CHAPTER I

INTRODUCTION

Titanium nitride (TiN), a non-oxide ceramic material, is an extremely hard (~85 Rockwell C Hardness or ~2500 Vickers Hardness), inert and biocompatible material. TiN is often used as a coating on titanium alloy, steel, carbide, and aluminum components to improve the substrate's surface properties. By far, the most common use for TiN coating, to enhance mechanical and chemical stabilities, is for edge retention and corrosion resistance of machine tooling, such as drill bits and milling cutters, which often improves the lifetime by a factor of three or more.

TiN has excellent infrared (IR) reflectivity properties, reflecting a spectrum similar to elemental gold (Au). Depending on the substrate material and surface finish, TiN has a coefficient of friction against itself (non-lubricated) in the range from 0.4 to 0.9. Typical formation of TiN is a rock-salt crystalline structure with a roughly 1:1 stoichiometry, but TiN can also exist over a wide composition range due to vacancies appearing on the nitrogen sublattice (Walker et al. 1998). TiN can be oxidized at 600°C in normal atmosphere, and has a melting point of 2930°C.

Because of metallic gold color of TiN, it is often used to coat costume jewelry and automotive trim for decorative purposes. TiN is also widely used as a top-layer coating, usually with nickel (Ni) or chromium (Cr) plated substrates, on consumer plumbing fixtures and door hardware. As a coating, it is also used to protect the sliding surfaces of suspension forks of bicycles and motorcycles. TiN is non-toxic, meets with FDA guidelines and has seen uses in medical devices and bio-implants, as well as aerospace and military applications. Such coatings have also been used in implanted prostheses (especially hip replacement implants). The TiN films are usually formed by either reactive growth (for example, annealing a piece of titanium in nitrogen) or physical vapor deposition (PVD), with a tickness often about 3 micrometers. Its high Young's modulus (600 Gpa) relative to titanium alloys

(100 GPa) means that thick coatings tend to flake away, making them much less durable than thin ones.

Though less visible, the thin films of TiN are also used in the semiconductor industry. In copper-based chips, such films find use as a conductive barrier between silicon devices and the metal contacts. While the film blocks diffusion of metal into silicon, it is conductive enough (30–70 $\Omega\cdot$cm) to allow a good electrical connection. In this context, TiN is classified as a "barrier metal", even though it is clearly a ceramic from the perspective of chemistry or mechanical behavior.

The methods for TiN powders production are classified as follows: (1) solid state methods, such as chemical reduction of titanium oxide by nitrogen and ammonia; direct reaction of Ti with N; and self-propagating high-temperature synthesis, (2) gaseous state methods, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) process, and (3) liquid state methods, such as thermal decomposition process (Xiang et al. 2000).

Bulk TiN objects can be fabricated by packing powdered metallic titanium into the desired shape, compressing it to the proper density, and then igniting it in an atmosphere of pure nitrogen. The heat released by the chemical reaction between the metal and gas is sufficient to sinter the nitrided product into a hard, finished item. However, there are many drawbacks for these methods. For example, powders obtained from solid state methods usually have large particle size and low purity. The processes of liquid and gaseous cannot be easily controlled and the raw materials are generally very expensive. So, there is a necessity to develop a new way to synthesize TiN powders conveniently and effectively (Xiang et al. 2000).

Sol-gel process is a versatile solution process for making high purity and homogeneity ceramic and glass materials. It has many benefits, for instance, good dispersion of the components, narrow distribution of particle sizes, larger specific surface and higher purity when compared with the conventional methods listed above. In addition, this process does not require special equipment and can be finished with low cost (Xiang et al. 2000). According to the fundamental nature of the sol-gel process, it is possible to generate ceramic material at temperature close to room temperature. By applying the sol-gel process, it is also possible to fabricate ceramic or glass materials in a wide variety of forms, e.g. ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials.

The conventional practice to make ceramic fibers is to extrude molten ceramic at very high temperature through a set of fine holes approximately 3 millimeters in diameter. However, in this process, a strict control of the diameter has not been possible. Moreover, ceramic fibers smaller than 1 micrometer in diameter are considered very carcinogenic and those finer than 3 micrometers in diameter can get ingested into the lungs during the manufacturing process and can cause serious respiratory diseases. They can also cause severe skin irritation. As a fair proportion of the fibers manufactured by the conventional process contain these small fibers, it is considered as health-hazards to those involved in manufacturing and handling of those fibers.

Recently, a team from Warwick University has developed a 'sol gel blow spinning technique' which produces fibers of very even diameters. The process uses sols, microsuspension of particles which consolidate to form the ceramics when finally heated to moderately high temperatures (much lower than the melting point). In the Warwick process, the sols are made more concentrated and viscous by the addition of a small amount of organic polymer which helps the formation of the fibers.

Nanofibres have great potential for a wide range of applications due to the small diameter providing very large surface area-to-mass ratio. Electrospinning, which was patented by Formhals in 1934 (Li and Xia 2004), is a simple and quick technique for producing fibers with nanoscaled diameters applicable for wide range of materials. It is a process that cerates nanofibers through an electrically charged jet of viscous solution or melt. It has also been applied to produce ceramic nanofibers. The electric field draws this droplet into a structure called a Taylor cone (Li and Xia 2004). In the continuous operation, the number of fibers can be formed with in short period of time, as short as a few seconds.

Carbothermal reduction of oxides has been recognized as an economical method for the production of non-oxide ceramic materials. The carbothermal reduction of titanium dioxide in inert or nitrogen-containing atmospheres is an economical method of producing carbide, oxycarbides, nitride, or carbonitride of titanium which represent a current field of interest in materials research of ceramics and hard materials (Xiang et al. 2006). In the carbothermal reduction processes, one solid and one gaseous reaction product are formed from two solid materials. For example, carbide and CO which are solid and gaseous, respectively, are formed form oxide and carbon (Berger et al. 1999).

In this research, sol-gel process and electrospinning technique are incorporated to prepare fiber mats of titania/polymer composites. Then, titanium nitride is synthesized by subsequent carbothermal reduction and nitridation of the obtained composites. This study intends to obtain material which combines the advantage of high strength ceramics and thin fiber together.

Effects of various parameters, such as Ti-to-C ratio of the composite fibers, pretreatment conditions for of titania fibers and conditions for the carbothermal reduction and nitridation on properties of titanium nitride produced are also investigated.

The present study is arranged as follows:

Chapter I is the introduction.

Chapter II describes the basic theory involved in this work such as sol-gel process, electrospinning process and carbothermal reduction and nitridation process. Furthermore, literature survey of the previous works related to this research is also presented in this chapter.

Chapter III shows materials, the experimental equipments, the preparation procedures of titanium nitride fibers and characterization techniques.

Chapter IV describes the experimental results and expanded discussion of the research.

In the last chapter, the overall conclusions of this research and some recommendations for future work are given.