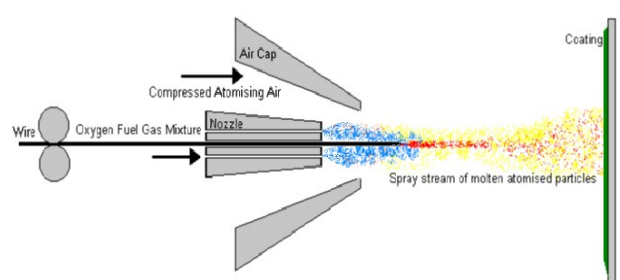
*D. Thermal Spray*

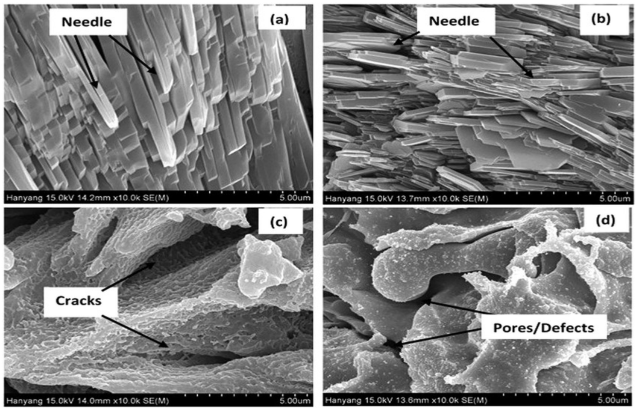
Thermal spray coating is usually used in industries. In This method the coating material is heated and melted into tiny droplets which are sprayed on coating surface with high velocity. The coating material is fed usually in powder or wire form. Thermal sprayed coatings can be applied to metal substrates, and some plastic substrates. Thermal sprayed coatings instantly enhance and improve the performance of the component. This process is known by many names including Plasma Spray, HVOF, Arc Spray, Flame Spray, and Metalizing. The coating material in the process can be tungsten carbides, stainless steels ceramics, (chrome oxide, aluminum oxide, zirconia, titanium) nickel- chrome carbides, pure metals (aluminum, zinc, copper). [16]

Electric wire arc thermal spraying works on the same principles as wire arc welding. The coating material which is in wire form is electrically charged to create an arc. Then the molten droplets of metal wire are sprayed onto the substrate using high velocity air stream.

Arc spray coatings are cheap and applied on metals like pure aluminum, zinc, copper, and metal alloys such as stainless steel. Arc spray also allows adjusting the coating texture from 200 micro inches to 800 micro inches. [16] The plasma spray process uses inert gases which are fed past an electrode in the "plasma" state. When these gases exit the nozzle of the gun they return to their normal state, releasing huge amount of heat. A powdered coating material is injected into the plasma "flame" and injected on the substrate.

Ceramic Coatings are applied using plasma spray because of their high melting temperatures. (Often above 3500 F). Several types of ceramic coatings can be applied using plasma spray. [16]






SEM images of Al coating applied by arc thermal spray process [17]

### E. Electrochemical Deposition

Electrochemical deposition is a method which is used for growth of metals and conducting metal oxides. They have the following advantages: the thickness and morphology of the nanostructure can be controlled by adjusting the electrochemical parameters; uniform and compact deposits can be made on template-based structures; higher deposition rates can be obtained; and the equipment is comparatively cheap as there is no requirement of high vacuum or a high reaction temperature layer.

A simple modification can be done by using pulse electroplating. This process involves an alternating current between two different values resulting in a series of pulses of equal amplitude, duration and polarity which are separated by zero current. By changing the pulse amplitude and width, the deposited film's composition and thickness can be changed.

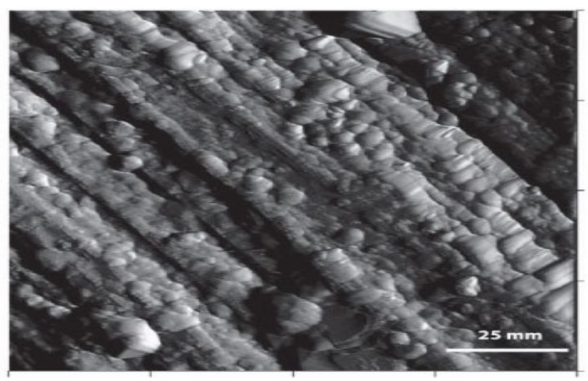
There are experimental parameters of pulse electroplating like peak current/potential, duty cycle, frequency and effective current/potential. Peak current/potential is the maximum set value of electroplating current or potential. Duty cycle is the effective interval of time in which the current or potential applied. The effective current/potential is calculated by multiplying the duty cycle and peak current/potential. Pulse electroplating also improves the quality of electroplated film and releases the internal stress built up during fast deposition process. Process with short duty cycle and high frequency decreases the surface cracks. However, to maintain the constant effective current or potential, a high performance power supply is required to provide high peak current/potential and fast switch. Another issue of pulse electroplating is that the anode material could get plated and contaminated during the reverse electroplating, especially for the costly electrode like platinum. [15]

Factors that could affect the pulse electroplating are temperature, anode-to-cathode gap and stirring. Pulse electroplating could also be performed in heated electroplating bath to increase the depositing rate since the rate in maximum chemical reactions increases exponentially with increase in temperature. The anode-to-cathode gap is in relation with the current distribution between anode and cathode. Small gap causes uneven distribution of current and affect the surface topology of plated sample. By stirring we can increase the transfer/diffusion rate of metal ions from bulk solution to the electrode surface. [15]

### F. Electro Spark Deposition

Electro spark Deposition (ESD) is a micro-bonding process that has the capacity of depositing wear and corrosion resistance coating to repair, improve and extend the service life of the component and tools. During the process, short duration of electrical pulses ranging from a few microseconds to milliseconds are used to deposit the electrode material on the component's surface as a protective layer. Advantages of ESD coating are low input heat and forming of metallurgical bond between coating and substrate. [14]

The Electro-Spark Deposition is usually described as a micro arc-welding process. During ESD process, the depositing electrode is momentarily contacted to the substrate surface with light pressure. This is necessary to maintain the electrode motion to prevent the electrode sticking to the substrate surface. Moreover, there are important process parameters that are unique in ESD process. These variables include electrode, substrate, environment, and electrical characteristics. Changing in any of these parameters will change the properties and quality of the resultant deposition [14].




AFM Image of electro spark deposition coating surface on stainless steel. [18]

## IV. INTERMETALLIC NANOPARTICLES

Intermetallic compounds are generally made of two or more metals or a metal and a nonmetal. There are examples like Aluminides and silicides of transition metals such as iron, nickel, titanium, and cobalt. Intermetallic bulk materials are used for several of high-temperature structural applications. They have properties which are useful in many applications like their low density, good electrical and heat conductivity and in some cases they are magnetic. Since these nanoparticles have a large specific surface area, they actively react with oxygen even at room temperature. The formation of oxide shells around intermetallic nanoparticles protects them against further oxidation at ambient temperature. On the other hand, metallic nanoparticles oxidize easily with increasing temperature and it prevents their application in higher temperatures. Intermetallic compounds, like aluminides and silicides of iron and nickel, exhibit good oxidation resistance which is important for their practical utilization. For example like Fe3Al nanoparticles covered with alumina (Al oxide) layer. The excellent oxidation and corrosion resistance properties of intermetallic phases is because of the formation of continuous and fully adherent oxide layer on surface when exposed to atmosphere at temperatures like 1000 C or even higher.[1]

## V. CERAMIC NANOPARTICLES OR NANOCERAMICS

Nano ceramic are made of nanoparticles of ceramic material. Ceramic material is hard, heat resistant and nonmetallic solid composed of metallic and nonmetallic compounds. These materials have unique properties and large variety of functions, including dielectric, ferroelectric, piezoelectric, pyro electric, ferromagnetic, magneto resistive, superconductive and electro-optical.

Initially Nano ceramics were made using sol-gel process. Later the sintering methods were developed where the pressure and heat was applied to form the structure of Nano ceramics. Since the particles are Nano scale the purity is high. [10-11]

## VI. EXAMPLE OF $ZrO_2$

Specific properties of ZrO2 nanoparticles such as low thermal conductivity, high coefficient of thermal expansion, high thermal stability, high oxygen ion conductivity, high strength, high fracture toughness and high thermal shock resistance, enables it to be used as thermal barrier coating, cutting tools, refractory material. Synthesis of ZrO2 nanostructures can be done by various methods such as sol–gel, hydrothermal, sputtering, Chemical Vapor Deposition (CVD) and electrical arc discharge method.

| Chemical Data | |
|---|---|
| Chemical symbol | $ZrO_2$ |
| CAS No | 1314-23-4 |
| Group | Zirconium 4<br>Oxygen 16 |
| Electronic configuration | Zirconium [Kr] $4d^2\ 5s^2$<br>Oxygen [He] $2s^2\ 2p^4$ |
| **Chemical Composition** | |
| **Element** | **Content (%)** |
| Zirconium | 74.03 |
| Oxygen | 24.34 |

The thermal properties of zirconium oxide nanoparticles are as per the table below.

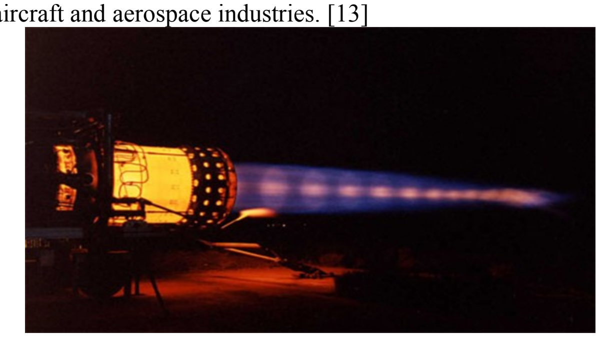
| Properties | Metric | Imperial |
|---|---|---|
| Melting Point | 2715°C | 4919°F |
| Boiling Point | 4300°C | 7772°F |

## VII. APPLICATIONS IN HIGH TEMPERATURE

Coatings and Depositions of Ceramic and Intermetallic nanoparticles on the surface of the material which is exposed to high temperature could make them highly resistant to heat. High temperature application includes Boilers, Turbines, Jet Exhausts, Engine Components, Furnaces, Reactors and some electrical components. Typical materials used in such application are alloys, ceramics, carbides or materials with high melting point. Such materials may not be economically suitable at large scale.

Maximum power generation plants are based on oil or coal fired steam turbines. They can achieve the maximum steam temperature of up to 600 Deg C. Certain components in these plants reach the higher temperature and are exposed to erosive and corrosive attacks. Such components include tubes and tube supports carrying the superheated steam, pipes and valves connecting boiler to turbine are exposed to thermal stresses and erosion. Rotors, turbine casing and casing bolts are exposed to stresses due to steam pressure and centrifugal forces. [13]

The term super alloys describe the materials which are resistant to creep and fatigue at high temperatures. The aircraft industries have always worked towards the development of these super alloys. Critical components like rotor and stator in aircraft gas turbine are usually made of these super alloys. Now days other engine components like disks, combustion chambers, casings and tail pipes are also being fabricated using super alloys. Space vehicles and shuttles also face the problems of high temperatures while leaving or entering the earth's atmosphere. Special refractory materials like tungsten and graphite are being used to resist these thermal stresses. However Nano material coatings can serve these issues of aircraft and aerospace industries. [13]



Material Processing industries use furnaces and ballasts for melting and reduction of metals. High temperature is also required while performing hot working and heat treatment processes. Other industries like glass and cement industry uses kilns and furnaces for process of their products. Such application in industries has given rise to use material which are durable and heat resistant even in the temperatures as high as 1500 Deg C. Not only heating components but the components which are coming into the direct contact like material handling components and conveyers also require being high temperature resistant. In such applications Nano Material lining and coatings could be used to resist high temperatures. [13]

## VIII. CONCLUSION

Nano materials, especially intermetallic nano materials and nano ceramics, can be used as coating materials for construction of components that are exposed to high temperatures, thermal stresses and corrosion. There are various techniques for synthesis of nano materials and any technique can be adopted depending upon the material to be fabricated and limitation of the method. The coating of nano materials not only enhances the mechanical or chemical property, but also allows us to save the costly material and alloys used in construction of such components.

Intermetallic nano material like Fe3Al, which has excellent oxidation and corrosion resistance properties, can be used in steam turbines blades, turbine casing and bolts as they are exposed to high temperature and moisture. Another example is ZrO2, a nano ceramic material which has the melting temperature around 2700 C. It can be used in gas turbines of jet engines, rocket propulsion, industrial furnaces and high temperature application areas.

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