CHAPTER 1

INTRODUCTION

1.1 Overviews

Recent Gamma Ti-Al alloy is increasing interested because of their low density, high stiffness, high oxidation resistance, high creep resistance, high melting temperature and excellent specific strength at high temperature. Hence, gamma Ti-Al alloy based on Ti_3Al and TiAl, which offers in many potential applications in aerospaces, automotive industries and high temperature applications such as turbine blades, engine valves and turbocharger rotors [1-3].

The major disadvantage of this alloy is low ambient temperature ductility and poor surface properties. Ductility can be improved by adding some elements like Nb, Cr, Mn, Mo, W, Ta and V. Surface properties such as hardness and wear resistance may be improved by surface modification. There are many processes used to modify alloy surfaces. Among those are chemical vapor deposition (CVD), physical vapor deposition (PVD), plasma immersion ion implantation and deposition, plasma-enhanced chemical vapor deposition, magnetron sputtering, ion implantation and others [4-9].

Plasma immersion ion implantation technique has become popular even in the industrial application. It has various features as a new methodology for physical surface modification. In the plasma immersion ion implantation and deposition processes, negative pulse voltages are applied to a processed target and the ions accelerated at the sheath are implanted onto the sample surface. This technique is highlighted with its advantages such as the non-line-of-sight processing, high energy bombardment, etc [10-12].

In this study, the plasma deposition technique is very interesting for surface modification of the gamma Ti-Al alloys due to no change and damage of bulk properties, easily coating for complex shape and purity over many other techniques. It is a clean technology as well.

Many researchers study on how to improve mechanical properties of the surface. The coating of TiN, TiC and TiCN have been widely used to improve the hardness, wear resistance and corrosion resistance. TiC has many merits, such as high hardness and melting temperature, thermal stability, low friction coefficient, high electrical and thermal conductivity as well as excellent chemical inertness. Because of its high hardness and low friction coefficient, it has great potential in surface modification on industrial components. Diamond-like carbon (DLC) is well known due to its excellent properties such as high microhardness, low friction coefficient and good chemical inertness. Therefore, DLC is suitable for coating on the surface. It can be prepared by using several methods such as RF-PECVD [13], pulsed laser deposition [14], reactive magnetron sputtering [15], magnetron plasma source ion implantation [16] and PBII-enhanced microwave ECR chemical vapor deposition [17]. DLC is a metastable form of amorphous carbon containing both sp^2 (graphite like) and sp^3 (diamond like) bonds [18]. In DLC films, sp^3 bonds are responsible for the mechanical properties. But for sp^2 bonds, which lie near the Fermi level, they control the optical and electronic properties of the films [19]. It is believed that the properties of DLC depend on the structure of the film [20]. However, it is not easy to grow amorphous carbon films with very high fraction of carbon atom in sp^3

hybridized tetrahedral bonding configuration [21]. The higher ratio of sp^3/sp^2 carbon atom, the closer the DLC film properties approach those of diamond. Therefore a large amount of work has been devoted to determine the sp^3 carbon content in DLC.

This section describes the general structure together with properties and applications of Ti-Al alloys. The key purpose is to describe the surface modification and classify surface deposition techniques prepared by the plasma deposition. Therefore, general background of the plasma and types of plasma deposition technique are given in this section.

1.2 Titanium aluminium alloys

Titanium alloys offer superior specific strength in high temperature (over 590^oC) and low temperature (-253^oC), which make them appropriate in ultra high-speed aircraft and account for their uses on the space shuttles. The superplastic nature of titanium allows it to deform over 200% without necking or cracking when it is heated at around 925^oC in a process known as superplastic forming. Advances in new technologies such as superplasticity forming and diffusion bonding have furthered the potential of titanium. Titanium is nonmagnetic and has a lower linear coefficient of expansion and lower thermal conductivity than steel or aluminium. Zirconium, beryllium and titanium are allotropic and exist in a hcp structure (alpha) at below 885^oC and a bcc structure (beta) above that temperature. The composition of any titanium binary alloy consists of three phase fields in the solid state: α, $(\alpha+\beta)$, and β. Various alloying elements alter the effect of the structure and stabilize the alpha or beta phases. Alpha alloys have superior creep resistance and heat treatable. Beta phase alloys have excellent forge ability and fracture toughness. Alpha-beta alloys have good superplastic elongation and good strength characteristics. Alloys that are based on the intermetallic compound gamma titanium aluminide (γ-TiAl) have good stiffness, high temperature strength, and low density. Their applications in advanced gas engines, airframes, and automotive components are quite easy to understand. Titanium is an example of a biomaterial that serves as implanted for joint replacements and dental reconstruction.

The intermetallic TiAl compound or γ–TiAl based alloys are highly interested in recent years. They are considered for use in aerospace applications in both structural (airframes) components (aircrafts, space satellites and missiles) and jet engine components (turbine blades, engine valves and turbocharger rotors) such as Boeing’s 777 composed of the largest amount of titanium ever in a Boeing aircrafts. In fact, commercial and military aircrafts now use 80% of American-made titanium [22]. Because their high temperature strength, low density, high melting point and adequate creep resistance at high temperature [23-28].

Currently, available γ alloys contain approximately 46 to 52 at% Al and 1 to 10 at% M, with M being at least one of the following: vanadium, chromium, manganese, niobium, tantalum, tungsten, and molybdenum. Single-phase γ alloys contain third alloying elements such as niobium or tantalum that promote strengthening and further enhance oxidation resistance. Third alloying elements in two phase alloys can raise ductility (vanadium, chromium, and manganese), increase oxidation resistance (niobium and tantalum), or enhance combined properties. Creep properties of γ alloys, when normalized by density, are better than those of superalloys, but they are strongly influenced by alloy chemical and thermomechanical processing. Increase of aluminium content and additions of tungsten or carbon increase creep resistance, but lower ductility [29].

The structures of these alloys could be verified by Ti-Al binary phase diagram [14]. The Ti-Al binary phase diagram is shown in Figure 1.1 [30].

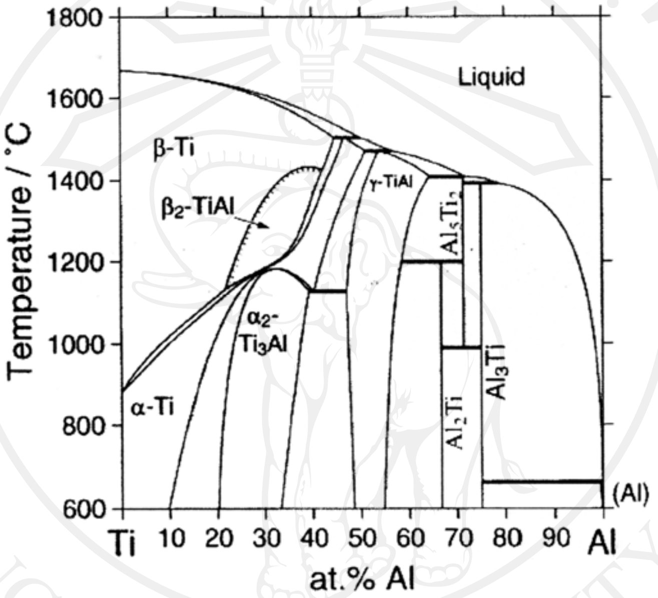
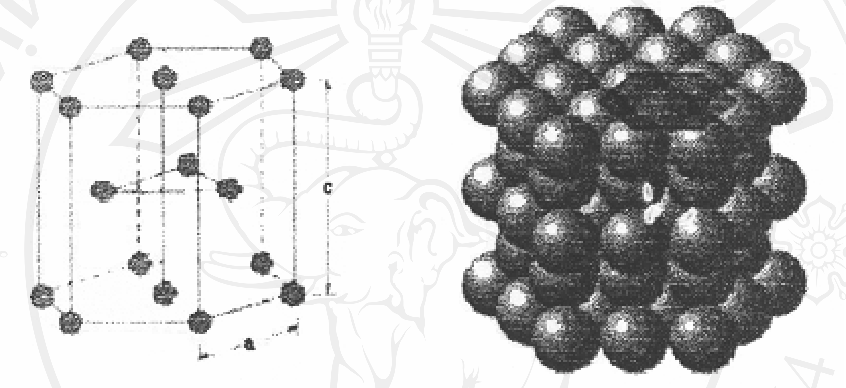


Figure 1.1 Ti-Al phase diagrams assessed by I. Onuma [30].

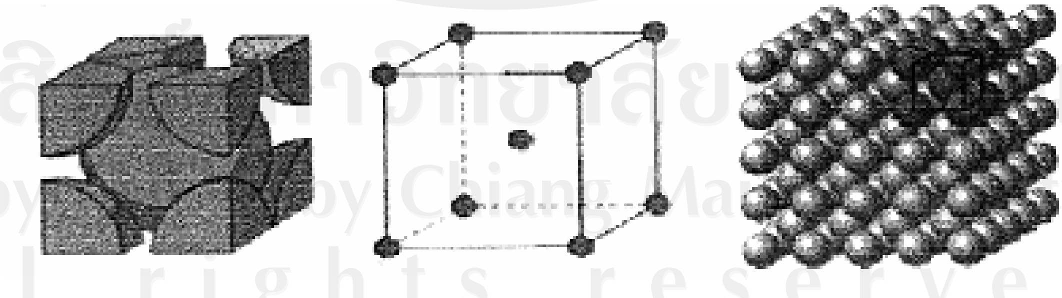
The phase in Ti-Al binary was categorized into 3 groups.

i) Disordered solution are α-Ti (hexagonal close-packed), β-Ti(body-centered cubic), liquid and Al (face-centered cubic) and are given in Figures. 1.2 to 1.4



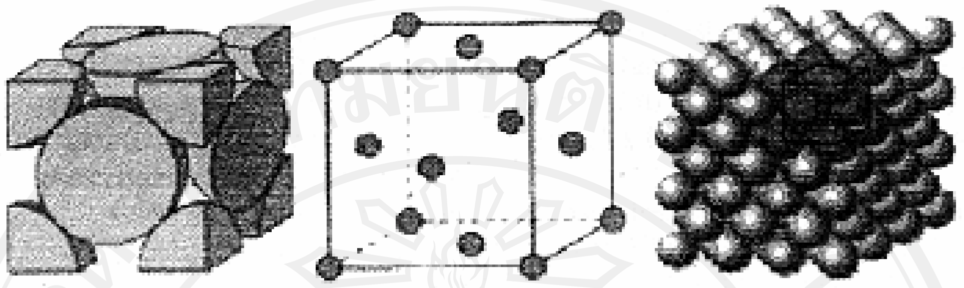
(a) (b)

Figure 1.2 The hexagonal close-packed crystal structure α-Ti phase [31].



(a) (b) (c)

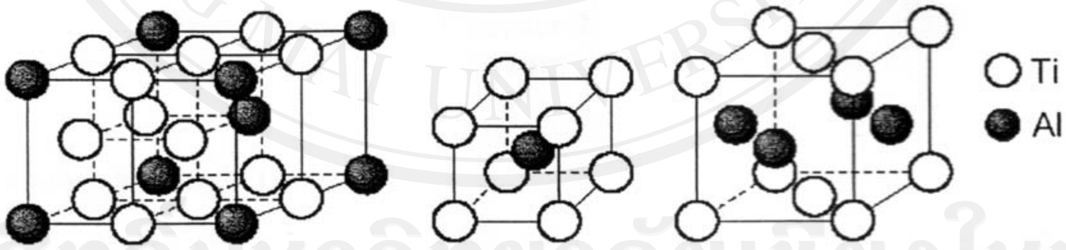
Figure 1.3 The body-centered cubic crystal structure β-Ti phase [31].



(a) (b) (c)

Figure 1.4 The face-centered cubic crystal structure Al phase [31].

ii) Ordered solution phases which are α_2-TiAl (hexagonal close-packed), β_2-TiAl (body-centered cubic) and γ-TiAl (face-centered cubic) and are given in Figure 1.5



(a) (b) (c)

Figure 1.5 Structure of ordered phase in the Ti-Al binary system: a) α_2-Ti Al b)β_2-Ti Al and c) γ-TiAl [31].

iii) Stoichiometric compound phase are Al_2Ti, Al_5Ti_2 and Al_3Ti.

The two alloys are consisted of the majority of γ-TiAl phase and the minority of Al_2Ti compound phase.

There are two major disadvantages for TiAl based alloys. They have very limited ductility at room temperature and poor surface properties at high temperature [24-27]. The former can be improved by the addition of some elements, but the latter by surface modification. Many studies have reported that addition of Nb, Cr, Mo, W, Ta, or V is to improve the fracture toughness, ductility and corrosion resistance in TiAl alloys [27-28] while the dispersion of hard boride particles, TiB_2 or CrB, is to improve the wear resistance.

Titanium carbide (TiC), titanium nitride (TiN) and titanium carbonitride (Ti(C,N)) coatings have been widely applied to improve hardness, wear resistance and corrosion resistance in many application such as cutting tools and dies [25-26, 27-31]. Ti(C,N) coating had a higher wear resistance than TiN coating. Very little internal stress TiC coating tends to peel off owning to the high internal compressive stress [27-29].

There are many methods to deposit these films, such as physical vapor deposition (PVD) [32-36], chemical vapor deposition (CVD) [37-38], plasma deposition [24,33-35], cathodic arc ion plating process (CA) [27-30, 39], ion implantation [40] and direct metal-gas reaction [25-26, 31]. The direct metal-gas reactions method is less costly and no toxic chemicals are used [25-26].

1.3 Thin film deposition

Thin films have been prepared ever since vacuum systems first became available, but deposition as a means of producing films for device purposed is a development of the past 40 years. Thin metallic film coatings on glass or plastic were among the first to be exploited for optical purposes, ranging from mirrors to sunglasses, and this still continues as a majority. Typically, high vacuum and high throughput business as thin film deposition processes have developed very rapidly over the past 25 years. The following sections describe some of these developments in outline.

1.3.1 Thermal evaporation and uniformity of deposits

This technique is the simplest concept, corresponding to raising the temperature of the source material, either in an open boat, suspended on a wire, or by any other convenient means so that the material evaporates or sublimes onto the substrate. The boat/wire is typically chosen as a high temperature material such as W or Mo, and must not react adversely with the evaporant. Unless particular precautions are taken, the evaporant will be deposited all over the inside of the vacuum system, and will therefore be both inefficient in the use of the source material, very messy for the vacuum system, and will not reduce a uniform deposit.

The production of uniform deposits with high throughput is required for industrial processes, and this usually means that the substrate has to be rotated. This movement is required because the emission from the source is more or less peaked in a particular (forward) direction, so that the deposited films are thinner at the edges.

In order to deposit high temperature materials, or materials which interact with the crucible, electron beam evaporation is required. The design typically includes a heavy duty filament to emit a number of milliamps of current, and several kilovolts of high voltage in order to deliver the necessary power. The electron beam is directed onto the sample surface by a shaped magnetic field, typically using an inbuilt permanent magnet. The heating is very localized, and care is required to ensure that it is localized where it should be; this is also the case when using pulsed ultra-violet eximer lasers. Laser ablation, sometimes called pulsed laser deposition (PLD), has typically been used to deposit ceramic materials, including high temperature superconductors. It produces very rapid deposition in which chunks of material can break off and be deposited during the immense peak powers which typically last for 10-20 ns. A particular advantage of rapid evaporation is the control of stoichiometry, since other species do not have time to reach the surface during the evaporation phase.

1.3.2 Sputtering and ion beam assisted deposition

There are many uses for ion in connection with the production of thin films. Sputtering with relatively low energy (100 eV-2 keV) ions is often used for cleaning samples, while higher energy (5-200 keV) ions is for doping layers with electrically active impurities. Ions can also be used for deposition. Individual ions, or changed clusters can be deposited at a range of energies. Clearly, the fact that the ions are charged allows extra control, and there are various methods by which this can be done. Directed ions beams from an accelerator from the most obvious possibility, but plasma and magnetron sources are also widely used.

One of the main claims for Ion Beam Assisted Deposition (IBAD) or Ion Beam Sputter Deposition (IBSD) is that better quality deposits can be obtained at lower temperature substrates, thus avoiding large scale interdiffusion which results from high temperature processing. However, the deposited films adhere well to the substrates because of the localized limited mixing caused by the ion impacts. This is one example of device engineers trying to reduce the 'thermal budget' and so produce sharper interfaces between dissimilar components. Another possibility is to produce cluster deposition with applied voltages. This has been termed Ionized Cluster Beam (ICB) technology by the inventors. Yet another possibility is to use ion beams to react with the substrate and grow compounds such as oxides or nitrides at and near surfaces.

Nonetheless, ion beam assisted methods are very widespread and are of great economic importance; sputter deposition, in particular, has high throughput for the production of (textured) polycrystalline thin films of a wide variety of materials. The language used to describe such as ion based processes necessarily starts from a similar superior point to that used to describe thermal evaporation [41].

1.3.3 Chemical vapor deposition (CVD)

CVD relies on reactive carrier gases to transport precursors of the desired material to the substrate surface. Here they react with other gases or decompose to produce stable reaction products, which are deposited on the substrate. CVD methods are among the most versatile deposition techniques because a wide range of chemical reactants and reactions can be used to deposit a large number of different types of films for a wide range of applications.

A number of variations on and subcategories of CVD techniques have been developed. Some of the more common techniques include:

- Metal-organic CVD (MOCVD) : This technique uses a thermally heated reaction chamber and sources that are organometallic in nature. Some examples of this technique are the deposition of III-V and II-VII compound semiconductors for device applications.

- Plasma-enhanced CVD (PEVCD) : This technique uses a plasma discharge to provide the excitation necessary for chemical reaction to occur. PECVD is often used for diamond deposition. Other applications of this technique include the deposition of silicides, silicon, and refractory metals.

- Atmosphere pressure CVD (APCVD) : This technique does not require a vacuum, and it can be performed in a continuous process with a belt transporting a continuous flow of substrates in and out of the deposition chamber. Applications of this technique include oxides and silicate glasses.

Many variations on these basic processes have been developed for and adapted to the deposition of a wide variety of materials.

A typical process flow for a CVD consists of the following:

1. The reactants are transported to the deposition reactor in a carrier gas flow.

2. Gas phase reactions are initiated in the reaction chamber by an energy source, such as a plasma discharge or thermal activation. The products of these reactions are the film precursors.

3. The film precursors are transported to the heated substrate surface in the carrier gas flow, and they are condensed or absorbed by the substrate surface.

4. Deposited species diffuse across the substrate surface to growth sites on the surface.

5. The deposited film grows and reaction by-products are desorbed and transported away from the deposition region by the carrier gas [42].

1.4 Plasma

On earth we live upon an island of “ordinary” matter. The different states of matter generally found on earth are solid, liquid, and gas. We have learned to work, play, and rest using these familiar states of matter. Sir William Crookers, an English physicist, identified a fourth state of matter, now called *plasma*, in 1879.

Plasma temperatures and densities range from relatively cool and tenuous (like aurora) to very hot and dense (like the central core of a star). Ordinary solids, liquids, and gases are both electrically neural and too cool or dense to be in a plasma state. The word “PLASMA” was first applied to ionized gas by Dr.Irving Langmuir, an American chemist and physicist, in 1929.

Plasma consists of a collection of free-moving electrons ions and neutral particles. Energy is needed to strip electrons from atoms to make plasma. The energy can be of various origins: thermal, electrical, or light (ultraviolet light or intense visible light from a laser). With insufficient sustaining power, plasmas recombine into neutral. Plasma can be accelerated and steered by electric and magnetic field, which allows it to be controlled and applied.

At present, the most important plasma application is in the production of large scale microelectronic circuits, which are used in almost any electronic device such as personal computers. Plasma processing of materials affects several of the largest manufacturing industries, including defense, automobiles, biomedicine, computer, hazardous waste, aerospace and telecommunications as show in Figure 1.6 [43].

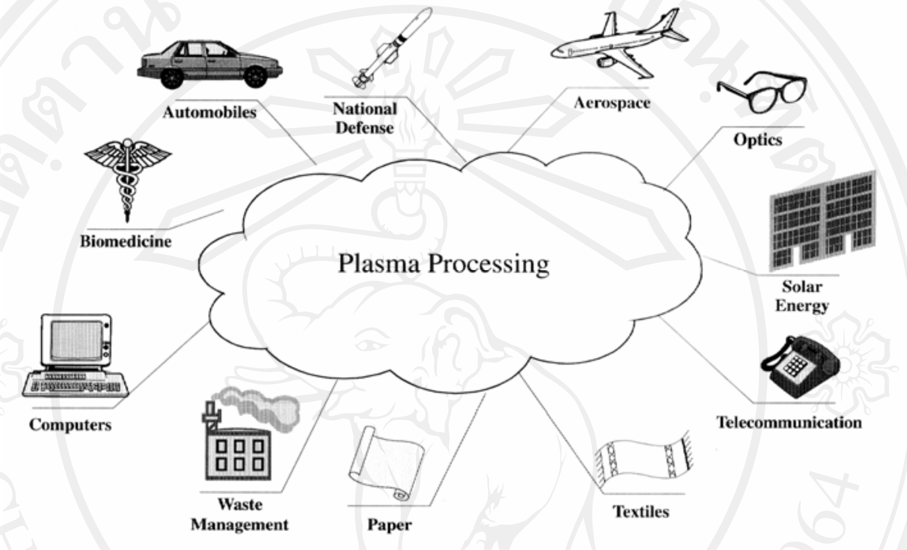


Figure 1.6 Plasma processing industry [43]

1.4.1 Plasma modification of materials

Plasma modification of materials is used to improve the surface properties without changing their bulk properties. These processes are carried out by ion implantation into the materials. This method has become economically having the power to attract in high technological centers and can be accomplished on metals and alloys, semiconductors, ceramics, insulators and polymers.

1.4.1.1 Plasma-assisted chemical vapor deposition (PACVD)

The refractory (i.e. unmanageable, difficult to melt, etc.) metals are best deposited by plasma using sputtering or *plasma-assisted chemical vapor deposition* (PACVD). Plasma is used in a reactor to initiate chemical reaction in gas with an electric discharge. For a standard chemical vapor deposition (CVD), the interaction between the substrate and the vapor occurs at high temperatures. Sometimes these high temperatures damage the substrate. By using the PACVD method the ions are attracted from the (hot) plasma toward the substrate, which can be kept at much cooler temperature than in the CVD method.

In a plasma atmosphere it is possible to produce materials that are difficult or impossible to produce with conventional chemistry. Furthermore, while in a pure chemical industry there are many subsequent processing steps, such as synthesizing, deposition, etc., in a plasma reactor all these processes are accomplished simultaneously in one step.

1.4.1.2 Plasma polymerization (PP)

PP is similar to PACVD. The main difference is that in the PP case the deposition is for organic materials (polymers) while the PACVD is for inorganic materials. For example, when tetrafluoroethylene gas is injected into a plasma, a Teflon-like film is deposited on a substrate. The plasma turns this starting gas into fragments which either nucleate into fragments which either nucleate into a polymer film at the surface of the substrate or polymerize into a chain of clusters.

Under suitable conditions, monomers (units of one compound) introduced into a plasma environment can combine to create polymers (many repeated unit of one or more compounds). Plasma processing can produce thin films of polymers necessary in many important applications such as coating on other materials, multiple layers for magnetic recording tapes or disks and plastic wrapping materials. The magnetic recording industry is also a multi-billion dollar enterprise.

The coating with the above polymers is very important in the biomedicine. It is possible for the development of new prosthetic devices, implants and tools for medical monitoring and diagnostics.

1.4.1.3 Ion implantation

Surface properties of materials are improved without having to change their bulk properties through implantation of specific ions into the materials. The following surface properties can be modified by plasma-assisted chemical vapor deposition:

1. the hardness of the material
2. fatigue (extreme weariness from prolonged exertion or stress)
3. toughness (the ability to withstand great strain without breaking)
4. adhesion (state of being united)
5. friction (the resistance of a surface to its relative motion with another surface)
6. dielectric properties (insulator materials capable of maintaining an electric field with minimum loss of power)
7. corrosion (deterioration through chemical action)
8. resistivity (the ability of opposing an electrical current)
9. oxidation (the ability to combine with oxygen)

A plasma source can be used to extract ions in order to implant them into the materials to be modified. A strong electric field exists in a plasma near the cathode (the cathode sheath) see Figure 1.7. This electric field accelerates the positive ions arriving from the plasma into the cathode. Inside the plasma tube, the pressure is kept very low (in a low density plasma). The ions can be accelerated to strike the cathode with very high energies of 100 keV or higher. At this level of energies, the ions can penetrate the cathode and be implanted. In this way, the hardness and lubricity of tools are improved. In a similar way, at lower energies, this technique is used for the microelectronic industry [43].

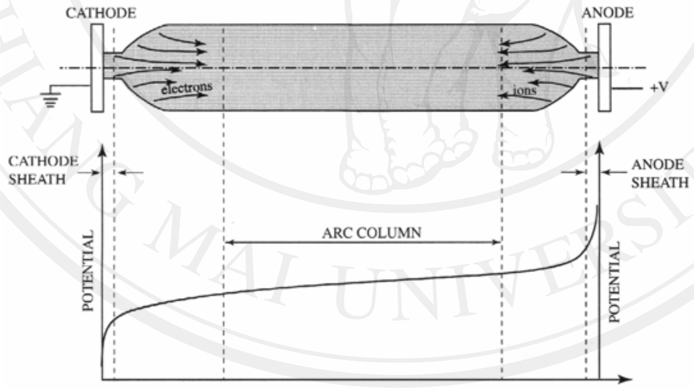


Figure 1.7 A schematic presentation of two sheath formations, near the anode and near cathode in an arc discharge [43].

It has been shown that the ion implantation can modify and improve the mechanical properties of steel. The wear resistances increased by the use of carbon, boron, titanium and molybdenum. They have also shown good results.

Today, scientists believe that it is cheaper and better to modify the surface of a material than to change its bulk properties. This can be better achieved by plasma modification of materials.

1.4.1.4 Plasma immersion ion implantation and deposition

In plasma immersion ion implantation and deposition (PIII-D), the target to be implanted is immersed in plasma and respectively pulsed to a high negative voltage. An expanding boundary layer (sheath) forms around the target during the voltage pulsing. The electric field within this expanding sheath accelerates ions toward all target surfaces simultaneously, emanating the need for target manipulation or masking. This allows a more uniform implantation, and also the treatment of a variety of shapes without a complex refixturing effort. A disadvantage of this process is that the ion energy and species can not be selected as in magnetically filtered beamline implantation, since the negative voltage pulse applied to attract all positively charged ions in the plasma [44].

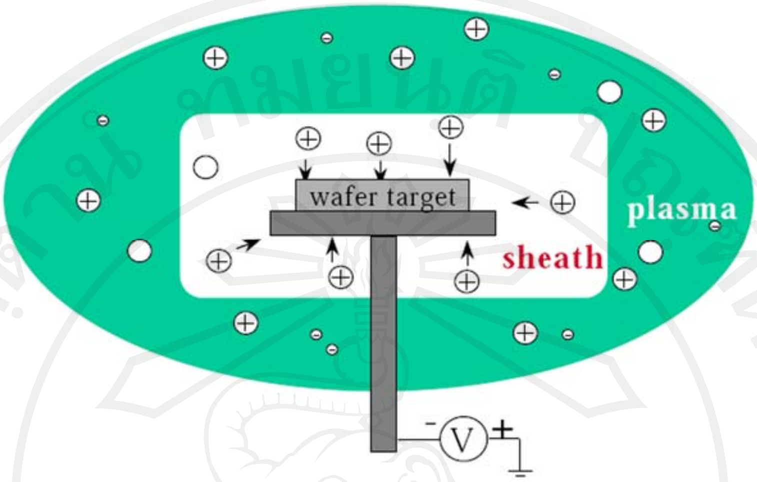


Figure 1.8 The feature of plasma immersion ion implantation technique.

1.5 The objectives of this research

In this study, emphasis is to improve the hardness of the gamma Ti-Al alloy surfaces by coating diamond like carbon and carbide thin films on the alloy surfaces. These films were synthesized by plasma deposition technique in a acetylene (C_2H_2) gas at various bias voltage and also deposition times. Additional, attention is to study phases, structure and morphology of the deposited films.