

CHAPTER II

THEORY AND LITERATURE SURVEY

TiN can be used in many kinds of application such as application in alloys and ceramics as an interlayer material (Ting and Vac 1982; Wittmer et al. 1981; Zhao et al. 2000), using as a diffusion barrier between Si and metals for integrated circuit technology (Shimada et al. 2000), utilizing in superalloys to prevent whisker growth of Al_2O_3 (Muller et al. 1999) and employed extensively in cutting tools to increase wear resistance (Huang et al. 2002). Therefore, it is important to discover appropriate conditions to produce TiN. There are several reported methods for synthesizing TiN, both in bulk and thin film, using solid state reaction, chemical techniques as well as chemical vapor deposition methods. The most common method reported for the production of TiN powder is the carbothermal reduction of TiO_2 (Yu and Lin 1998).

Titania can be synthesized by various techniques, such as precipitation (Kim et al. 1999), chemical vapor deposition (Ding et al. 2000), hydrothermal method (Yang et al. 2001), glycothermal method (Iwamoto et al. 2000) and sol-gel method (Xiang et al. 2000). Among these techniques, sol-gel method is the technique that can result in titania with extremely high surface area (Djaoued et al. 2002; Il-seok and Kumta 2003; Jung and Park 2000; Xiang et al. 2000).

Nanoscale materials, such as nanowires, nanorods and nanofibers have recently attracted attention due to their exceptional properties and novel potential applications. An electrospinning technique is a simple method for fabricating nanofibers, frequently polymer nanofibers. However, it is recently applied to fabricate ceramic nanofibers by using the appropriate blend of polymer and ceramic solution in sol-gel fashion.

2.1 Sol-Gel Process

Traditional ceramic and glass processing use high temperature to transform inorganic powder into dense object by melting or sintering. High temperature and agglomeration of powders often limit control of microstructure, properties, shape, and surface feature obtained. The goal of sol-gel technology is to use low temperature chemical processes to produce net-shape, films, fibers, particulates, or composites that can be used with minimum number of additional processing steps. The traditional ceramic processing produces materials having microstructure typically in the range of 1-10 micrometer in diameter. On the other hand, sol-gel processing can provide control of microstructures in the nanometer range, which approaches the molecular level. These materials often have unique physical and chemical characteristics.

Although the origin of the chemical-based ceramic processes may be dated to as early as 4000 BC, the concept of control of shape and molecular structure of ceramics and glasses by use of sol-gel chemistry probably dates from Bergman's studies on water glasses in 1779. Ebelman and Graham studied on silica gels in 1874 and 1876, respectively, and they studied a large body of work on the science of colloids in the mid-1800s. These early studies led to the following definitions:

Sols are dispersions of colloidal particles with size ranging from 1 nm to 1 μm in liquid. Sol particles are typically small enough to remain suspended in liquid by Brownian motion. Sol can be obtained by the hydrolysis and partial condensation of precursor such as inorganic salt or metal alkoxide (e.g. TMOS, TEOS, Zr(IV)-Propoxide, Ti(IV)-Butoxide, etc.).

Gels, which are a diphasic material with a solids encapsulating liquid or solvent, are viscoelastic bodies that have interconnected pores of submicrometered dimensions. A gel typically consists of at least two phases, a solid network that entraps a liquid phase. The term gel embraces numerous combination of substances which can be classified into the following categories: (1) well-ordered lamellar structure; (2) covalent polymeric networks that are completely disordered; (3)

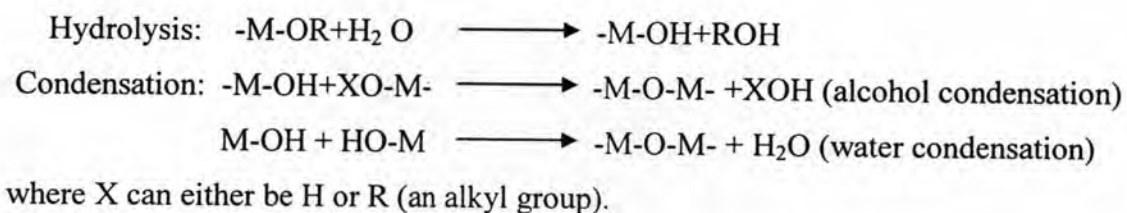
polymer networks formed through physical aggregation that are predominantly disordered; and (4) particular disordered structures.

The sol-gel process involves the formation of sol following by that of gel. Further condensation of sol particles into a three-dimensional network produces gel. Alternatively, gel can be produced by destabilizing the solution of preformed sols. In either case, the materials are referred as aquasol (or aquagel) if water is used as a solvent, and alcosol (or alcogel) if alcohol is used. The encapsulated liquid can be removed from gel by either evaporative drying or drying with supercritical extraction (supercritical drying for short). Potential advantages of the sol-gel process include:

- (i) high homogeneity owing to the use of molecularly tailored, usually liquid compounds;
- (ii) high purity owing to the use of chemically prepared precursor;
- (iii) lower temperature of processing that lead to savings in energy, reduction of risk of crystallization and phase separation, and combination between ceramics and low-temperature materials such as organic compounds and polymers;
- (iv) preparation of new crystalline phases and new noncrystalline solids;
- (v) fabrication of special products such as fibers, films, and aerogels;
- (vi) ultrastructural control of materials by manipulating network formation from early stages of sol formation;
- (vii) production of net-shape optics such that complex geometries and surface replication can be achieved, and lightweight optics formed involving reduced grinding and polishing operations;
- (viii) preparation of materials having improved physical properties, such as lower coefficient of thermal expansion and lower UV cutoff and higher optical transmission;
- (ix) preparation of transparent porous materials (e.g. porous silica) that allow impregnation using organic compounds and polymers at controlled chemical doping and oxidation states of dopants, as well as production of refractive index.

The four key steps in converting a precursor to a particular product form via sol-gel preparation are: formation of gel, aging of gel, removal of solvent, and heat treatment. The versatility of this preparative approach lies in the number of parameters that can be manipulated in each of these steps.

As mention earlier, the precursor in sol-gel preparation can be either metal salt/alkoxide dissolved in an appropriate solvent or a stable colloidal suspension of preformed sols. Metal alkoxides have been the most extensively used because they are commercially available in high purity and their solution chemistry has been documented. At its simplest level, sol-gel chemistry with metal alkoxides can be described in term of two classes of reactions:



Such a description oversimplifies the overall process because it does not correctly represent the molecular formulae of intermediates and end products, nor does it depicts the simultaneous occurrence of the two reactions. However, this oversimplification captures the key phenomenological idea that a three-dimensional gel network comes from the condensation of partially hydrolyzed species. Any parameters that affect either or both of these reactions are thus likely to impact on properties of the product. In fact, the important variables are the reaction rates of hydrolysis and condensation.

Because hydrolysis and condensation are both nucleophilic displacement reactions, the reactivity of metal alkoxides depends on the positive partial charge of metal atom and its coordination number. For example, tetraethyl orthosilicate (TEOS), which contains small positive partial charge on silicon, is the least reactive among the common alkoxides. In general, the longer and bulkier the alkoxide group attached to a particular metal atom, the less reactive that precursor is in hydrolysis and

condensation. Changing the type of precursor and/or its concentration are thus effective means of controlling the reaction rates.

The amount of water used in the sol-gel preparation and the rate by which it is added also influence gel characteristics. The former is usually expressed in term of the hydrolysis ratio h , defined as moles of water per mole of metal alkoxide, $M(OR)_m$. There are three specific regions of interest:

- (i) $h < 1$: An infinite network seldom forms due to the low functionality of the precursor towards condensation. Because there are few M-OH groups for cross-linking, gelation or precipitation cannot occur when there is no local excess of water.
- (ii) $1 < h < m$: Polymeric gels can form.
- (iii) $h < m$: Cross-linked polymers, particulate gels, or precipitates can form when an excess of water is added to the alkoxides.

For a given amount of water, another level of control comes from the rate of addition. Common approaches to slowly add water are: using a micropipette, absorbing moisture from a controlled humidity environment, and generating water in the solution with another chemical reaction.

Two other important sol-gel parameters are temperature and type of solvent. Both hot and cold plates are commercially available, which can be used to increase and decrease the reaction rate, respectively. Varying the temperature is most effective when it can alter the relative rate of competing reactions. Solvent can change the nature of an alkoxide through solvent exchange or can affect the condensation reaction directly. It is also possible to prepare gel without solvent as long as another mean, such as ultrasound irradiation, is used to homogenize an otherwise immiscible alkoxide/water mixture.

Using preformed sols instead of metal alkoxides as precursors is an attractive alternative in sol-gel preparation because recent advances in inorganic colloidal dispersions allow some control over the characteristic of the starting sols. Colloidal suspension of sol particles is often stabilized (i.e. prevented from flocculation) by pH adjustment. Thus, pH of the solution, which can be changed by the addition of either acid or base, is the single most important parameter in obtaining gel from preformed sols. Other parameters that influence gel quality are size and concentration of the starting sol particles.

For any of the sol-gel parameters discussed so far, its effect on gel properties can often be observed by an experimental parameter known as gel time. Gel time is defined as the time that the solution undergoes rapid rise in viscosity which is corresponding to the transition from viscous fluid to elastic gel. At the gel point, the solid phase forms a continuous structure that reflects the formation and branching of particles under specific growth condition. This particular phase is important because it is the genesis of structural evolution that takes place in all subsequent processing steps (Ertl et al. 1999).

However, if polymeric components are directly added into the ceramic sol, it is usually thought that it will risk reducing the connectivity of the sol-gel network and decreasing condensation reaction rates (i.e., a longer time) during the gellation which, in turn, will result in a less dense microstructure of gel network upon the removal of solvent. If the impregnation of polymer takes place after the gel process, it is believed that it will prevent the reduced adhesion between the coating and substrate, and decrease the permeability.

There are many applications of sol-gel process. The important one is application in the fabrication of fiber. During sol-to-gel evolution, changes in the rheology of the sol can be used to allow fiber pulling. Formation of elongated polymer in a solution is a requirement for spinnability, i.e, the ability to form fibers. Reduced viscosity for solutions of chain-like or spherical polymers is independent of concentration, whereas linear polymers give a direct relation between reduced

viscosity and concentration. Acidic pHs and low values for the molar ratio between water and alkoxide result in the production of linear polymers that exhibit spinnability. High molar ratios of water/alkoxide and basic media lead to the production of spherical and ramified polymers that form a three-dimensional network. Low molar ratios of water/alkoxide allow the production of a functionality of two in the inorganic polymers; whereas acidic medium reduces the immiscibility gap in the alcohol-alkoxide-water system and provides a catalytic effect important in the development in the development of linear polymers.

Nanoparticles of titania could be synthesized by sol-gel process in many forms such as film (Choi et al. 2006), hollow sphere (Zhang et al. 2005) and microballoon (Kimura et al. 2005).

Choi et al. (2006) prepared mesoporous photocatalytic TiO₂ films and membranes via a simple synthesis method that involved dip-coating of appropriate substrates into an organic/inorganic sol composed of isopropanol, acetic acid, titanium tetraisopropoxide, and polyoxyethylenesorbitan monooleate surfactant (Tween 80) following by calcination of the coating at 500°C. The advantageous properties included high surface area (147 m²/g) and porosity (46%), narrow pore size distribution ranging from 2 to 8 nm, homogeneity without cracks and pinholes, active anatase crystal phase, and small crystallite size (9 nm).

Zhang et al. (2005) reported that TiO₂ hollow spheres could be prepared by a convenient sol-gel method at room temperature. It was found that these spheres had outer diameters of 200–500 nm. The wall of the sphere was mesoporous with average pore diameter about 9.8 nm. TiO₂ sample was amorphous after drying at 60°C, but it was in anatase structure after calcination at 500°C for 4 h. No characteristic peak of impurities or other phase such as rutile and brookite was observed, which indicated that the products had high purity.

Mine et al. (2005) studied a synthesis method for preparing submicrometer-sized titania particles. Submicrometer-sized spherical titania particles with particle sizes of 143–551 nm were synthesized by hydrolysis and condensation of titanium tetraisopropoxide. Annealing at 100–1000°C led to shrinkage and crystallization of titania particles, which consequently resulted in an increase in the refractive index of titania particles. Colloidal crystals of the spherical titania particles prepared by the gravitational sedimentation showed the Bragg reflection peak, which indicated monodispersity of the titania particles. Shrinkage and crystallization of titania particles took place when annealed at high temperature, and shift of the Bragg reflection peak angle could be explained by a decrease in the particle size and a increase in the titania refractive index.

Kimura et al. (2005) prepared titania microballoons by sol–gel process of titanium tetra-2-propoxide in reverse dispersion. The products were confirmed as titania microballoons of 76 nm in mean diameter and 4 nm in wall thickness without any crack or dimple. The specimen calcined at 500°C was identified as anatase. Scanning electron microscopy showed that the products were hollow microspheres or microballoons. The effects of preparation duration, dispersion stabilizer concentration, and pH on the yield and the mean diameter were investigated. It was predicted that titanium tetraisopropoxide concentration in the continuous phase should be controlled to a level, below which fine particles were not formed by homogeneous nucleation.



2.2 Electrospinning Process

Electrospinning is a process that creates nanofibers through an electrically charged jet of polymer solution or polymer melt. This process is a simple and quick technique for producing fibers with nanoscaled diameters for wide range of materials. The process was patented by Formhals in 1934, where the experimental set up was outlined for the production of polymer filaments using electrostatic force. The small diameter provides large surface area to mass ratio, in the range from $10 \text{ m}^2/\text{g}$ (when the diameter is around 500 nm.) to $1000 \text{ m}^2/\text{g}$ (when the fiber diameter is around 50 nm). Following this, investigations of the process have been carried out by a number of researchers. The electrospinning process, in its simplest form, employs a set of equipments consisting of a pipette to hold the polymer solution, two electrodes and a DC voltage supply in the kV range, as shown in Figure 2.1. The polymer drop from the tip of the pipette is drawn into a fiber under the influence of strong electric field, as high as several kV/cm. The electric field draws this droplet into a structure called a Taylor cone (Li and Xia 2004). Electrostatic charges built up on the surface of a droplet induces to form of a jet, which is subsequently stretched to form a continuous ultrathin fiber (Wattanaarun et al. 2005). The jet is electrically charged and the charge caused the fibers to bend such that every time the polymer fiber loops, its diameter is reduced. In the continuous operation, the number of fibers can be formed within short period of time, as short as a few seconds. The fiber is collected as a web of fibers on the surface of a grounded target.

If viscosity and surface tension of the solution are appropriately tuned, varicose breakup is avoided (if there is varicose breakup, electrospray occurs) and a stable jet is formed. A bending instability results in a whipping process which stretches and elongates the fiber until it has a diameter of micrometers or nanometers. The fiber is then deposited on a grounded collector to form non-woven mat that has high surface area (Li and Xia 2004). There are various techniques for collecting oriented fibers, including patterning a collector electrode to cause the fibers to jump between specific positions on the substrate and rotating the substrate to allow deposition of fibers in a spiral or linear pattern.

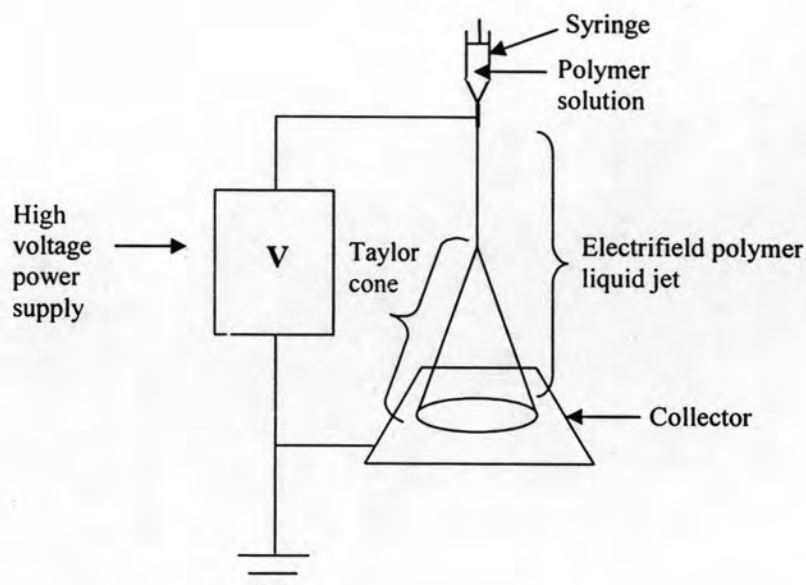


Figure 2.1 Schematic diagram of the electrospinning process.

Important limits of electrospinning are (Ramakrishna et al. 2005):

- Suitable solvent should be available for dissolving the polymer.
- Vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.
- Viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.
- The power supply should be adequate to overcome viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette.
- The gap between the pipette tip and the grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form.

2.2.1 Mechanism of Electrospinning Process

The electrospinning process involves polymer science, applied physics, fluid mechanics, electrical engineering, mechanical engineering, chemical engineering, material engineering and rheology. Many parameters, including electric field, solution viscosity, resistivity, surface tension, charge carried by the jet and relaxation time can affect the process. A comprehensive mathematical model of this process was developed by Reneker et al (Reneker et al. 2000).

The electrospinning process consists of three stages: (1) jet initiation and the extension of the jet along a straight line; (2) the growth of a bending instability and the further elongation of the jet, which allows the jet to become very long and thin while it follows a looping and spiraling path; (3) solidification of the jet into nanofibers.

2.2.1.1 Jet initiation and diameter of a single jet

In a typical experiment, a pendent droplet of polymer solution is supported by surface tension at the tip of the spinneret. When the electrical potential difference between the spinneret and the grounded collector is increased, the motion of ions through the liquid charges the surface of the liquid. If the electrical forces at the surface overcome the forces associated with surface tension, a liquid jet emerges from a conical protrusion that formed on the surface of the pendant droplet. The jet is electrically charged. It carries away ions that are attracted to the surface when the potential is applied. Increasing the potential increases both the charge density on the jet and the flow rate of the jet.

The jet diameter decreases with the distance from the orifice. Higher electric fields and a lower surface tension coefficient favor the formation of a thicker jet. Addition of salt (NaCl) to the solution, with other parameters held constant, reduces the diameter of the jet. Increasing the viscosity of the solution does not always increase the diameter. The largest jet diameter occurs when the solution viscosity is in a medium range. Both higher and lower viscosity favors a thinner jet.

2.2.1.2 Bending instability and elongation of the jet

After initiation, path of the jet is straight for a certain distance. Then, an electrically driven bending instability grows at the bottom end of the straight segment. The bending allows large elongation to occur in small region of space. The electrically driven bending instability occurs in self-similar cycles. Each cycle has three steps and it is smaller in scale than the preceding cycle.

The three steps in each cycle are:

Step 1. A smooth segment that is straight or slightly curved suddenly develops an array of bends.

Step 2. As the segment of the jet in each bend elongates, the linear array of bends becomes a series of spiraling loops with growing diameters.

Step 3. As the perimeter of each loop increases, the cross-sectional diameter of the jet forming the loop gets smaller, and the conditions for Step 1 are established everywhere along the loop.

After the first cycle, the axis of a particular segment might lie in any direction. The continuous elongation of each segment is most strongly influenced by the repulsion between the charges carried by adjacent segment of the jet. The externally applied field, acting on the charged jet, causes the entire jet to drift toward the collector, which is maintained at an attractive potential.

2.2.2 Parameters and Conditions for Electrospinning Process

Variables that must be controlled in order to electrospin uniform fibers include the spinning voltage, the collection distance and the solution viscosity and conductivity. Proper choices of processing parameters such as surface tension, viscosity and conductivity, concentration of the solutions, molecular weights, applied fields and electrode configurations allow the formation of fibers having diameter down to a few nanometers (Li and Xia 2004).

2.2.2.1 Parameters for Polymer Solution

Properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology.

Molecular Weight and Solution Viscosity: One of the factors that affect viscosity of the solution is molecular weight of the polymer. Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer but of a lower molecular weight. Another way to increase viscosity of the solution is to increase the polymer concentration. One of the conditions necessary for the formation of fibers via the electrospinning is that the solution must consist of polymer of sufficient molecular weight or concentration and solution must be of sufficient viscosity. Viscosity has an important role in the formation of smooth fibers. At low viscosity, it is common to find beads along the fibers deposited on the collection plate.

Surface Tension: The initiation of the electrospinning requires the charged solution to overcome its surface tension. The surface tension has a part to play in the formation of beads, which will occur if the solution is not fully stretched, along the fiber length.

Solution Conductivity: The electrospinning involves stretching of the solution caused by repulsion of the charges at its surface. Thus if the conductivity of the solution is increased, more charges can be carried by the electrospinning jet. The increased charges carried by the solution will increase the stretching of the solution. As a result, smooth fibers are formed which may otherwise yield beaded fibers. The increased in the stretching of the solution also will tend to yield fibers of smaller diameter.

Dielectric Effect of Solvent: Generally, a solution with a greater dielectric property reduces the beads formation, as well as diameter of the resultant electrospun fiber. The bending instability of the electrospinning jet also increases with higher dielectric constant.

2.2.2.2 Processing Conditions

Other important parameters that affect the electrospinning process are the various external factors exerting on the electrospinning jet. These parameters have a certain influence in the fiber morphology although they are less significant than the solution parameters (Ramakrishna et al. 2005).

Voltage: The high voltage will induce the necessary charges on the solution and, together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. In most cases, a higher voltage will lead to greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field. These factors have the effect of reducing diameter of the fibers and also encourage faster solvent evaporation to yield drier fibers. But at a higher voltage, it has been found that there is a greater tendency for beads formation. Another factor that may influence the diameter of the fiber is the flight time of the electrospinning jet. A longer flight time will allow more time for the fiber to stretch and elongate before it is deposited on the collection plate. Thus, at a lower voltage, the reduced acceleration of



the jet and the weaker electric field may increase the flight time of the electrospinning jet which may favor the formation of finer fibers.

Feed rate: The feed rate will determine the amount of solution available for electrospinning. When the feed rate is increased, there is a corresponding increase in the fiber diameter or beads size. This is apparent as there is a greater volume of solution that is drawn away from the needle tip. A lower feed rate is more desirable as the solvent will have more time for evaporation.

Temperature: The temperature of the solution has both the effect of increasing its evaporation rate and reducing the viscosity of the polymer solution.

Effect of Collector: There must be an electric field between the source and the collector for electrospinning to initiate. Thus in most electrospinning setup, the collector plate is made out of conductive material such as aluminum foil which is electrically grounded so that there is a stable potential difference between the source and the collector. The charges on the fibers are dissipated thus allowing more fibers to be attracted to the collector. The fibers are able to pack closely together as a result.

Diameter of Pipette Orifice/Needle: A smaller internal diameter has been found to reduce the clogging as well as the amount of beads on the electrospun fibers. The reduction in the clogging could be due to less exposure of the solution to the atmosphere during electrospinning. Decrease in the internal diameter of the orifice was also found to cause a reduction in the diameter of electrospun fibers. However, if the diameter of the orifice is too small, it may not be possible to extrude a droplet of solution at the tip of the orifice.

Distance between Tip and Collector: Varying the distance between the tip and the collector will have a direct influence in both the flight time and the electric field strength. For independent fibers to form, the electrospinning jet must have time for most of the solvent to be evaporated. When the distance between the tip and the collector is reduced, the jet will have a shorter distance to travel before it reaches the

collector plate. Moreover, the electric field strength will also increase at the same time and this will increase the acceleration of the jet to the collector. As a result, they may not have enough time for the solvent to evaporate when it hits the collector. When the distance is too low, excess solvent may cause the fibers to merge when they contact to form junctions resulting in inter and intra layer bonding.

2.2.2.3 Ambient Parameters

Any interaction between the surrounding and the polymer solution may have an effect on the electrospun fiber morphology. Since electrospinning is influenced by external electric field, any changes in the electrospinning environment will also affect the electrospinning process (Ramakrishna et al. 2005).

Humidity: At high humidity, it is likely that water condenses on the surface of the fiber when electrospinning is carried out under normal atmosphere. As a result, this may have an influence on the fiber morphology especially polymer dissolve in volatile solvents. However, an increased in the humidity during electrospinning will cause circular pores to form on the fiber surfaces. The humidity of the environment will also determine the rate of evaporation of the solvent in the solution. At a very low humidity, a volatile solvent may dries rapidly.

Type of Atmosphere: The composition of the gas in the electrospinnig environment will have an effect on the electrospinning process. Difference gases have different behavior under high electrostatic field.

Pressure: When the pressure is below atmospheric pressure, the polymer solution in the syringe will have a greater tendency to flow out of the needle and causes unstable jet initiation. As the pressure decreases, rapid bubbling of the solution will occur at the needle tip. At very low pressure, electrospinning is not possible due to direct discharge of the electrical charges.

2.2.3 Applications of Electrospinning

Nanofibers made from many new synthetic polymers and biologically derived polymers are being considered for the use in tissue engineering, artificial organ applications, drug delivery, and for wound dressings. Nanofibers of DNA were made by Fang and Reneker (Fang and Reneker 1997).. The growth of cells on nanofibers was reported by Ko and Reneker (Ko et al. 1998).

Many kinds of bio-generated and bio-compatible materials are currently interested in many field of applications. Conventional methods for making fibers require so much material that they are often impractical. Electrospinning provides a convenient way to fabricate nanofibers using as little as a few hundred milligrams of the starting materials.

Nanofibers have found use in filters to remove particles and droplets smaller than 100 nm from liquids or gases. They are also being considered for the absorption of noxious molecules, since their specific surface area is so large, and their surface chemistry can be tailored to be selective to many kinds of substances. The application of pesticides to plants is another area where nanofibers may find large-scale applications. Nanofibers, spun in the field, and directed onto plants by a combination of electrical forces and air stream, will attach to plants with nearly 100% efficiency. This contrasts with the 3 to 5% sticking efficiency of conventional application methods for applying pesticides in form of dusts or sprays. The use of nanofibers to carry and attach pesticides could make the use of sophisticated but expensive pesticides cost effective. The burden placed on the environment by wasted pesticides would also be reduced.

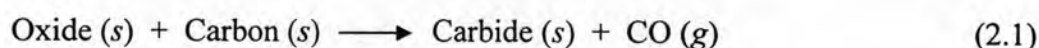
Nanofibers, perhaps at the scale of single polymer molecules, can be expected to play a role in micro-electro-mechanical devices (MEMS). The possibility of making ceramic material by chemical routes that use linear polymers as intermediates provides suggestions for ways to make ceramic nanofibers.

There are many studies in synthesizing titania nanofibers via the combination of electrospinning and sol-gel techniques (Lee et al. 2005; Li and Xia 2003; Watthanaarun et al. 2005). Titania nanofibers have been derived from titanium oxide/poly (vinyl pyrrolidone) (PVP) composite nanofibers prepared by using solution containing PVP and titanium tetraisopropoxide as precursors (Li and Xia 2003; Watthanaarun et al. 2005). This solution was injected through a needle under strong electrical field and the composite nanofibers made of PVP and amorphous TiO_2 were formed as a result of the electrostatic jetting. Calcination of these fibers, in the range from 500-800°C for 2-3 h, resulted in pure anatase TiO_2 nanofibers without contamination by other phase (Lee et al. 2005; Li and Xia 2003; Watthanaarun et al. 2005). The product transformed to rutile upon the calcinations above 800°C (Madhugiri et al. 2004). High calcination temperature resulted in shrinkage of fibers and the fiber was no longer straight (Watthanaarun et al. 2005). It was found that, after calcined at 500°C, the nanofibers remained as continuous structures with their average diameter reduced. This size reduction could be accounted by the loss of PVP from the nanofibers and the crystallization of titania (Li and Xia 2003). They also reported the followings: diameter of nanofibers increased and fibers obtained had boarder size distribution as the PVP concentration was increased; thinner nanofibers and narrow the size distribution were obtained when the strength of the electric field was increased; faster feeding rate of PVP solution often resulted in thicker fibers; and the use of titanium tetraisopropoxide at lower concentration led to the formation of thinner ceramic nanofibers (Li and Xia 2003; Watthanaarun et al. 2005). Furthermore, it was suggested that the electrospinning procedure could be extended to provide a generic route to nanofibers made of other oxides such as SnO_2 , SiO_2 , Al_2O_3 , and ZrO_2 (Li and Xia 2003).

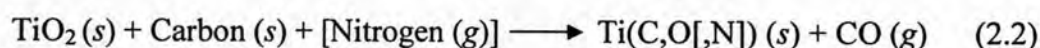
2.3 Carbothermal Synthesis of Titanium Nitride

Carbothermal reduction of oxides has been recognized as an economical method for the production of non-oxide ceramic materials. It was developed by Sanders Rosenberg and colleagues at Aerojet-General Corporation in the mid-1960s. The carbothermal reduction process can be used to synthesize nitrides and carbides of transition metals. The carbothermal reduction of titanium dioxide in inert or nitrogen-containing atmospheres is the most cost-effective method to produce titanium carbide, titanium carbonitride and titanium nitride powders for application in composite materials, such as cermets or black ceramics (Berger and Grunur 2002).

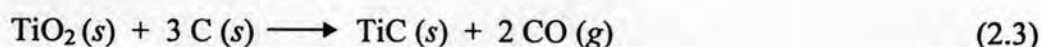
The carbothermal reduction in an inert atmosphere follows the general equation shown below:



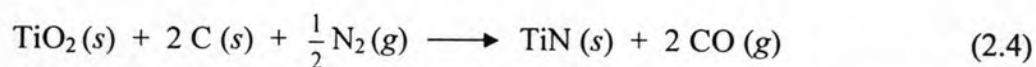
For the preparation of cubic phases in the pseudoternary system TiC–TiN–TiO, the reaction must be performed in a nitrogen-containing atmosphere in order that incorporation of nitrogen into the product can occur. This process can be described by the general equation shown below:



In both cases, one solid product is formed from two solid starting materials (oxide and carbon). In particular, the formation of titanium carbide can be described according to Eq. (2.3),



and the formation of titanium nitride is according to Eq. (2.4).

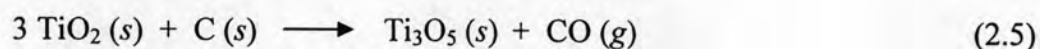


Both reactions are regarded as the boundary cases for the same process (Berger and Grunur 2002).

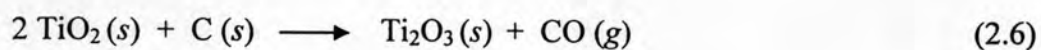
Several parameters affect the process. The kinetics of the reaction and the thermodynamically favoured products are mainly determined by temperature. According to thermodynamic calculations, the temperature at which reaction (2.4) becomes spontaneous is about 1160°C, while the temperature where carbon starts to react with TiO₂ according to reaction (2.3) is about 1260°C (Xiang et al. 2000). Morphology of the products is determined by the morphology and character is TiC of the starting materials as well as by the addition of catalysts. The reaction is also influenced by the preparation rate for the raw materials and by the residence time of the reaction (Shaviv 1996).

The sequence of solid intermediate reaction products obtained in argon is TiO₂, Ti_nO_{2n-1} (n>10), Ti_nO_{2n-1} (10>n>4), Ti₃O₅, may be Ti₂O₃, and TiC_xO_y, respectively (Berger et al. 1999).

It has been recently shown that the carbothermal reduction of titanium dioxide, either in anatase or rutile phase, by the global equation shown by Eq (2.3) is consisted of three successive reactions. Firstly, the reduction of the dioxide into suboxides, Ti₃O₅ or Ti₂O₃ if coarse TiO₂ powder is used, according to:

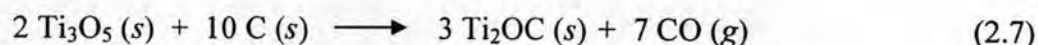


or

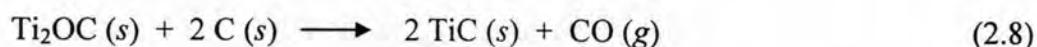


These reactions are rapid at temperatures higher than 1000°C and their rates are limited by the volumic diffusion of oxygen inside the oxide grains.

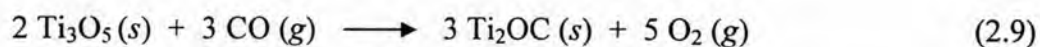
After that, a second solid-solid reaction occurs between carbon and the suboxide providing a well-defined oxycarbide Ti_2OC , such as:



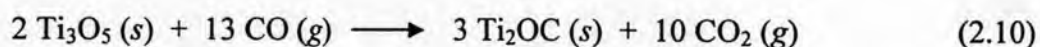
Using different grain sizes, it has been proved that the limiting step of this reaction is located on the surface of carbon. Lastly, the oxycarbide converts into titanium carbide through a slow diffusional process, according to the following equation:



Looking at these three reactions, it is appeared that the carbothermal reduction of the suboxide is a very interesting and it is a somewhat original mean to approach carbon oxidation at high temperatures and for low pressures of oxidizing gas. Actually, the formation of oxycarbide involves two simultaneous reactions. An equilibrium located on the suboxide's surface with an oxygen or carbon dioxide emission with a limiting reaction on the carbon's surface (Maitre and Lefort 1999):



Or



The very small amount of CO_2 that was present in addition to the CO at starting temperatures of about 900°C probably resulted from the reaction of adsorbed or bound oxygen species on the carbon black powder surface

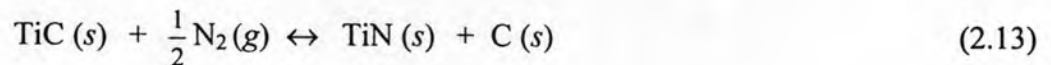


The Equation (2.11) is assumed to occur in all of the systems under investigation, starting also from lower temperatures (about 600°C). In the presence of carbon, the amounts of CO and CO₂ formed are governed by the Boudouard equation (Gruner et al. 2000)



The overall result is Equation (2.7).

The important problem of titanium nitride synthesis by carbothermal reduction and nitridation is associated with the formation of titanium carbide, because titanium carbide can also be produced by reaction of titanium monoxide with carbon (Equation (2.3)). Furthermore, titanium nitride can be converted to titanium carbide in the presence of carbon as well, according to the following reaction (Yu and Lin 1998):



Therefore, the reaction conditions are particularly important in establishing which compound will be formed during the carbothermal reduction and nitridation process.

Full conversion using titania and carbon according to stoichiometric ratio (1:2) can occur only if there is perfect contact between carbon and titania particles. Hence, an excess amount of carbon is always required for full transformation of titania to titanium nitride, and free carbon can remain in titanium nitride powder. Although the remaining carbon can be removed by heat treatment in air, the titanium nitride would be oxidized as well. Consequently, the powder synthesized by this method often suffers from purity problem associated with residual carbon and oxygen content.

As mention earlier, TiO_2 can be converted to TiN by the carbothermal reduction and nitridation. Yu and Lin (1998) had synthesized TiN from the mixture of pure titanium dioxide (anatase) and acetylene carbon black by the carbothermal reduction and nitridation at 1523 K for 1 h. It was found that anatase phase was transformed to rutile phase before it reacting with C and N_2 to produce TiN. The solid products were TiN and TiC. The fraction of TiN in the solid product could be increased by increasing reaction temperature or decreasing initial molar ratio of C/ TiO_2 . The gaseous products from the reaction were mostly CO and trace amount of CO_2 , which could be extending by increasing the reaction time or increasing the reaction temperature (Yu and Lin 1998).

Xiang et al. (1999) reported that $\text{TiC}_{1-x}\text{N}_x$ ultrafine powders could be synthesized by carbothermal reduction of TiO_2 , derived from sol-gel process, at high temperature in flowing nitrogen gas. $\text{TiC}_{0.5}\text{N}_{0.5}$ powders with particle size smaller than 100 nm were produced at 1550°C. Increased C content in the raw materials, elevated synthesizing temperature, prolonged holding time and low flow rate of nitrogen gas were beneficial in the production of $\text{TiC}_{1-x}\text{N}_x$ powders with low x value (Xiang et al. 2000).

Djaoued et al. (2001) studied phase transition and the thermal nitridation of nanocrystalline sol-gel titania films. Titanium tetraisopropoxide was used as the starting material in sol-gel process. Titanium oxide films prepared by the sol-gel method were heated to temperature in the range between 500 and 1100°C (heating rate of 5 or 20°C/min) in dry ammonia gas (with flow rate of 200-300 ml/min) in a quartz tube. The samples were held at the peak temperature for a time ranging from 1 to 5 h before cooled to room temperature under flow of dry nitrogen. Titania films heated to 400°C were found by XRD that they were crystallized in anatase phase but organic material was not completely eliminated. Heating to 800°C caused anatase phase to change to rutile phase. The thermal nitridation process yielded $\text{TiN}_x\text{O}_{1-x}$ ($x < 1$) and the lattice parameter was found to be sensitive to the composition of the coating solution. At constant heating rate, the conversion of titania to TiN depended not only

on the temperature but also on the composition of the coating solution and the time of nitridation (Djaoued et al. 2002).