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STRUCTURE AND PROPERTIES OF TITANIUM
NITRIDE STRENGTHENED MICROLAMINATE COMPOSITES

by

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ABSTRACT

This investigation examines the structure and properties of titanium nitride strengthened microlaminate composites. Reactive ion plated titanium nitride (TiN) was deposited onto titanium, nickel, and aluminum foils which were subsequently hot pressed to form microlaminate composites. The TiN volume percent was varied and its effect upon the structure and properties of the composites investigated. Scanning electron microscopy (SEM) has been used to characterize the film morphology, the fracture behavior of the composites, and the ceramic/metal interfaces formed during reactive ion plating and hot pressing. The mechanical properties of the microlaminate composites were determined by standard tensile testing. Correlations between the microstructures, mechanical properties, and processing parameters are presented.

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TABLE OF CONTENTS

Section	Page
I. INTRODUCTION	1
II. REVIEW OF LITERATURE	4
A. COMPOSITES	4
1. Metal-matrix Composites	5
2. Laminated Composites	7
B. INTERFACES	9
C. LAMINATE FABRICATION METHODS	13
D. ION PLATING	15
E. MATERIAL EVALUATION	17
F. DEFORMATION AND FRACTURE ANALYSIS	19
III. EXPERIMENTAL PROCEDURE	23
A. MATERIALS DESCRIPTION	23
B. ION PLATING SYSTEM	23
C. DEPOSITION PROCEDURE	26
D. HOT PRESSING	31
1. System Description	31
2. Pressing Procedure	31
IV. ANALYTICAL PROCEDURE	33
A. MECHANICAL TESTING	33
1. Sample Fabrication	33
2. Uniaxial Tensile Testing	33
B. ELECTRON MICROSCOPY	34

Section	Page
V. RESULTS AND DISCUSSION	36
A. MECHANICAL PROPERTIES	36
1. Ti/TiN Microlaminate Composites	37
2. Al/TiN Microlaminate Composites	41
B. SCANNING ELECTRON MICROSCOPY	42
1. Ti/TiN Microlaminate Composites	42
2. Al/TiN Microlaminate Composites	51
VI. SUMMARY	56
A. COMPOSITE FABRICATION	56
B. PROPERTIES	56
C. STRUCTURE AND CHEMISTRY	57
VII. CONCLUSIONS	58
VIII. REFERENCES	60

I. INTRODUCTION

The research described in this thesis involves a study of the structure/property/processing relationships for microlaminate metal matrix/titanium nitride composites fabricated by reactive physical vapor deposition (reactive ion plating). Specific composite systems chosen for the investigation are Al/TiN, Ni/TiN, and Ti/TiN, with the titanium nitride (TiN) phase deposited by reactive ion plating [1]. A major objective of the study is to determine how accurately existing laminate composite mechanics theories correlate with the microstructure/mechanical property relationships for these materials. Since the interface between the matrix and strengthening material greatly influences the properties of the composite, the interfacial microstructure and microchemistry formed during reactive ion plating and after hot pressing are analyzed. The role of interface structure and chemistry on the composite's deformation behavior is addressed.

Reactive ion plating was chosen as the TiN deposition technique by virtue of its ability to produce highly adherent films (i.e., a strong interface). Hot pressing was subsequently utilized to densify and diffusion bond the individual metal/ceramic layers to produce a microlaminate composite suitably sized for mechanical testing. The metal matrix composite systems of titanium, nickel, and aluminum have possible aerospace applications [2,3], but were chosen primarily for their different but simple crystal structures. TiN, an electrically conductive, high elastic modulus, and high melting point ceramic [4], has commercial hard-facing and electrical applications [5,6]. It is also potentially useful as a dispersed strengthening phase for high temperature composite materials.

Mechanical properties analyzed in this program include the ultimate tensile strength, uniform strain and strain to failure. These properties are correlated with controlled variations of the composite's TiN volume percent. Scanning electron microscopy (SEM)

has been used to characterize film morphology, fracture behavior of the composites, and differences in the structure and chemistry of the reactive ion plated and hot pressed ceramic/metal interfaces. Correlations between the microstructural information and the physical properties are presented.

The results of this research will be applied in future work towards improving the microstructure, chemistry, and processing of these engineered microlaminate composite materials for optimum mechanical properties and performance. Fundamental questions addressed by this research program include:

1. How effective is ion plating as a technique for producing metal/ceramic microlaminate composite materials?
2. How are the microstructures and chemistries of the ion plated films and metal/ceramic interfaces affected by the processing parameters? How does the ion plated interface differ chemically and structurally from that of the hot pressed interface?
3. How effectively does hot pressing form a metallurgically sound bond between the ion plated film and the substrate? What processing parameter combinations (mainly time, temperature, and pressure) optimize this step of the fabrication process?
4. What type of testing and fracture analysis should be conducted to provide the necessary mechanical and physical property information to best characterize the composite material and its fabrication process? Does the laminate structure generally provide desirable mechanical properties? What is the mode of failure of the composite material?

5. How can the mechanical behavior of these microlaminate materials be interpreted by composite theory? Does the composite conform to conventional theories such as "rule-of-mixtures" or does its behavior deviate and require more complex analyses?

6. Do these engineered microlaminate metal/ceramic composite materials with their novel fabrication processes possess the necessary mechanical properties to justify further study for industrial or military applications?

II. REVIEW OF LITERATURE

A. COMPOSITES

Composites encompass a wide range of materials internally arranged in certain specific configurations to obtain mechanical or other properties tailored to specific applications. According to Broutman and Krock [7], a material must meet the following criteria in order to be categorized as a composite material:

- It must be man-made.
- It must be a combination of at least two chemically distinct materials with a distinct interface separating the constituents.
- The separate materials forming the composite must be combined three-dimensionally.
- It should be created to obtain properties which would not otherwise be achieved by any of the individual constituents.

The advantage of composite materials is that they usually do exhibit the best qualities of their constituents and often some qualities that neither constituent possesses alone. For example, the properties that can be improved by forming a composite material include:

- Strength
- Stiffness
- Fatigue life
- Wear resistance
- Weight
- Corrosion resistance

- Temperature-dependent behavior
- Thermal conductivity
- Attractiveness.

Composite materials generally consist of a bulk material, called the matrix, and a filler of some type, for example, fibers, whiskers, particles, or films. The composite material can consist of fibers, whiskers, particles, or films in a matrix forming a single thin lamina, or a laminated composite consisting of layers of various laminae. The filler material usually carries the major stresses and loads, while the matrix protects the usually brittle filler material from damage and holds these laminae together to enable the transfer of stresses and loads [8]. Composite materials are generally grouped into three broad groups identified by the matrix material: plastic, metal, and ceramic.

1. Metal-matrix Composites

Metal-matrix composite (MMC) materials have been under development for more than 30 years. They were first developed for applications in aerospace, followed by applications in other industries [9]. In the development of these composite materials, one must consider problems of chemical and mechanical compatibility of the two constituents. Because of the high strength and modulus of the reinforcement, there is a high degree of interaction between the matrix and reinforcement.

Chemical compatibility problems (inertness of the reinforcement to the matrix under the processing conditions) have been solved in MMCs in two ways: either using low-temperature (solid-state) fabrication techniques or by selecting thermodynamically stable constituents that are at equilibrium with each other. A corresponding thermal-mechanical compatibility problem has been solved either by using a ductile matrix that yields and takes up all the differential strain necessary in thermal cycling

or by selecting a matrix and a reinforcement having nearly matching thermal-expansion coefficients [10].

MMCs have several advantages that are very important for their use as structural materials. These advantages include a combination of the following properties:

- High strength
- High modulus
- High toughness and impact properties
- Low sensitivity to temperature changes or thermal shock
- High surface durability and low sensitivity to surface flaws
- High electrical and thermal conductivity.

As compared to organic matrix composites, the high strength and high moduli of pure metals and engineering alloys (as compared to organic materials) can be utilized in composite materials. The matrix strength is particularly important with respect to composite properties at some angle away from the reinforcement direction. Properties such as transverse strength, torsional strength, and interlaminar shear strength are generally matrix controlled. This is true in creep and fatigue loading as well as under static loading. The higher strength of metal can be used to conserve the amount of high-cost reinforcement necessary for a given structure. The high moduli (stiffness ratios) of metal alloys are particularly significant in dynamic structures such as turbine-engine fan blades and large airfoils. The high toughness and impact properties of metal alloys are very important in composite materials, since the reinforcement is generally a brittle solid and does not have good impact properties by itself. Ductile metal matrices undergo energy-absorbing plastic deformation under impact, which is important in many dynamic structural applications. The ductile matrix also permits the blunting of cracks and stress concentrations by plastic deformation and gives the material improved fracture toughness.

The relative insensitivity of metal properties to changes in temperature is an important asset of metals as matrix materials for high-modulus structural composites (organic materials require low temperatures and their temperature range of operation is very limited; and structural ceramics are susceptible to thermal shock). Poor resistance to thermal shock, oxidation, corrosion, or erosion at elevated temperatures could lead to catastrophic failure in the structural application. Structural engineering alloys generally have a low sensitivity to surface flaws, and the surfaces are more durable than structural ceramics. Small cracks at the surface, started by erosion, abrasion, or corrosion are blunted by plastic deformation. The small cracks are significant stress risers and weaken the material. Also, metal-matrix alloys have high electrical and thermal conductivity, which permits the diffusion and elimination of high thermal and electrical concentrations [10]. Compared with organic and ceramic composite materials, the most obvious advantages of MMCs are their resistance to severe environments, toughness, and retention of strength at high temperatures.

MMCs can be reinforced by strong second phases (oxides, carbides, nitrides, etc.) of three-dimensional shapes (particulate), two-dimensional shapes (laminar), or one-dimensional shapes (fibrous). Each of these classes of reinforcement has its own advantages and characteristics. Generally, these classes of composites fall into differing areas of application, not only because of the differing mechanical properties of the classes but also because of the contrasts in fabrication techniques.

2. Laminated Composites

Laminated composite materials are considered to be reinforced by a repeating lamellar reinforcement of high modulus and strength, which is contained in the more ductile and formable metallic matrix material. Spacing of the lamellae is microscopic, so that in the structural component the material can be considered as an anisotropic, homogeneous material at the proper scale. These

composites are structural composites and therefore do not include the many types of coated materials in which the lamellae can be considered as a structural member with an environmental-protection coating as a second constituent of the structural material.

The elastic constants of a structural lamellar composite have been predicted by laminate theory [11]. In either of the principal directions of the reinforcing plates, the elastic modulus is given by the rule of mixtures:

$$E_R V_R + E_M V_M = E_C \quad (1)$$

where E_R , E_M , and E_C are the elastic moduli of the reinforcement, matrix, and composite respectively, and V refers to the volume fraction. Other elastic constants of the anisotropic material are somewhat more complex to derive but can be accurately predicted.

The strength of laminated composite materials relates more closely to the bulk reinforcement than to the small-volume (one-dimensional) properties that can be developed in whiskers or filaments. Since the reinforcing lamellae can have two dimensions that are comparable in size to the structural part, flaws in the reinforcement can nucleate cracks of lengths similar to that of the part. This action is in contrast to the action of a flaw that nucleates a crack in a filamentary material. In a filament loaded in axial tension, the crack propagates through the cross section of the filament, which is quite small in area in relation to the whole piece. Since the most important reinforcing materials are brittle in nature, their strength is related to the statistical population of their flaw density and intensity. Therefore, they obey classical fracture mechanics as stated by Griffith [12], and their strength is related inversely to their size.

The strength of laminated structural composites has been limited by the somewhat lower strengths of film reinforcements compared to filamentary reinforcements. In addition, the low strain to failure of the brittle reinforcement limits the elongation and ductility of the composite in all directions in the plane of the

reinforcement. The reinforcement strength and modulus, however, are present in all directions of the plane and offer a significant advantage compared to the unidirectional reinforcement of a filament array.

B. INTERFACES

Compatibility (chemical and thermal-mechanical) of the reinforcement and the matrix is one of the most important considerations in the development of composite materials. Adequate bonding between matrix and filler is essential to permit loading the filler material to its maximum strength. Metallurgical reactions between the matrix and the reinforcement may greatly affect the composite properties. The importance of interfacial reactions in MMC materials was recognized early, and mutually insoluble components were often chosen for strengthening studies [13,14]. Mutually insoluble systems were selected to avoid the effects of interfacial reactions. However, there are few mutually insoluble or nonreactive metal/metal-metal/filler systems. Many ceramics, particularly oxides, are thermodynamically more stable than metals and consequently less susceptible to interfacial reaction with metal matrix materials. Even the most thermodynamically stable oxides may dissolve in metal matrices under some conditions. Generally, ceramics exhibit poor adherence to metals, causing difficulties in the transfer of stresses across the ceramic/metal interface. For example, sapphire ($\alpha\text{-Al}_2\text{O}_3$) exhibits considerable resistance to metal wetting. Alloying additives to the matrix or reinforcement coatings have been used to promote bonding between the matrix and the filler. Although alloying or coatings may promote bonding for adequate stress transfer by causing reactions at the interface, they also tend to reduce composite strength by adversely affecting the filler [15].

A general scheme for the classification of interfaces, based on the type of chemical reaction occurring between a filament and

matrix, has been suggested by Metcalfe [16]. The term "reactive" is restricted to systems that result in the formation of a new chemical compound or compounds residing between the filament and matrix. The three proposed classes are:

Class I -- filament and matrix mutually nonreactive and insoluble

Class II -- filament and matrix mutually nonreactive but soluble

Class III -- filament and matrix mutually react to form compound or compounds at the interface.

For these three general classes of interfaces, the following definition of an interface is given:

An interface is the region of significantly changed chemical composition that constitutes the bond between the matrix and reinforcement for transfer of loads between these members of the composite structure.

The general descriptions of interface bonding classes avoid the considerations of the physical element and mechanical aspects of bonding [17]. The type of bonding occurring in a composite material can be identified with one of the following six bonds [18].

Mechanical bond.

A purely mechanical bond requires that all chemical sources of bonding be absent. This bonding can arise from mechanical interlocking or from frictional effects arising from the concentration of the matrix on the reinforcement.

Dissolution and wetting bond.

A contact angle less than 90 degrees occurs in wetting and is also characteristic of dissolution. If wetting is assumed to be accompanied by some dissolution, however small, then this bonding characteristic covers both extremes of mutual solubility. Elimination of adsorbed gases and contaminant films must be achieved before element-to-element contact can occur and result in wetting and dissolution.

Reaction bond.

The reaction bond occurs when a new chemical compound is formed at the interface, such as the formation of titanium diboride at the interface between boron and titanium.

Exchange reaction bond.

This is a special case of the reaction bond in which two or more reactions may occur.

Oxide bond.

The oxide bond may not involve new principles other than those described earlier. It may appear to be purely mechanical, such as the silver/alumina whisker bonds. Moore [19] showed that the introduction of traces of oxygen converted the nickel-alumina bond to reaction bond by formation of the $\text{Ni}\cdot\text{Al}_2\text{O}_3$ spinel. Another example is the bond formed between the oxide-coated surface of aluminum and boron by solution or reaction between two oxides. The product exists as an oxide film at the interface and constitutes the bond in this pseudo-stable Class I composite system.

Mixed bonds.

This may be one of the most important categories. Breakdown from one type to another is one source of mixed bonds, such as the

partial transition from a pseudo-Class I system to Class II or Class III system.

Interfacial reactions may affect the properties of the components of the composites in three ways:

One or more of the materials in the combination may be strengthened by the reactions

One or more materials in combination may be weakened by the reactions

The properties of the components may remain unchanged subsequent to consolidation (fabrication).

For example, weak matrix materials can be strengthened by solution of reinforcement materials. Removal of surface imperfections of fibers by solution into the matrix may promote higher fracture stress of some brittle fibers. Unfortunately, the converse possibility of degrading the properties of composites appears more likely. With fibers, interfacial reactions can degrade the properties of the fiber by reducing the stored energy of cold work, causing notch imbrittlement, and/or forming a brittle alloy or recrystallized zone at the interface. Between the two extreme possibilities of a beneficial and a deleterious effect is the possibility of relatively unchanged properties, even where reactions take place. Proper choice of matrix and fiber composition might reduce the driving force for a catastrophic reaction, diffusion barriers can be placed between reinforcement and matrix materials that are particularly incompatible, and fabrication process can be selected to reduce reactions and diffusion rates.

C LAMINATE FABRICATION METHODS

Fabrication techniques used to make composites can influence the extent of the interfacial reaction and the amount of change to the properties. Commercial metal laminates have been fabricated by a variety of methods, the most common of which are roll bonding, coextrusion, explosive welding, and brazing.

Roll bonding

In the roll bonding process, the metals are bonded by rolling under heat and pressure so that an integral bond is formed over the entire interfacial area. The specific rolling techniques and conditions (temperature, rolling pressure) depend on the properties (melting point, ductility, thickness ratio) of the metals composing the laminate.

Coextrusion

Coextrusion is the particularly well adapted to the formation of long, continuous wire, rod, and flat rectangular shapes. The extrusion pressure, temperature, and the amount of reduction depend on the materials being coextruded. The primary bonding mechanism is pressure diffusion bonding, in which clean metal surfaces are brought into intimate contact under pressure [20].

Explosive welding

Explosive welding or explosive bonding permits the rapid economical bonding of dissimilar metals, many of which could not be bonded otherwise because of their widely different properties. Basically this process involves the formation of a high-velocity metal jet through removal of a surface layer of one of the metals to be joined. As this jet shoots across the surface of the other metal to be joined, it also removes a thin surface layer from it. The resulting clean surfaces are then forced together by the explosive pressure to form a sound metallurgical bond. Bonding by this method is not

limited by large differences in melting points or plastic properties of the metals to be joined [21].

Brazing

Brazing basically involves the use of a wetting liquid-metal phase which, on solidification, bonds the two laminae together. When the brazing material has a melting point that is lower than that of the two surfaces to be bonded, the technique is known as high-temperature brazing. The system is heated to a temperature between the melting point of the brazing alloy and that of the laminae to be bonded. The brazing alloy may be in the form of foil or wire and may be used with or without a flux. When the brazing alloy is used to form a low-melting eutectic between the metal layers, the process is known as eutectic brazing. This method has been used to bond titanium to steel, using a copper-silver eutectic alloy without a flux in a high vacuum.

MMCs with ceramic reinforcement have been fabricated by many methods, however the proper technique must be selected since key problems can result. In order to optimize the properties of the composite, one has to introduce the ceramic into the metal matrix without any mechanical damage and eliminate the reinforcement degradation; uniformly distribute the filler; and produce strong bonding between the ceramic reinforcement and metal matrix which is the most important and most difficult problem associated with the fabrication of composite materials. The well developed bond should be achieved without any detrimental chemical attack or reaction at the interface. Techniques such as roll diffusion bonding (described above) and hot pressing have been used to fabricate metal/ceramic composites [3].

Hot pressing

Hot pressing as a fabrication procedure describes the enhancement of densification by coincident application of external

pressure with temperature [22]. This pressure serves to augment the normal driving force for densification (reduction of internal surface area). The increased rates of densification permit practical firing times while the temperature is much lower than normally required. Hot pressing is accomplished by placing the material in a suitable chamber and applying pressure from one or more directions while the entire system is held at an elevated temperature. The selection of hot pressing as a desirable procedure is usually based on the need for stringent microstructural control in addition to the requirement of high density. In many cases, hot pressing is used as an attempt to maintain uniform starting materials and thermal history. However, hot pressing is, in general, expensive, time consuming, and rather limited in the variety of shapes that can be processed.

D. ION PLATING

Ion plating is a plasma assisted physical vapor deposition technique, combining elements of vacuum evaporation and sputtering. This deposition process, which incorporates the benefits of both sputter etching and ion beam mixing, can produce metal, alloy, ceramic, and metal/ceramic composite coatings which are fully dense, have equiaxed grain structures and exhibit excellent coating/substrate adhesion. Ion plating was first introduced into the literature in 1963 by Mattox [23]. A generic description for the term ion plating given by Mattox [24] is "a film deposition process in which the substrate surface and/or the depositing film is subjected to a flux of high energy particles sufficient to cause changes in the interfacial region or film properties compared to non-bombarded deposition." Some of the benefits of ion plating are the ability to: "sputter clean" the surface; provide a high energy flux to the surface, achieving high temperature properties while maintaining low bulk temperatures; and alter the surface and interfacial structure by creating defects, mixing the film and substrate material and

influencing the nucleation and growth conditions [25]. Another advantage of ion plating is its good "throwing power," which is the ability to deposit a film on all surfaces of the substrate [26]. This is unlike most other high vacuum techniques, such as evaporation and sputtering, and is due primarily to scattering events with the working gas atoms.

The ion plating process is conducted in a high vacuum chamber, with base pressures in the 10^{-6} Torr range. Typical systems are evacuated using a mechanical (rotary) - diffusion pump combination, as shown in Figure 1. Substrates are mounted on a high voltage cathode, which is generally water cooled. Source material is evaporated using either resistive heating, electron beam evaporation, or a sputtering target. If an electron beam system is employed, modifications in the basic chamber design are necessary to maintain adequate high vacuum (10^{-5} Torr) at the electron gun filament while plating is occurring at approximately 10^{-2} Torr. This is accomplished by using a two chamber design, introduced by Chambers and Carmichael [27]. A pressure of approximately 1×10^{-2} Torr of inert working gas, generally high purity argon, is maintained in the upper chamber during plating in order to support the glow discharge. An inert gas/reactive gas combination (e.g. Ar + N₂) is used to produce ceramic compound coatings like TiN by reactive ion plating. The glow discharge is ignited by biasing the cathode negatively to 1.0 to 5.0 kilovolts, while the remainder of the apparatus is at ground. The high negative potential causes positive ions from the glow discharge to be accelerated toward and strike the substrate with sufficient average kinetic energies to sputter atoms off the substrate surface [28]. It is the presence of this glow discharge at the substrate which distinguishes ion plating from most other deposition techniques. The discharge is established prior to deposition in order to sputter clean the surface, and may be continued during deposition to modify the film morphology.

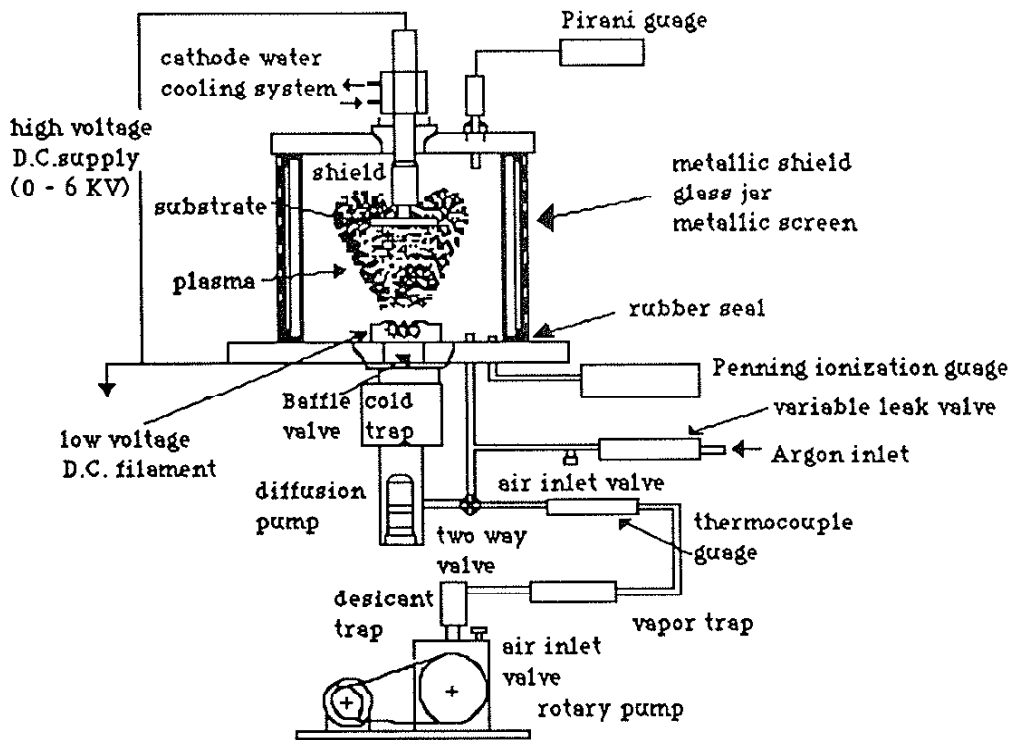


Figure 1 - Schematic of a typical ion plating system [29].

E MATERIAL EVALUATION

Material evaluation by experimental characterization refers to the determination of the material properties through tests conducted on suitably designed specimens. The data obtained from the tests are appropriately reduced to evaluate various material properties that can later be used for analysis and design of practical structures. Understanding the material behavior is necessary for efficient material utilization. In the case of composite materials, it may be desirable to begin the design of the structure with constituent material properties and arrive at the composite macromechanical properties through micromechanics analyses. Other purposes of the

experimental characterization are to check the adequacy of fabrication procedures, assure material uniformity, and as a comparative measure for various candidate materials.

Elastic constants and strengths are basic mechanical properties of materials. For a unidirectional lamina or composite, there are four independent elastic constants: the elastic moduli in the longitudinal and transverse directions; the shear modulus; the major Poisson ratio; and five independent strengths, namely, tensile and compressive strengths in the longitudinal and transverse directions and the in-plane shear strength [30]. In the case of a laminate, the interlaminar shear strength is also an important property. These properties are generally determined by subjecting suitable material specimens to in-plane loads. Composite material structures are often subjected to bending loads, it is desirable to characterize flexural properties in addition to the properties just mentioned. From first principles, all the properties should be established for a single ply or lamina of the composite material, which is the building block for composite structures, with laminate theory subsequently used to calculate the properties of laminates. However, practical considerations often prevent the construction of single layer test specimens. It becomes necessary to conduct tests on multilayer specimens and use appropriate laminate theory to reduce the results in terms of lamina properties. If the laminates are unidirectional, their behavior simulates the lamina behavior [31].

The static uniaxial tension test is probably the simplest and most widely used mechanical test. This test is conducted to determine the elastic modulus, tensile strength, and Poisson ratio of the material. In the case of composite materials, the tension test is generally performed on flat specimens. The most commonly used specimen geometries (ASTM 1988 Designation E8) are the dog-bone specimen and straight sided specimen with end tabs [32]. A uniaxial load is applied through the ends by providing a pin-type or serrated-jaw-type end connection [33]. The specimen must be of sufficient length to ensure that the tensile load is uniform in the strain gauge

region. The data recording in a tension test consists of measuring the applied load and strain both parallel and perpendicular to the load. The applied load is usually measured by means of a load cell that is generally provided with the testing machine. The strains can be measured by means of an extensometer or an electrical-resistance strain gauge. From these data taken until specimen failure, a stress-strain curve can easily be plotted for the material and the required material properties determined [34].

F. DEFORMATION AND FRACTURE ANALYSIS

The analysis of strength of laminates has been investigated primarily through the approach of translating laminate loads into laminar (and interlaminar) stress states and utilizing those stress states in criteria for initiation of local failure. Conversely, experimental strength determination has dealt primarily with overall laminate failure rather than any localized failure [35].

Fracture is a complex subject even in homogeneous, metallic materials. However, most metallic materials can be modelled by a single linear elastic fracture mechanics (LEFM) theory. LEFM is based on the concept that the relevant mechanical property, the fracture toughness, is the force necessary to extend a crack through a structural member. This theory does not concern itself with the prevention of crack nucleation [36]. It assumes that defects will always be present in a structural element and an answer is sought to the following question: Given a certain stress, what is the largest size of a defect (crack) that can be tolerated without the failure of the member?

The LEFM theory is based upon the following assumptions:

1. The cracks are inherently present in a material.

2. A crack is a free, internal, and plane surface in a linear elastic stress field. With this hypothesis, the linear elasticity furnishes stresses near the crack tip as

$$\sigma_{r\theta} = \frac{K}{\sqrt{(2\Pi r)}} f(\theta)$$

where r and θ are polar coordinates and K is a constant called the stress intensity factor (SIF).

3. The crack growth leading to the failure of the structural member is then predicted in terms of the tensile stress acting at the crack tip. In other words, the stress situation at the crack tip is characterized by the value of K . It can be shown by elasticity theory [37] that

$$K = \alpha\sigma\sqrt{(\Pi a)}$$

where σ is the applied stress, a is the half crack length, and α is a constant that depends on the crack opening mode and the specimen geometry.

Unlike homogeneous metallic materials, the fracture of laminate composite materials may not be modeled by a single linear elastic fracture mechanics (LEFM) theory [38]. This is true because laminate composites exhibit multiple fracture modes and because self-similar crack propagation is not assured due to the anisotropic and heterogeneous nature of the material microstructure. For a given interlaminar defect, crack propagation may be accomplished in the opening (mode I), shearing (mode II), tearing (mode III), and mixed modes [39]. Delamination, sometimes also called interlaminar cracking, is one of the most frequently encountered types of damage in advanced composite materials [40]. The problem is not only of great theoretical interest but also of significant technical importance.

The presence and growth of delamination cracks in composite laminates may lead to severe reliability and safety problems, such as reduction of structural stiffness, exposure of the interior to adverse conditions, and disintegration of the material, which may lead to final failure. Thus, understanding the basic mechanics of composite failure is of critical importance in characterization of advanced composite materials and structures.

The starting point for an understanding of failure is the individual lamina, or unidirectional fiber composite material (very good first approximation for a two-dimensional thin film composite material). The simplest model for the tensile failure of a unidirectional fiber composite subjected to a tensile load in the fiber direction is based upon the elasticity solution of uniform axial strain throughout the composite [35]. Generally, the fibers have a lower strain to failure than the matrix, and composite fracture occurs at the failure strain of the fibers alone. This results in a rule-of-mixtures value for composite tensile strength.

The problem with this approach is the variability of fiber strength. The statistical distribution of single filament strength is considered to result from a distribution of imperfections along the length of these brittle fibers. There are two important consequences of a wide distribution of individual fiber strengths. First, all fibers will not be stressed to their failure strength simultaneously. Thus, the load for a group of fibers will not equal the sum of loads for the individual fibers (nor will strength equal mean fiber strength). The second important factor is that those fibers which break earliest during the loading process will cause perturbations of the stress field in the vicinity of the break, resulting in localized high fiber-matrix interface shear stresses. These shear stresses transfer the load around the break, and also introduce stress concentrations into adjacent unbroken fibers.

At each local fiber break, the stress in the vicinity of the broken fiber changes so that the axial stress in the fiber vanishes at the fiber break and gradually builds back up along the fiber length

to its undisturbed stress value. The shear stress is a maximum close to the fiber break and decays rapidly along the length of the fiber. As a result, the axial fiber stress builds up to its initial undisturbed value over a relatively short dimension [35]. This stress distribution may cause several possible failures to occur. The shear stresses may cause a crack to progress along the interface. If the interface is weak, such propagation can be extensive. This undesirable mode of failure can be prevented by a strong fiber-matrix interface or a soft, ductile matrix which permits the redistribution of the high shear stresses. When the interface does not fail, the local stress concentrations may cause the fiber break to propagate through the matrix, to and through adjacent fibers. Alternately, the stress concentration in adjacent fibers may cause one or more of such fibers to break prior to the occurrence of failure of the intermediate matrix. If such a crack or such fiber breaks continue to propagate, the strength of the composite may be no greater than that of its weakest link [36]. If the matrix and interface properties are of sufficient strength and toughness to prevent or arrest these failure mechanisms, then continued load increases will produce new fiber failures at other locations in the material, resulting in an accumulation of dispersed internal damage as the loading continues. It can be expected that all of these effects will occur prior to material failure. That is, local fractures will propagate for some distance along the fibers and transverse to the fibers. These fractures will initiate and grow at various points within the composite. Increasing the load will produce a statistical accumulation of dispersed damage regions until a sufficient number of such regions interact to provide a weak surface, resulting in composite failure [37].

III. EXPERIMENTAL PROCEDURE

A. MATERIALS DESCRIPTION

The source material used to grow the TiN reinforcement films was 99.7% pure titanium, obtained from Aesar, Inc. The titanium was in the form of 6.4 mm diameter rod of 1.0 m length, which was subsequently cut with a band saw into 25.0 mm lengths. The titanium pieces were placed in the ion plating system's electron beam crucibles for consolidation and evaporation. The titanium reacted with research grade (99.995%) nitrogen to form TiN.

The substrate materials, composite matrices, were in the form of metal foils obtained from Aesar, Inc. The specific metals used in this investigation were Al, Ti, and Ni. The aluminum foil was 99.5% pure, 0.0077 mm thick, and in an annealed state. The titanium foil was Grade 2, 99.7% pure, 0.025 mm thick, and also in an annealed state. The nickel foil was 99.95% pure, 0.006 mm thick, and was electroformed. These foils were machined into 76.2 mm (3.0 inch) diameter discs and TiN was deposited onto these discs in their as received condition.

B. ION PLATING SYSTEM

All of the TiN films used in this study were grown using the ion plating facility of the Construction Engineering Research Laboratory (CERL), operated by the United States Army Corps of Engineers, located in Champaign, Illinois. The plating system was built by InterTec, Inc (formerly Torr Vacuum, Inc). The vacuum chamber of the system is a split chamber design, allowing easy access to the interior. A power driven hoist is used to raise the upper chamber, which may then be pivoted about the hoist axis as desired. The chamber is cylindrical with a diameter of 0.66 m. The source to

cathode distance can be varied, but was typically at a distance of 0.30 m. All vacuum seals in the system, with the exception of the conflat feedthroughs, are made via viton O-rings. Both the upper and lower halves of the chamber have a variety of ports to accommodate accessories to the system. In addition, the upper chamber has two 0.115 m diameter viewports to allow observation of the chamber interior during an experiment. Disposable glass inserts are fitted to the inside of the viewports to minimize down time between runs due to coating of the windows. A "baffle plate" is placed in the lower chamber to isolate the electron gun assemblies from the soft vacuum in the upper chamber. The cathode, onto which substrates or substrate holder can be mounted, is a machined cylindrical stainless steel disc with a pattern of tapped holes in its lower face. The holder, which is water cooled, is welded to a pipe which passes through the chamber lid. Electrical isolation and vacuum integrity are achieved via a machined block of teflon, designed similar to a conflat feedthrough.

The pumping system for the ion plater consists of 0.254 m (10 inch) and 0.152 m (6 inch) diffusion pumps working in parallel, backed by a single rotary pump. The pumping sequence is automated with manual override capabilities. Liquid nitrogen is supplied to the diffusion pumps to achieve maximum pumping efficiency. Evaporation is conducted via two diametrically opposed electron beam evaporation sources allowing alloy and multilayer films to be deposited without breaking vacuum. Each gun assembly consists of a water cooled copper crucible, a thermionic emission filament, and a magnetic beam deflection system. They are powered and controlled by an Airco Temescal CV-14 power supply, generally operated at 10 kilovolts and 0.1 to 0.6 Amperes per gun. Power to the cathode, needed to support the glow discharge is provided through either a d. c. power supply or an r. f. generator. The d. c. power supply is capable of delivering 7.5 kilovolts and 0.75 amps and the r. f. generator (operating frequency is 13.56 MHz) can provide 1000 Watts of forward power. The system is equipped with

safety interlocks to prevent contact with any of the high voltage components while in operation. Gases are delivered to the system through stainless steel lines with the flow rates adjustable via mass flow controllers. High purity argon, nitrogen, oxygen, and acetylene can be admitted into the chamber, with each gas having its own calibrated mass flow controller capable of flow rates up to 100 sccm. The argon gas is further purified by a titanium gettering furnace through which the argon flows before entering the chamber. Upon completion of the experiment, the ion plating system is returned to atmospheric pressure by delivering dry nitrogen to the chamber through a vent valve.

Accessories to the system include a residual gas analyzer (RGA), Inficon Model 1000, used to monitor gas content and composition prior to and during deposition. It is primarily used to monitor consumption rates of gases during reactive ion plating (monitors nitrogen during the reactive ion plating of titanium nitride). Also, the RGA allows leaks to be detected by locally injecting helium around the seal in question and monitoring the helium signal on the RGA. A capacitance manometer accurately measures the upper chamber pressure and coupled with the RGA can provide the partial pressures of the gas species. A triode enhancement system may be connected to the system when the cathode is biased negatively by the d. c. power supply. The triode increases the ionization efficiency of the power supply. It consists of a copper ring mounted concentrically with the cathode and biased positively. Four Hewlett-Packard d. c. power supplies, each rated at 60 V and 5 A, are used to drive the anode, with typical operating voltages being 50 to 120 volts. Other options being evaluated or installed include a quartz crystal thickness monitor to provide in situ deposition rate information and an optical spectroscopy system to characterize the constituents of the plasma during deposition. A complete schematic of the ion plating system is shown in Figure 2.

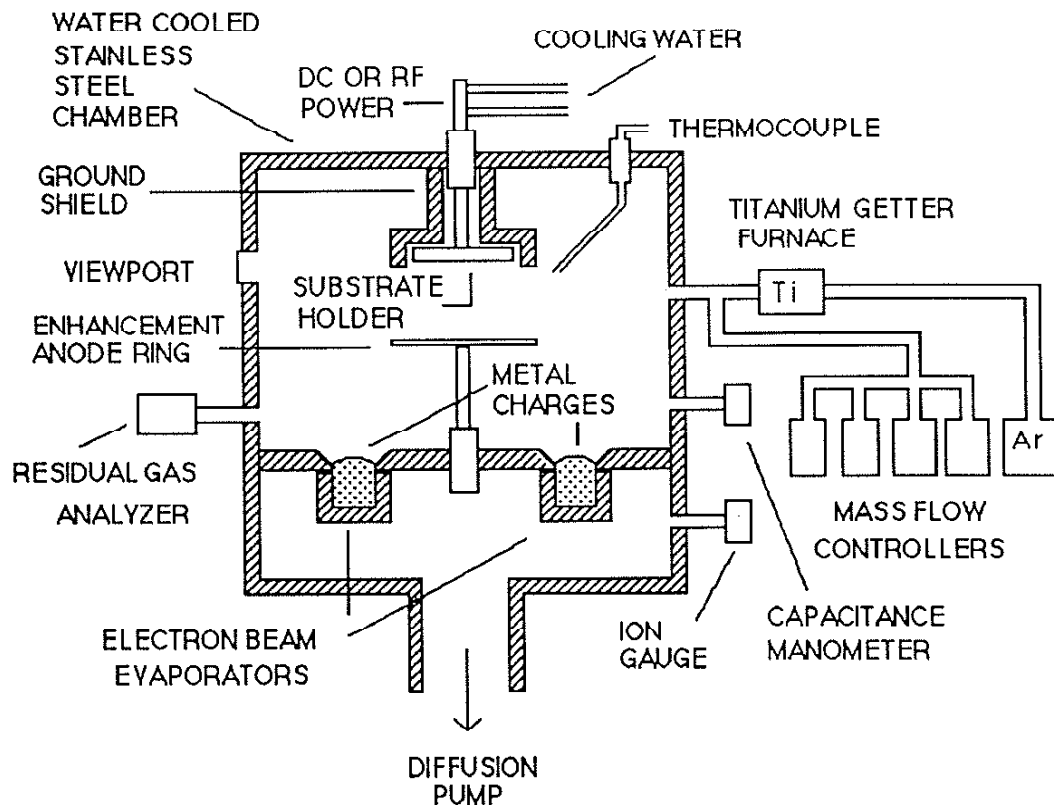


Figure 2 - Schematic diagram of the U of I / USA-CERL ion plating system

C DEPOSITION PROCEDURE

Prior to each set of deposition runs, the interior of the vacuum chamber is covered with clean aluminum foil. This allows for minimal down time when changing material systems, as the old aluminum foil may be removed and discarded. Either a previously melted charge or fresh titanium pieces are placed in both of the electron beam crucibles, and a dummy deposition of titanium is conducted. This serves two purposes: to consolidate the charge without having to worry about splattering from an unstable charge

ruining a substrate; and to coat all exposed aluminum foil and fixtures with titanium to effectively negate the possibility of contamination due to backsputtering. Next, the parametric space of reactive ion plated TiN must be investigated in order to determine the acceptable processing window for the deposition of TiN. This task is accomplished by examining the "consumption curves" of the titanium and nitrogen reaction. For the reactive formation of TiN, one must monitor the evaporation rate of Ti, flow rate of nitrogen, the residual nitrogen partial pressure, and the subsequent interaction of these ion plating parameters. Typical consumption curves are shown in Figure 3.

Figure 3(a) is a plot of the partial pressure of nitrogen (N_2) as a function of the nitrogen flow rate for a constant, titanium evaporation rate. The partial pressure of nitrogen is determined by observing the nitrogen signal (ion current) displayed by the RGA. The signal level shows the amount of unreacted (residual) nitrogen left in the upper chamber. This is a valid deduction and is shown by the direct correspondence between the nitrogen ion current and the total system pressure in Figure 3(a). The total pressure is monitored by a capacitance manometer. The changes in the evaporation rate of titanium are determined by observing the gun current (power) to the electron beam crucibles. Obviously, this method does not give direct or absolute evaporation rates, but it has proven most reliable in the determination of the TiN consumption curves. Returning to Figure 3(a), this graph shows a knee in the residual nitrogen curves at approximately 40 sccm. This is the optimal level of operation for these particular reactive ion plating conditions. Below this point, the consumption rate of nitrogen is too great and other depositing species (Ti and Ti_2N) besides TiN will be grown. Above the knee, too much nitrogen has been introduced into the system. Evaporant poisoning (titanium and nitrogen reacting on the surface of the source material) results which severely diminishes the evaporation rate. Figure 3(b) shows the nitrogen partial pressure changing as a function of the evaporation rate for a given nitrogen flow rate. This

is significant since it shows that the optimal conditions for the formation of TiN will be shifted to a higher flow rate of nitrogen for an increased evaporation rate. Figure 3(c) depicts the shifting of the consumption curve to a higher nitrogen flow rate (from 40 sccm to 85 sccm) after the power to the electron beam evaporators has been increased.

Figure 3(a)

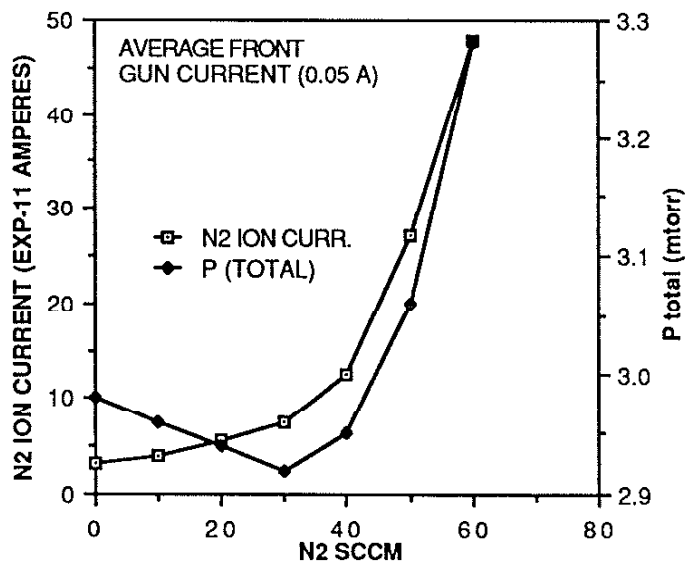


Figure 3(b)

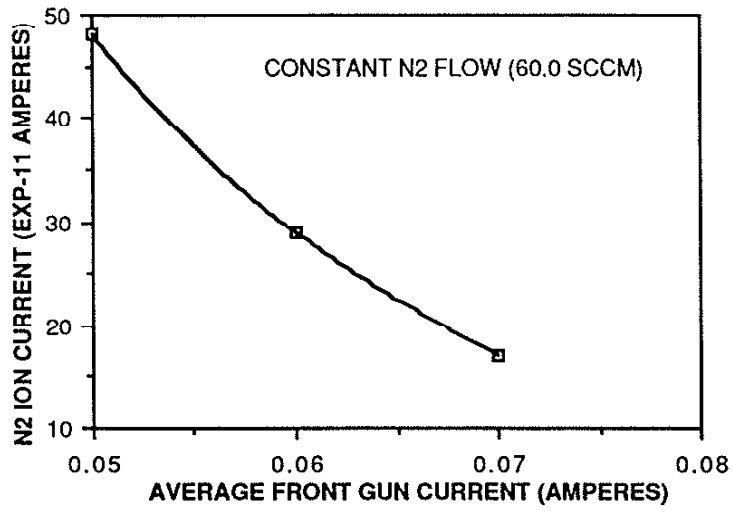


Figure 3(c)

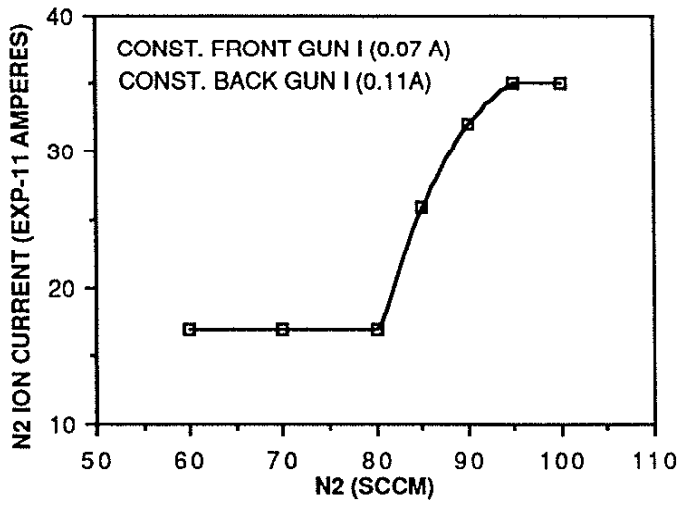


Figure 3 - Consumption curves for reactive ion plated TiN

Once the TiN processing window has been determined, the chamber is then vented, after being allowed to cool to approximately 40°C, and substrates are mounted to the cathode using titanium nitride coated hardware. Precautions such as using gloves and tweezers were taken to preserve cleanliness. Once the sources and substrates are loaded into the system, the chamber is evacuated to its base pressure. During this pumpdown procedure, the RGA is turned on, the liquid nitrogen traps of the diffusions pumps are filled, and the gas lines are opened and evacuated. When the base pressure is attained, the gas lines are purged and the purity of the gases is monitored on the RGA. The desired flow rate of gas is then introduced and the system is allowed to equilibrate. If sputter cleaning of the substrates is to be done, the bias to the cathode is applied, igniting the glow discharge. A few minutes prior to the start of evaporation, the electron beams are turned on. This allows the sources to be slowly and uniformly heated to the vaporization temperature. When deposition is to be started, the power to the electron beams is increased, and evaporation commences quickly since the sources have already been preheated. However, just prior to this point for the reactive ion plating of titanium nitride, the desired flow rate of nitrogen is set (the working gas is still present) and the enhancement power levels are attained. During deposition, the reaction rate of titanium and nitrogen is monitored on the RGA by observing the nitrogen signal as a function of time. Upon completion of the deposition, the gun power is turned off, the discharge is extinguished, and the chamber is allowed to cool. When the chamber has reached approximately 40°C, it is vented and the specimens removed. The chamber is exposed to the atmosphere as little as possible between runs to minimize the adsorption of water molecules to the chamber walls.

D. HOT PRESSING

1. System Description

The composites fabricated in this study were diffusion bonded using the hot pressing facility operated by the Materials Research Laboratory at the University of Illinois, Champaign-Urbana. The unit is a Vacuum Hot Press Sintering Furnace Series 3600 manufactured by GCA Corporation, Vacuum Industries Division. This high temperature, high pressure furnace has temperature capabilities of 2300°C and pressure capabilities of 34.5 MPa (5000 psi). This is an automated system which controls the vacuum, temperature, and pressure simultaneously. The materials can be pressed in a vacuum (1 mPa) or in an inert argon atmosphere. An insulated heating element encases the die configuration and heats the material to the desired temperature. The temperature is monitored by an optical pyrometer for temperatures up to 1500°C; beyond that temperature a thermocouple is used. The pressure limit of 34.5 MPa is determined by the strength of the die materials (namely graphite) not the furnace capabilities. This furnace uses hydraulic pressure in lieu of pneumatic pressure for compressing samples. The opposing hydraulic rams transmit pressure against graphite punches which are contained inside an appropriate die with the sample in between the punches. This contains the sample and shapes it to the configuration of the die being used while at pressure and temperature. Many sizes and shapes can be pressed. The system has successfully pressed samples as large as 152.4 mm diameter and as small as 19.0 mm square (samples for this research were 76.2 mm in diameter).

2. Pressing Procedure

Each material is consolidated separately due to considerations of melting points and vapor pressures. The hot press furnace is vented and the appropriate die is assembled. The graphite die is first lined with graphfoil before the samples are loaded. Next,

graphite spacers topped with graphfoil are placed between each experiment as it is loaded into the die. The graphfoil protects the graphite die material against any possible reaction that may occur with the samples under the hot pressing conditions. The graphite spacers separate experiments and transmit the load through the volume of the specimens. Once the loading of the samples is completed, the graphite punches are brought to rest upon the die and the furnace is evacuated. After reaching the base pressure, a one-half atmosphere of argon is admitted into the furnace to prevent possible oxidation of the material. At this point, the operating parameters are entered into the controller. The temperature is ramped up at 25°C per minute to the desired soaking temperature (Al = 440°C, Ni = 850°C, and Ti = 950°C) and then held for 60 minutes. The pressure ramps up to reach 34.5 MPa just as the soaking temperature is attained. However the pressure is maintained until the samples are removed. Upon completing the soaking time, the samples are allowed to cool to approximately 30°C. The hydraulic pressure is then released, the system is vented, and the samples are removed.

IV. ANALYTICAL PROCEDURE

A. MECHANICAL TESTING

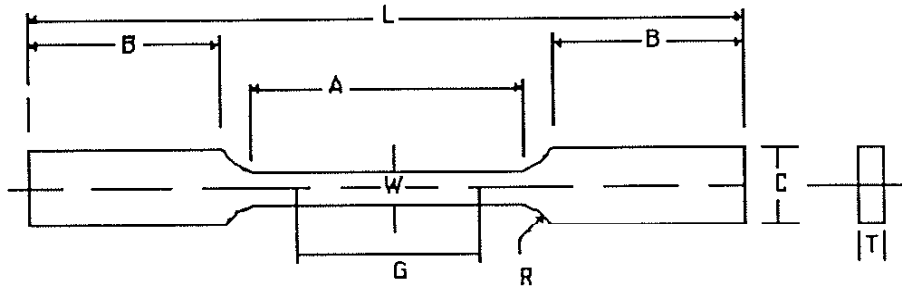
1. Sample Fabrication

After each experiment's group of metallic discs (Al, Ni, and Ti) had been successfully reactive ion plated with TiN, these foils were subsequently stacked and hot pressed. The stacking sequence was such that all interfaces formed were either ion plated metal/ceramic or hot pressed metal/ceramic. These microlaminate composite materials were consolidated to a final thickness of approximately 0.400 mm. From these hot pressed composite discs, samples were sheared with the free edges subsequently machine milled into sub-size dog bone tensile specimens, according to ASTM specifications E 8, by the Department of Materials Science and Engineering Machine Shop. Figure 4 provides the dimensions of these specimens.

2. Uniaxial Tensile Testing

Uniaxial tensile testing is used to evaluate the mechanical integrity of the microlaminate structure. Tensile tests are conducted using a United Calibration Corp. TM-1-10 table top tensile machine. The tensile specimens are inserted into the serrated mechanical grips and properly aligned for uniaxial testing. The testing parameters consisted of a 138.25 N (1000 lb) load cell with a strain rate of 0.254 mm/mm/sec. The load was applied parallel to the plane of the film reinforcement until failure. An analog plotter recorded the load versus displacement and the tensile machine displayed the maximum load. Knowing the specimen dimensions and cross-sectional area, the ultimate tensile strength, uniform strain, and strain to failure were calculated.

SUBSIZE TENSILE DOG-BONE SPECIMEN



DIMENSIONS

SUBSIZE SPECIMEN	
UNITS=mm	
G -- Gage Length	12.50 +/- 0.08
W -- Width	6.125 +/- 0.050
T -- Thickness	thickness of material
R -- Radius of fillet, min	3
L -- Over-all length, min	50
A -- Length of reduced section, min	16
B -- Length of grip section, min	16
C -- Width of grip section, approximate	5

DIMENSION RATIOS MEET ASTM STANDARDS

Figure 4 - Specifications for the subsize tensile specimens (T = 0.400 mm for these composite materials)

B. ELECTRON MICROSCOPY

Scanning electron microscopy was utilized in this study in order to characterize the microlaminate composite materials. The SEM micrographs were taken using an Hitachi S-800 scanning electron microscope, located at the University of Illinois Center for Microanalysis of Materials. This high resolution instrument is

equipped with a field emission gun assembly which provides a smaller probe diameter and greater brightness. SEM micrographs were taken of the fracture surfaces and polished cross-sections of the laminate structures. The fracture surfaces of the tensile specimens were mechanically sheared from the specimens and mounted vertically on SEM mounting stubs. The micrographs of the fracture surfaces provided information concerning the mode of failure and the mechanical stability of the ion plated and hot pressed metal/ceramic interfaces. Cross-sections of the composite materials were mechanically polished through a standard metallographic series of grit sizes and diamond pastes to a final 0.25 micron diamond polish. Chemical etching was then performed according to the following specifications:

Etchant for pure Ti: reveals general structure
10 ml HF
30 ml HNO₃
60 ml H₂O
swab 3-20 seconds
rinse in H₂O [41]

with the specimens subsequently mounted vertically on SEM mounting stubs. The micrographs of the cross-sections provide information in regard to the structure of the TiN film reinforcement and the chemical differences of the ion plated and hot pressed metal/ceramic interfaces.

V. RESULTS AND DISCUSSION

A. MECHANICAL PROPERTIES

For each metal matrix (Al, Ni, and Ti), the amount of TiN was varied from 0 to approximately 20 volume percent by controlling the coating to substrate thickness ratios. This was accomplished by performing a series of reactive ion plating depositions at three different periods of time (0.5 hr, 1.0 hr, and 2.0 hr) and comparing the composite results to similarly processed (hot pressed) uncoated metal foils. Each condition (metal foils with the different deposition times) had three tensile coupons tested to provide a reasonable measure of the statistical error. The results of these experiments are based on the information gained from testing the Ti/TiN and Al/TiN composites and are summarized in Tables (1), (2), and (3). A malfunction of the hot press equipment during the hot pressing of the Ni/TiN samples destroyed that series of experiments.

Table 1 - Mechanical data for Ti/TiN microlaminates

<u>Deposition Length</u>	<u>Volume Percent</u>	<u>UTS Observed</u>	<u>Uniform Strain e_u</u>	<u>Total Strain e_f</u>
0.0 hr	0.00%	453.2 MPa	0.21	0.47
0.0 hr	0.00%	453.4 MPa	0.22	0.45
0.0 hr	0.00%	462.8 MPa	0.21	0.45
0.5 hr	1.96%	625.8 MPa	0.16	0.24
0.5 hr	1.96%	633.7 MPa	0.18	0.26
0.5 hr	1.96%	637.3 MPa	0.19	0.24
1.0 hr	3.85%	636.8 MPa	0.2	0.24
1.0 hr	3.85%	641.6 MPa	0.2	0.24
1.0 hr	3.85%	664.5 MPa	0.2	0.24
2.0 hr	7.41%	645.4 MPa	0.18	0.2
2.0 hr	7.41%	660.5 MPa	0.17	0.18
2.0 hr	7.41%	660.7 MPa	0.17	0.19

Table 2 - Mechanical data for Ti/TiN microlaminates

Volume Percent	Average UTS (MPa)	Average e_u	Average e_f	UTS Theory
0.00%	456.5+/-7.4			345 MPa
0.00%		0.21+/-0.01		
0.00%			0.46+/-0.01	
1.96%	632.3+/-5.9			355 MPa
1.96%		0.18+/-0.02		
1.96%			0.25+/-0.01	
3.85%	647.6+/-15			365 MPa
3.85%		0.20+/-0.00		
3.85%			0.24+/-0.00	
7.41%	655.5+/-8.8			383 MPa
7.41%		0.17+/-0.01		
7.41%			0.19+/-0.01	

Table 3 - Mechanical data for Al/TiN microlaminates

Deposition Length	Volume Percent	UTS Observed	Average UTS	Standard Deviation	UTS Theory
0.0 hr	0.00%	39.8 MPa			35 MPa
0.0 hr	0.00%	43.6 MPa	42.5 MPa	+/- 2.3	
0.0 hr	0.00%	44.2 MPa			
0.5 hr	6.10%	48.3 MPa			85 MPa
0.5 hr	6.10%	49.3 MPa	50.5 MPa	+/- 3.0	
0.5 hr	6.10%	53.9 MPa			
1.0 hr	11.49%	54.7 MPa			130 MPa
1.0 hr	11.49%	54.9 MPa	54.8 MPa	+/- 0.1	
2.0 hr	20.62%	39.2 MPa			205 MPa
2.0 hr	20.62%	49.8 MPa	47.6 MPa	+/- 7.6	
2.0 hr	20.62%	53.9 MPa			

1. Ti/TiN Microlaminate Composites

Figures 5 and 6 show the mechanical behavior of the Ti/TiN microlaminate series. In Figure 5, the ultimate tensile strength

(UTS), experimental and theoretical, is plotted as a function of the volume percent of TiN. The addition of TiN increases both the experimental and theoretical UTS, however the explicit behaviors are very different. The experimental UTS shows a knee at approximately 2 vol. % TiN (The exact nature of the knee cannot be determined at this point in the research program. Future work will include testing and analyzing of composites with TiN reinforcement between zero and two volume percent in order to characterize the initial strengthening behavior of the composite material.). The initial rate of observed strengthening is very significant with this effect due to the unique nature of the laminate structure [42]. However, after the knee, the experimental UTS shows a rate of change similar to that which has been predicted for these composites by rule-of-mixtures (ROM). This knee is significant because it can be explained by more than one phenomenon. One explanation is that the volume percent for this point is at a critical coating thickness above which the tensile stress to fracture the reinforcement is relatively constant [43]. Thus, one would expect to see the UTS greatly increase for volume percents of TiN below this critical thickness; and the UTS should follow the rule-of-mixtures for larger thicknesses. Another possible cause for the observed behavior is that the fabrication process is limiting the strengthening effects of the film reinforcement by allowing premature failure of the composite. The critical material parameter of these composites is the adhesion between the ceramic film reinforcement and metal matrix. Low levels of adhesion would allow interfacial separation between the filler and matrix and produce composite fracture at lower stress levels [44]. The validity and applicability of these statements for these composite materials will be discussed in a later section.

The theoretical UTS shown in Figure 5 has been derived from the rule-of-mixtures (ROM). The calculation of the theoretical UTS resulted from the use of the following equation [11] and values:

$$UTS_m V_m + UTS_r V_r = UTS_c$$

For Ti/TiN: (Ti) $UTS_m = 345$ MPa [45]; (TiN) $UTS_r = 860$ MPa [4]

For Al/TiN: (Al) $UTS_m = 35$ MPa [45]; (TiN) $UTS_r = 860$ MPa [4].

The rule-of-mixtures predicts a maximum strengthening of ≈ 380 MPa compared to an observed 660 MPa (7.4 volume percent TiN). Despite the discrepancies between the ROM and observed UTS, this theory is a valid and applicable first approximation to explain the mechanical behavior of these microlaminated composites [46]. However, it must be used as a lower bound since it does not take into account interfacial stresses [16]

Returning to the discussion of the observed UTS of Figure 5, one notices that the uncoated, hot pressed, titanium foils exhibited strengthening also above that which was expected from rule-of-mixtures. Since titanium is very susceptible to interstitial pick-up, precipitation of interstitials (carbon, oxygen, and nitrogen), due to the hot pressing procedure, could cause an observed increase in the UTS. The UTS would be increased due to the interaction of dislocations with these very hard particles [47]. Also, interfacial strengthening and/or oxide contaminants could cause this observation. After the hot pressing of the Ti foils, remnants of the foil surfaces would still be present resulting in a structurally and/or chemically different interfacial area. This interfacial area would increase the UTS of the material because of the increased work hardening ability of the material [10]. Also, since the foils were diffusion bonded in their as-received condition, the surface oxide of the Ti foils could act as a ceramic reinforcement causing the observed UTS to be larger than expected.

Figure 6 shows the uniform strain and strain-to-fracture for the Ti/TiN microlaminated composites. The uniform strain is relatively independent of the volume percent TiN. This indicates that the mechanical behavior of the composite is not a function of coating thickness or that the mechanical behavior of the composite is

determined by the matrix only. More accurate mechanical testing is needed to differentiate these two effects. The strain-to-fracture data shows that reasonable ductility is obtainable even after a few volume percent additions of the brittle, ceramic reinforcement. Also shown in the strain-to-fracture curve is a knee similar to that of the UTS data. The same two explanations of a critical coating thickness or a strengthening limitation due to the fabrication process would justify this observed behavior.

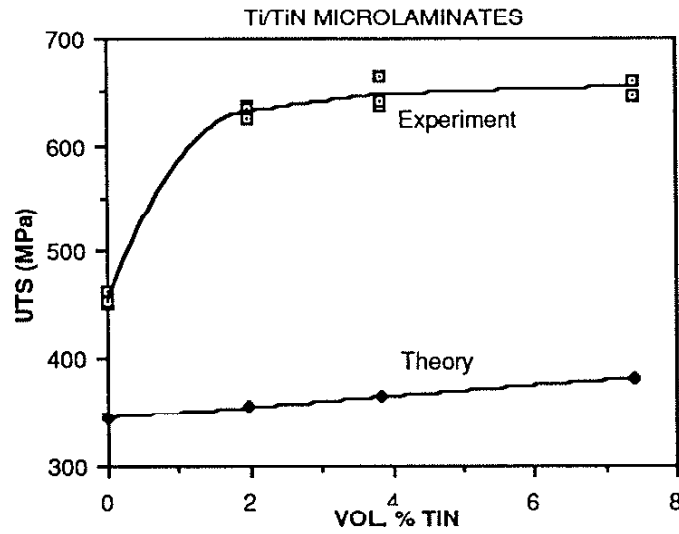


Figure 5 - Ultimate tensile strength as a function of volume percent TiN for the Ti/TiN microlaminate series

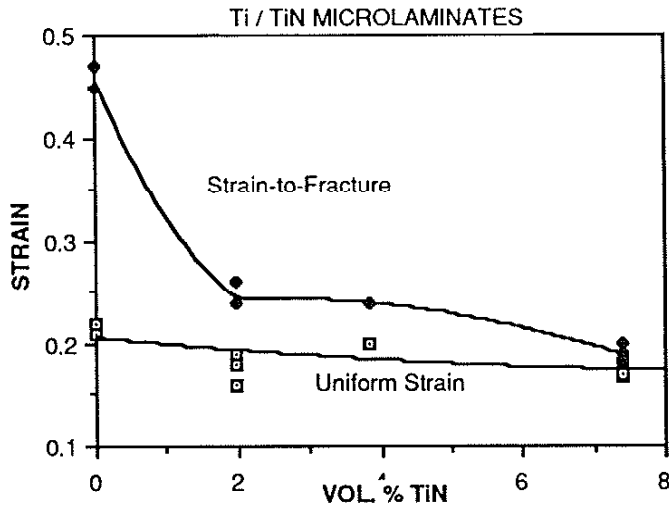


Figure 6 - Strain as a function of volume percent TiN for the Ti/TiN microlaminate series

2. Al/TiN Microlaminate Composites

The mechanical behavior of the Al/TiN is shown in Figure 7. Due to the limitations of the tensile machine and the analog chart recorder (strain rate was too high and chart recorder was not sufficiently sensitive), the strain data could not be tabulated. For the Al/TiN microlaminate composite series, the addition of TiN did not significantly increase the ultimate tensile strength beyond that of pure, annealed aluminum (UTS \approx 35 MPa) [45]. The specific cause(s) of these results is thought to be that the strengthening mechanism may be limited by the fabrication process. As discussed in the Ti/TiN mechanical section, poor adhesion between the reinforcement and the matrix would result in deleterious effects upon the mechanical behavior of the composite. Also, internal flaws and edge damage introduced in the processing, machining, or testing of the composite would decrease the observed UTS. These defects act as nuclei for cracks and delaminations which greatly lowers the failure stress [2,48]. Therefore, for this composite series, due to the weak

matrix and the inadequacies of the tensile apparatus, damage to the composites may have been introduced during the gripping of the specimens which would have emphasized the strengthening limitations.

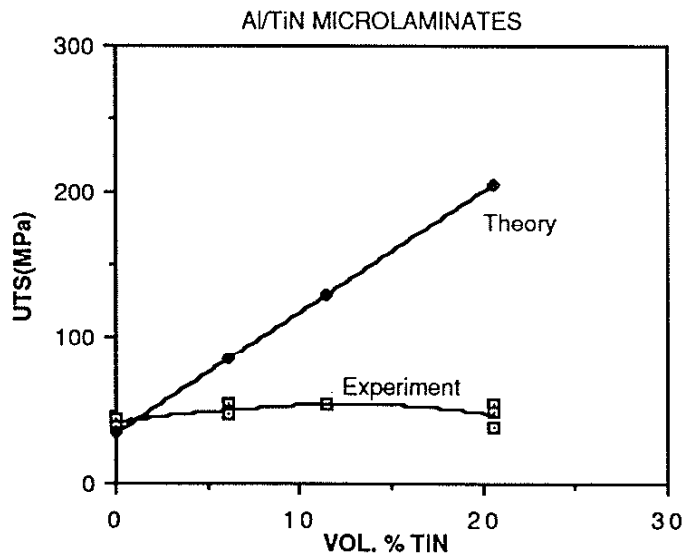


Figure 7 - Mechanical data for the Al/TiN microlaminate series

B. SCANNING ELECTRON MICROSCOPY

1. Ti/TiN Microlaminate Composites

After tensile failure, SEM fractography of the microlaminate composite fracture surfaces was used to evaluate the failure mode of the composites. Figures 8 and 9 are SEM micrographs of the fracture surface of the hot pressed, uncoated Ti foils. The specimen exhibits the expected ductile fracture and shows shearing across the remnants of hot pressed foil surfaces. The latter observation shows that the hot pressing conditions were severe enough to cause metallurgical bonding of the Ti foils.

Figures 10 and 11 show the fracture surface of the Ti/TiN composite strengthened with 7.4 volume percent TiN. The metallic component exhibited a ductile fracture and the TiN phase had an abrupt, brittle fracture. The delamination between the individual foils is shown in both micrographs. However, the TiN remained adherent to the ion plated surface which is evident by the growth direction of the film depicted in Figure 11. Thus, failure of the composite occurred in or near the hot pressed metal/ceramic interface.

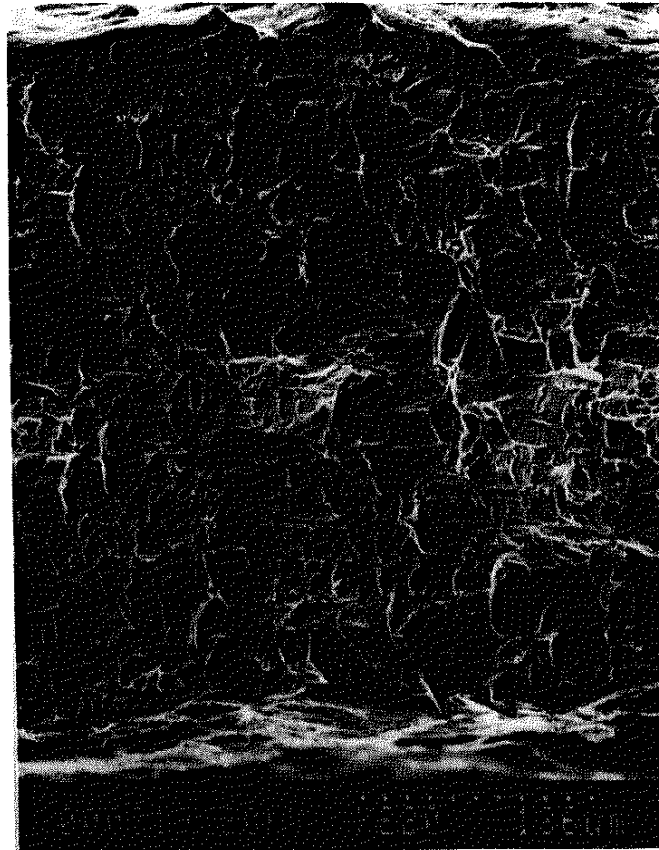


Figure 8 - Scanning electron micrograph of the fracture surface of the hot pressed, uncoated Ti foils

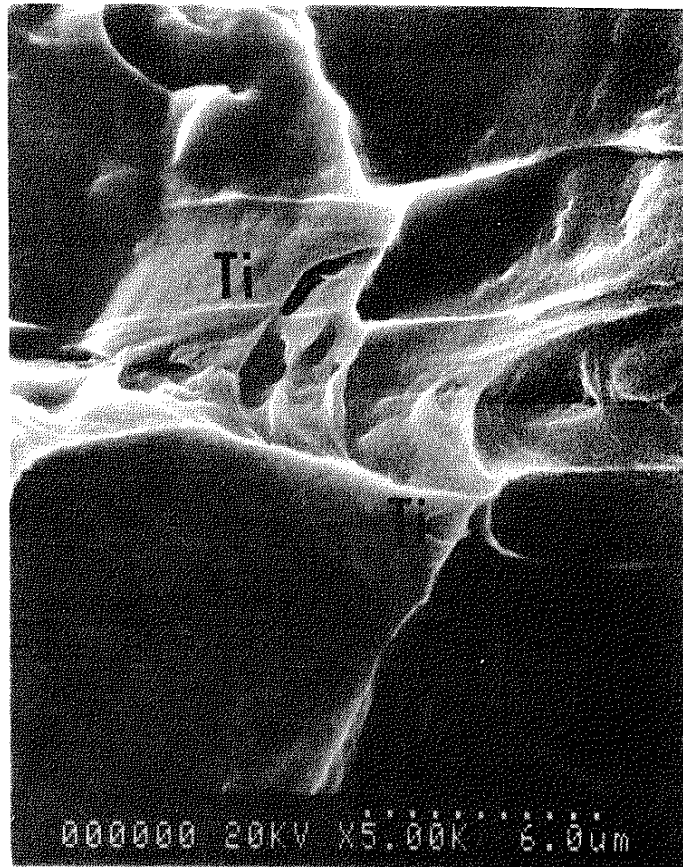


Figure 9 - SEM of the fracture surface of the hot pressed, uncoated Ti foils

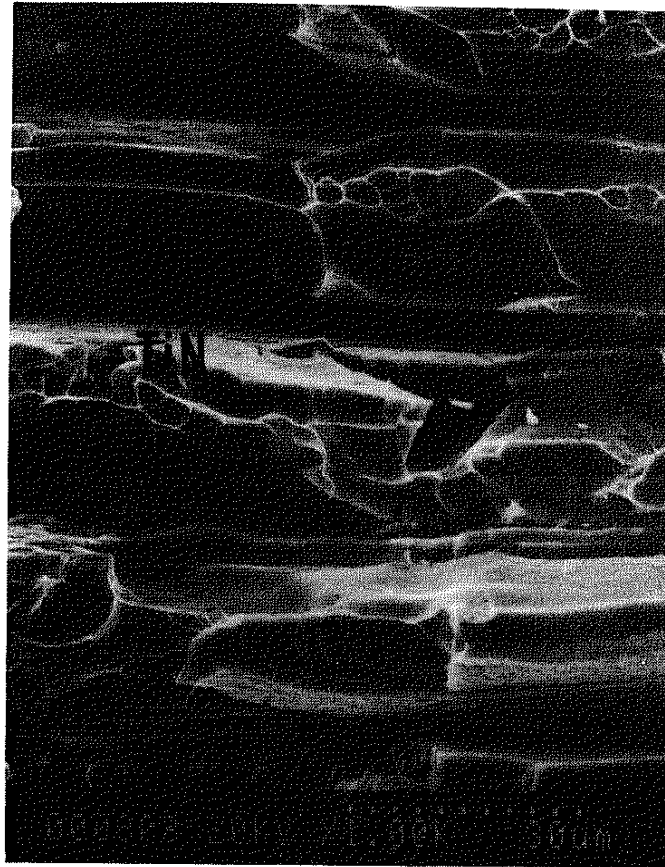


Figure 10 - Scanning electron microscopy of the fracture surface of the Ti/TiN composite strengthened with 7.4 volume percent TiN

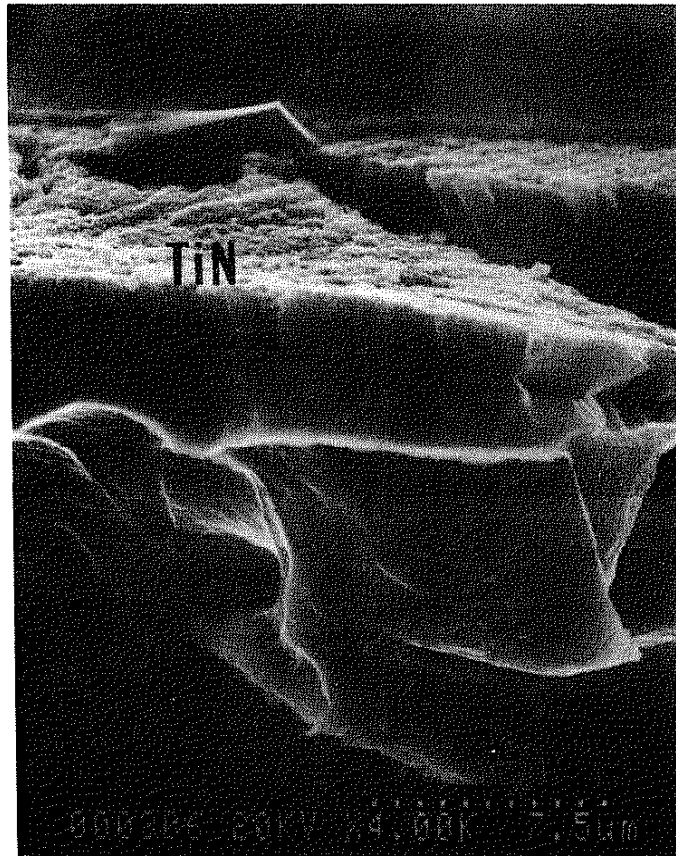


Figure 11 - SEM of the fracture surface of the Ti/TiN composite strengthened with 7.4 volume percent TiN

Mechanically polished and chemically etched cross-sections of this microlaminate composite series were prepared for SEM evaluation to provide more insight concerning the mechanical behavior of the composite materials. Figures 12 and 13 are micrographs of the mechanically polished and chemically etched, uncoated Ti, hot pressed specimen. Depicted in these micrographs is the preferential attack of the hot pressed interfaces indicating a change in structure and/or chemistry and the presence of a thin, film phase at the interface. This film could be the surface oxide that would be present on the Ti foils in their as-received condition. Cross-sectional transmission electron microscopy (X-TEM) would clarify this finding. Also shown in the micrographs is a possible interstitial precipitation. During the hot pressing procedure, the uncoated Ti foil will pick-up carbon from the graphite die. This free carbon will diffuse into the Ti foil from the samples free edges and form TiC precipitates. These precipitates will not be present in the Ti/TiN materials, since the free carbon diffuses in from the sample surface it will react with the TiN layer [47]. X-TEM and further surface-chemical analysis, such as secondary ion mass spectroscopy (SIMS), are needed to better characterize this observation. However, if these secondary phase(s) present are real and the interface itself is of different chemistry and/or structure, the possible explanations, discussed earlier, for the increased ultimate tensile strength of the uncoated Ti foils observed in Figure 5 would be valid.

At this time it is not clear what the microstructural and microchemical differences are between the ion plated and hot pressed interfaces. It will be shown however that substantial differences do exist. Figure 14 is an SEM micrograph of the mechanically polished and chemically etched cross-section of the Ti/TiN composite strengthened with 7.4 volume percent TiN. Bonding is observed between the metal/ceramic phases for both the ion plated and the hot pressed regions. However, preferential attack of the hot pressed Ti/TiN interface by the etchant gives direct evidence that a chemical and/or microstructural difference exists

between the ion plated and the hot pressed interfaces (comparison of the etchant attack in Figures 12 and 13 with Figure 14 shows that the hot pressed interface is the preferentially attacked interface). Since these chemical and/or microstructural differences are so clearly shown with SEM analysis, X-TEM combined with EDS would allow proper characterization of the possible reaction phases, deformation processes, and structural changes that have occurred at these metal/ceramic interfaces. Samples of these composites are being prepared for X-TEM in order to better understand these preliminary findings.

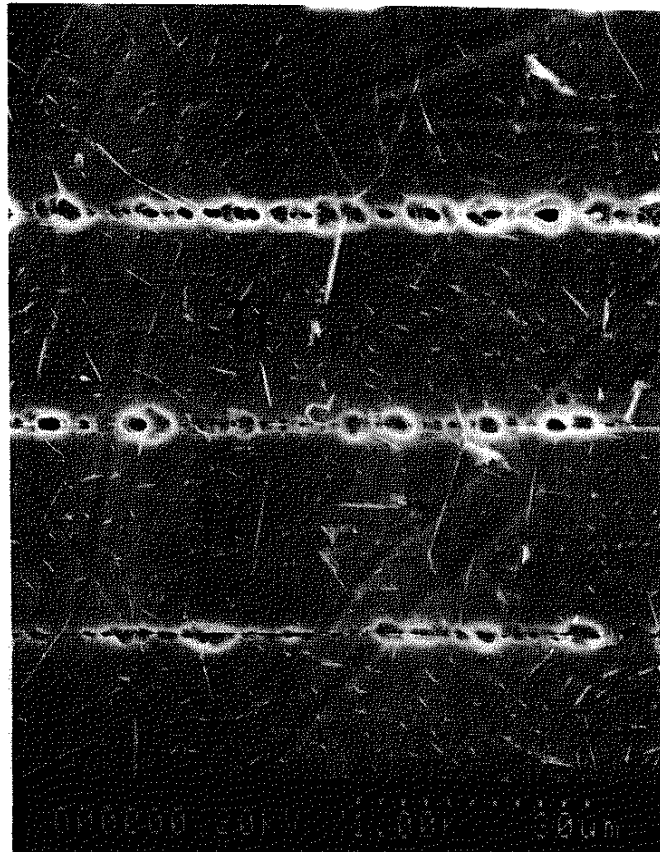


Figure 12 - Scanning electron micrograph of a mechanically polished and chemically etched Ti hot pressed specimen

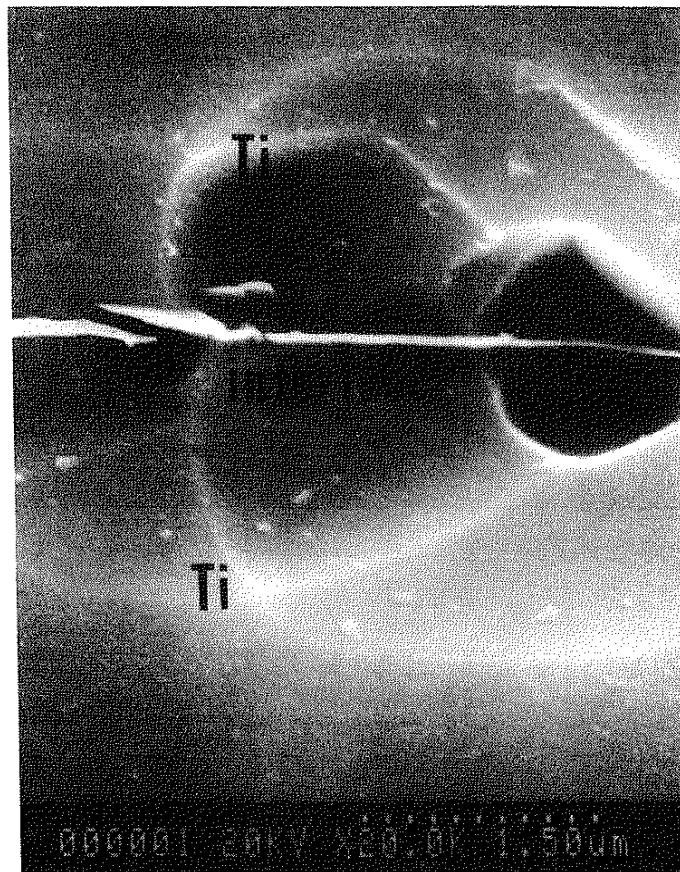


Figure 13 - SEM of a mechanically polished and chemically etched Ti hot pressed specimen

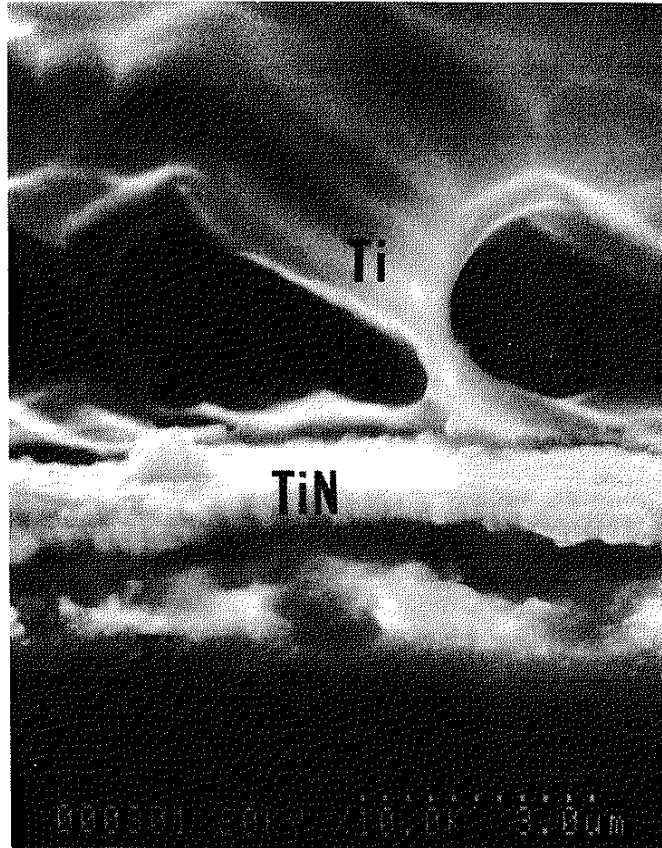


Figure 14 - SEM of the mechanically polished and chemically etched cross-section of a Ti/TiN composite strengthened with 7.4 volume percent TiN
RIP: reactive ion plated interface
HP: hot pressed interface

2. Al/TiN Microlaminate Composites

Figure 15 is an SEM micrograph of the fracture surface of the uncoated, hot pressed, aluminum foils. The material exhibits failure by ductile tearing, typical of a low modulus material, and debonding caused by the stress concentrations due to the necking of the foils.

Figure 16 is an SEM micrograph of the fracture surface of an Al/TiN composite strengthened by 20.6 volume percent TiN. The metallic component exhibited a ductile fracture and the TiN phase had an abrupt, brittle fracture. It can be seen that the TiN remained adherent to the foil, indicating strong adhesion at the ion plated metal/ceramic interface. This suggests that the composite failed due to delamination of the relatively weak metal/TiN hot pressed bond interface. Such a result is consistent with other ion plating research programs where it has been clearly shown that ion plating often greatly (up to 100 times or more) enhances the strength of the film/substrate interface [49].

Also depicted in Figure 16 are the islands of TiN on the surface of the aluminum substrate. This observation is indicative of an important mechanical property of these microlaminate composite materials. The breaking of the film reinforcement into segments dissipates a significant amount of stress build-up during the deformation process. This film fracturing allows the metal-matrix to work harden and the composite to maintain a high load bearing capacity [43]. This multiple fracture phenomenon will continue until the film segments reach a critical size. At this point, matrix failure will occur because of favorable stress requirements; the stress to fracture the film segments is greater than the stress needed for matrix failure..

Figure 17 is an SEM micrograph of the fracture surface of an Al/TiN composite strengthened by 20.6 volume percent TiN. This micrograph depicts a mixed-mode failure involving brittle fracture of the TiN layer and localized delamination along the hot pressed Al/TiN interfaces. This locally delaminated interface leads to a concentration of stress on the adherent regions and eventual failure

by localized plastic flow (necking) and tearing along the hot pressed interface. This finding supports the earlier claim that the strengthening mechanism was limited by an aspect of the fabrication process (in this example, the limitation is the strength of the hot pressed Al/TiN bond). The deformation processes observed in this micrograph are similar to those for mylar laminate sheets. Bhateja and Alfrey [50] report that poor adhesion results in a deformation response involving partial or complete delamination. However, even though these observations support the statement that the strengthening mechanism was limited by an aspect of the fabrication process, the validity and applicability of the critical coating thickness theory cannot be resolved at this time. In our future work, more precise and thorough mechanical testing coupled with methodical SEM and X-TEM analysis is needed to further define these preliminary results.

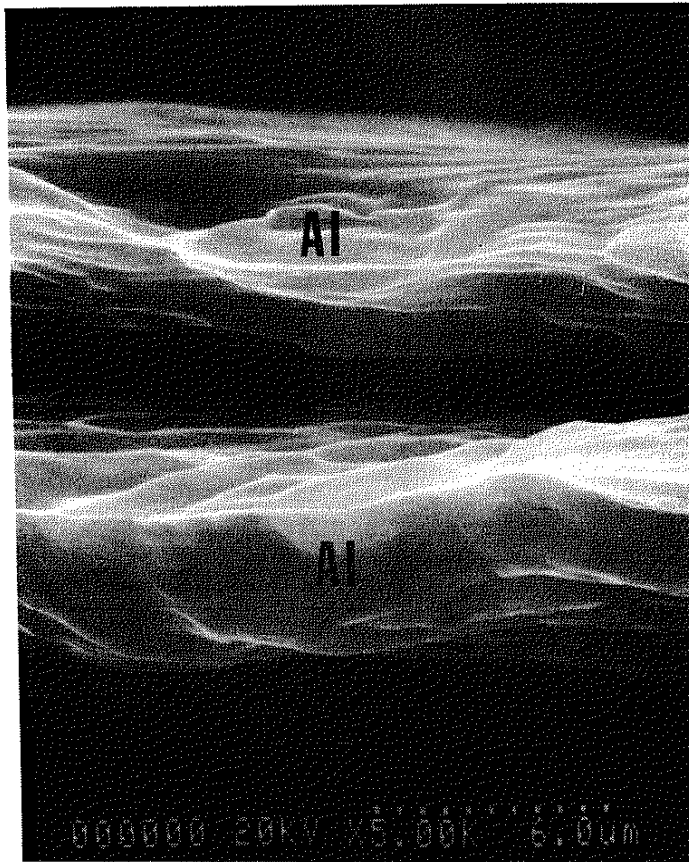


Figure 15 - Scanning electron microscopy of the fracture surface of the hot pressed, uncoated Al foils.

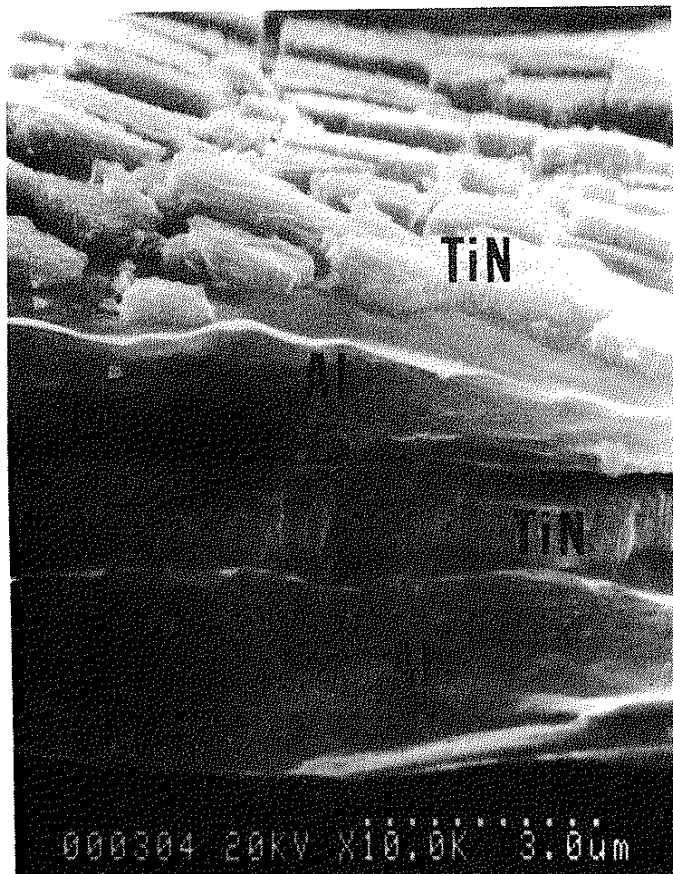


Figure 16 - SEM of of the fracture surface of an Al/TiN composite strengthened by 20.6 volume percent TiN

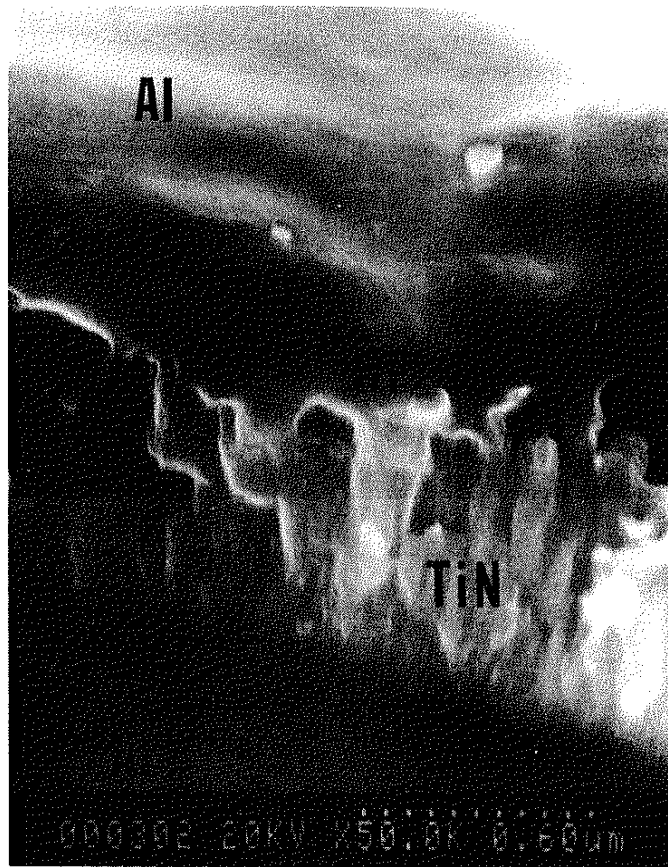


Figure 17 - SEM of the fracture surface of an Al/TiN composite strengthened by 20.6 volume percent TiN
RIP: reactive ion plated interface
HP: hot pressed interface

VI. SUMMARY

A. COMPOSITE FABRICATION

Microlaminate TiN strengthened metal matrix composites have been fabricated via a combined reactive ion plating and hot pressing process. The reactive ion plating procedure deposited a dimensionally uniform, thin film reinforcement of TiN on selected metallic foils. This step allowed controlled variations in the volume percent of the two-dimensional filler by changing the film/substrate thickness ratios (length of deposition time was varied). Also, most importantly, the reactive ion plating technique produced a very adherent metal/ceramic interface.

The hot pressing procedure was utilized in order to metallurgically bond the individual metal/ceramic layers and provide a suitably sized laminate composite for mechanical testing. This process did provide the necessary metal/ceramic bonding to form the microlaminate structure. However, the hot pressing process has not been optimized and thus a weak metal/ceramic interface was formed which failed and hindered the performance of the composite.

B. PROPERTIES

Uniaxial tension testing was conducted on sub-size tensile specimens machined from the microlaminate composite materials. Data concerning the ultimate tensile strength (UTS), uniform strain, and strain to failure was obtained for the Ti/TiN and Al/TiN composites. The Ti/TiN laminates exhibited strengthening greater than that predicted by rule-of-mixtures while maintaining some ductility with the brittle TiN phase present. However, after the initial few volume percent of TiN, the mechanical response of the composites produced knees in the mechanical property curves.. This

effect is due to the failure of the weak, hot pressed Ti/TiN interface and/or a mechanical property dependence upon a critical coating thickness.

The Al/TiN composites did not exhibit the expected increase in the UTS. Due to the weak metal matrix and the poor diffusion bonding, failure of the hot pressed metal/ceramic interface was readily obtained at very small loads. Also, with the weak matrix, damage to the composite structure could have occurred before testing which would have intensified the poor strengthening.

C STRUCTURE AND CHEMISTRY

Fracture surfaces and polished cross-sections of the microlaminate composite materials were examined with a scanning electron microscope. The fracture surfaces depicted the mode of failure of the composites. The composites exhibited a mixed-mode failure involving brittle fracture of the TiN layers and delamination along the hot pressed metal/ceramic interfaces. The mechanically polished and chemically etched cross-sections of the composites were used to show differences in the metal/ceramic interfaces. The etchant preferentially attacked the hot pressed metal/ceramic interface giving direct evidence that a chemical and/or microstructural differential exists between the ion plated and the hot pressed interfaces.

VII. CONCLUSIONS

Microlaminate metal/ceramic composites have been successfully fabricated using reactive ion plating and hot pressing. The composite materials have been mechanically tested and characterized structurally and chemically. It has been observed that these laminate composites exhibit strengthening much greater than that predicted by the simple rule-of-mixtures and still maintain reasonable ductility. However, composite strengthening is limited by delamination of the hot pressed TiN/substrate bond and elimination of this problem will likely result in a major improvement in mechanical properties.

The results of this research will be applied towards improving the microstructure, chemistry, and processing of these engineered composite materials for optimum mechanical properties and performance. This research program has revealed the following statements:

1. Ion plating is an effective technique for producing unique metal/ceramic microlaminate composite materials by virtue of its ability to deposit controlled volume percents of film reinforcement and produce a highly adherent metal/ceramic interface.
2. The ion plated metal/ceramic interfaces and hot pressed metal/ceramic interfaces differ structurally and/or chemically as shown by the preferential etchant attack of the hot pressed interfaces.
3. The hot pressed bonds of these composites were very weak and the processing conditions of the hot press must be improved to strengthen the solid state bonding.

4. The laminate structure provided favorable strengthening while maintaining reasonable ductility. When failure occurred, it was a mixed-mode failure involving brittle fracture of the filler and delamination along the hot pressed interface.
5. The mechanical behavior of these microlaminate materials does not conform to conventional theories such as "rule-of-mixtures" and will require more complex analyses.
6. The evaluation of these engineered microlaminate composites has shown that they possess the necessary mechanical properties (increased strengthening and reasonable ductility by a two-dimensional reinforcement) to justify further study.

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