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NUCLEATION AND GROWTH MECHANISMS IN ION-PLATED TiN FILMS ON STEEL SUBSTRATES

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ABSTRACT:

Cross-sectional transmission electron microscopy (XTEM) was used to investigate the nucleation and growth characteristics of TiN films, ion plated on tool and stainless steel substrates with and without an α-Ti underlayer ($\approx$100 nm thick). It was found that (1) at lower deposition temperatures, the underlayer α-Ti remains unchanged and exhibits a layer + island growth mode; (2) at higher deposition temperatures, the underlayer may transform into a TiC phase on M50 steel and into a δ'-TiN phase on 316L stainless steel; (3) the growth behavior of TiN films was controlled primarily by the reaction thermodynamics and diffusion kinetics of Ti and N adatoms. Based on microscopic evidence together with the kinetic and thermodynamic considerations a mechanistic model is presented to describe the nucleation and growth mechanisms of ion-plated TiN films under the deposition conditions explored in this study.

INTRODUCTION

The nanometer-scale probing of interfaces where thin films originate from and intimately bond to substrates can provide us with important information on the nature of atomistic processes occurring during the early stages of film nucleation and growth. A strong attraction among film atoms is known to favor an island type growth mode (also known as Volmer-Weber growth mode), a strong atomic attraction between film and substrate atoms is known to give rise to layer or Frank-van der Merwe growth, and a diminishing interatomic attraction between substrate and film atoms but an increasing attraction among film atoms with increasing film thickness is known to prompt Stranski-Krastanov or layer + island growth mode [1]. These growth modes have been well-established on several films, vacuum evaporated onto amorphous or cleaved solid surfaces [1]. When energetic ions, atoms and ionized clusters are used during the vapor-phase deposition, it has been observed that (1) the Volmer-Weber type growth modes in vacuum evaporated films can be forced into a Frank-van der Merwe and/or a Stranski-Krastanov type growth mode [2,3], (2) the nuclei density in Volmer-Weber growth mode can be increased dramatically [4-6], and the grain size [7] and morphology [8], as well as the internal defect and void densities [9,10] can effectively be modified.

Apart from model coating-substrate systems, recent studies on commercially important coatings, such as magnetron sputtered TiN, have shown that (1) as a result of epitaxial nucleation on some carbide particles, a bimodal grain size distribution may exist in films deposited on high speed tool steels [11,12]; (2) increasing substrate temperature may result in substantial grain growth [12], (3) biasing of substrates during deposition can disrupt the bimodal growth behavior, increase the nuclei and defect density, and reduce the average grain size and void densities [13,14].

Despite comprehensive studies of model film-substrate systems as well as the sputtered TiN coatings, our knowledge base is somewhat poor on the nucleation and growth behavior of TiN films, ion plated on steel substrates in an enhanced plasma environment. Furthermore, despite the fact that the deposition of an initial Ti underlayer has become a fairly routine practice among many commercial coaters, its influence on thin film growth behavior is not known. In this study, we will focus on these key points in a systematic manner and present a mechanistic model to increase our predictive capabilities in achieving better film structure and performance.

II. EXPERIMENTAL DETAILS

2.1. Preparation of the Substrates and Coatings

The substrates for ion plating were sliced from M50, 440C and 316L steel rods (9.5 mm in diameter) into 4 mm thick discs. After grinding and polishing progressively to a mirror-like surface finish, the specimens were ultrasonically cleaned in acetone, methanol and distilled water and were eventually loaded into the ion plating unit for TiN deposition.

Ion plating of TiN was carried out in a unit that was equipped with a hollow cathode discharge (HCD) electron beam gun for the evaporation of source material, Ti. The specimens were ion sputter cleaned by creating an argon glow discharge around the specimens for 10 minutes. Next, the specimens were heated up to desired temperatures (100^0 and 500^0C) by means of a radiant heater. Finally, the HCD gun was energized to evaporate pure Ti into the plasma, sustained by a substrate bias voltage of 100 V negative dc. and a chamber pressure of 0.11 Pa. A thin layer of pure Ti was first deposited on M50 and 316L substrates immediately before admitting nitrogen gas into the chamber. The 440C specimens were directly ion-plated with TiN at 500^0C.

2.2. Cross-sectional Transmission Electron Microscopy

The TiN coated specimens were first sliced into 2 mm x 1 mm slabs. Two slabs were then epoxy-glued together so that the TiN coated sides were facing each other. This assembly was then cast into a 3-mm-diameter stainless steel tube filled with an epoxy. Discs (approximately 0.5 mm thick) were then cut from this tube and were progressively thinned down by mechanical grinding and dimpling to a thickness of about 20 μm in the center. Ion beam milling of these samples was accomplished by utilizing an Ion Technology Inc. mill operated at a voltage of 6 kV and an ion current of 2 mA. To avoid preferential etching of one phase over another, a Ta mask was used to cover at least one half of the specimen surface. The XTEM imaging was performed with a Philips EM420 analytical electron microscope operated at 120 kV.

III. RESULTS

3.1. TiN Films Deposited on M50 Steel Substrates

Figure 1a shows that at a deposition temperature of 100^0C, the initially deposited α-Ti exists as an undisturbed crystalline phase. Near the substrate surface, there exists a zone (about 10 nm thick) with no grain boundaries detectable. Some small grains displaying equiaxed morphology are located above this zone. Their size ranges from 30 to 50 nm. The interface separating α-Ti from

TiN appears quite sharp and the TiN phase consists of fine columnar grains with diameters ranging from 10 to 20 nm.

Films ion plated at 300^0C, exhibit an underlayer composed of α-Ti and TiC phases. The grains of TiC phase are quite large (approximately 100 nm across) and the grain boundaries are well-defined (see Figure 1b). The α-Ti phase is made up of two types of grains; large grains which span the entire underlayer thickness and very fine grains (denoted by an arrow in Figure 1b) which are sparsely scattered within the underlayer. The grain morphology within the TiN phase is again columnar and the diameter of each column is between 20 and 30 nm.

After ion plating at 500^0C, the underlayer is composed entirely of TiC phase. The grains are equiaxed and exhibit sizes ranging from 2 nm at or near the interfaces between TiC and substrate and TiN and TiC phases to 100 nm near the center (see Figure 1c). The TiN phase on top of the underlayer TiC phase consists of coarse columnar grains originating from the corner points of the grains of TiC phase. Near the TiC phase, the diameter of columnar grains is about 50 nm and it increases gradually with increasing distance from the TiC phase.

3.2. TiN Ion Plated at 500^0C on 316L Stainless-steel

Figure 2 shows that the α-Ti underlayer was transformed into a δ'-TiN phase when plating was done at 500^0C. The grains that make up this underlayer phase are predominantly equiaxed and smaller (about 20 nm across) near the 316L substrate, but larger near the center of the δ'-TiN underlayer. The interface between the underlayer δ'-TiN and overlayer TiN phases appears sharp. The TiN phase itself was made up of columnar grains whose diameters ranged from 30 to 50 nm. The growth mode of the grains in the TiN phase appears to have been unaffected by the grain morphology of the underlying δ'-TiN phase.

3.3. TiN Deposited at 500^0C on 440C Stainless-steel

The TiN films deposited at 500^0C without an α-Ti underlayer possessed very poor adhesion to the substrate. Because of the poor adhesion, there existed a gap between film and substrate sides of the TEM sample. Separation somewhere along the interface always occurred during sample preparation. The XTEM micrograph in Figure 3 reveals that direct deposition of TiN results in a columnar growth pattern somewhat different from those with an underlayer deposited at 500^0C. The grains near the substrate display a smaller width-to-length ratio than those far from it. The length of the grains increases substantially with increasing distance from the interface.

4. DISCUSSION OF RESULTS

Principally, ion plating of TiN coatings in an enhanced plasma involves subjecting the substrate to intense ionic and atomic bombardments which give rise to sputtering, heat generation, and to increased solid state diffusion and chemical reaction rates. In our study, we kept these plasma conditions constant for all the films, but varied the deposition temperature, the substrate material and the presence or absence of an α-Ti underlayer. In this manner, we could elucidate the influence of these variables on the nucleation and growth characteristic of films emerging from various steel substrates as well as underlayers.

4.1. TiN Deposited on M50 Steel

The XTEM micrographs of the TiN films involving an underlayer (see Figures 1a, b and c), suggest that the deposition temperature has a dominant influence on the atomistic processes occurring at interfaces. This is because both solid-state diffusion and chemical reaction rates are thermally activated.

We believe that at 100^0C, owing to relatively low bulk diffusion rates, neither substrate nor the film atoms are capable of interdiffusion in substantial amounts. Further, the activation energy for chemical reaction is also relatively low, so that the probability of forming a new phase is low. However, because of the intense ionic and atomic bombardment in ion plating, the Ti adatoms can diffuse long distances in the lateral direction. We believe that high surface diffusion capability of the Ti adatoms combined with an interatomic attraction between Ti and substrate atoms initially promotes a layer-by-layer growth mode. It is possible that beyond a certain thickness, the Ti atoms may regroup themselves to form a few equiaxed grains within the underlayer as seen in Figure 1a. This type of growth behavior is known as the Stranski-Krastanov, or layer plus island type growth mode and has been observed on several other coating-substrate systems [1].

According to the Ti-TiC phase diagram, α-Ti and TiC can coexist as stable phases [15]. The observation of an underlayer composed of α-Ti and TiC phases in Figure 1b is hence consistent with the phase diagram. We believe that this composite phase primarily results from an increased bulk atomic diffusion rate for C. Compared to all the other atomic species within the system, C is smaller in size and has a greater diffusion coefficient. It is also somewhat abundant ($\approx$0.85% by weight in M50 steel substrate) and thermodynamically attracted to Ti atoms. Hence, it preferentially diffuses into the α-Ti phase and reacts with Ti to form the TiC phase. It is possible that the α-Ti phase grows initially layer-by-layer, at the same time as C diffuses into the growing film. Upon supersaturation, the TiC precipitates as a stable phase and grows laterally by means of grain boundary migration. The infusion of N atoms from the overlayer TiN phase is also a distinct possibility. Nevertheless, at 300^{0}C, the diffusion coefficient of N in Ti is 1/1000th that of C [16]. Further, most N atoms are chemically bound to Ti. Therefore, at this intermediate temperature, C that comes from the substrate steel plays a dominant role in the growth kinetics of the grains within the underlayer. Because of the large influence of C, the growth mode of films deposited at higher temperatures cannot be fit into any of the universal growth modes mentioned earlier.

At 500^{0}C, both bulk and surface diffusion rates are relatively high. We believe that the Ti adatoms that arrive at the start of ion plating react with C, thereby forming the very fine grains adjacent to the substrate steel (see Figure 1c). The larger grains seen farther from the interface are the result of two interrelated phenomena: (1) the availability of C is considerably reduced because of the depletion of C in the near surface region and because the first row of TiC grains act as a diffusion barrier; (2) owing to the much increased bulk and surface diffusion rates plus the longer time available, the Ti adatoms can migrate longer distances and construct larger grains before they too react with C and transform into TiC. It is concluded that at 500^{0}C, the initial nucleation was dominated by reaction kinetics, whereas the subsequent growth was dictated by an interplay between surface and bulk diffusion rates at this high deposition temperature.

Regardless of the chemical as well as morphological nature of the underlying phases (e.g., α-Ti, α-Ti+TiC, iron, etc.), we believe that in general, the growth mode of the grains within the TiN phase was predominantly controlled by the thermodynamic and kinetic constraints imposed upon Ti and N adatoms at each deposition temperature. From the micrographs in Figure 1a-c, the influence of the α-Ti and/or α-Ti+TiC underlayers is not very obvious. But at 500^0C, some small grains similar to those seen on top of the steel substrate appear between TiC and TiN phases plus the TiN grains preferentially originate from the corner points of these grains, suggesting that the shape and orientation of underlying grains may have some influence in the nucleation and growth behavior of TiN phase at higher temperatures (see Figures 1c).

A chemical reaction between Ti and N adatoms on a surface growing outwardly, results in the formation of TiN, hence greatly immobilizes these atoms and possibly stabilizes the morphological shapes of the resulting grains. At low deposition temperatures (e.g., 100^0C), owing to much lower bulk and surface diffusion rates, thin columnar grains with large defect density result (see Figure 1a). At 500^0C, because of the higher bulk and surface diffusion rates, atomic and/or molecular species can migrate further and construct coarse columnar grains possessing a low defect density as shown in Figure 1c. Similar observations were made on sputter deposited TiN coatings prepared at different temperatures [14]. In short, the growth behavior of the overlayer TiN films is largely governed by the thermodynamic and kinetic constraints imposed upon adatoms Ti and N. It is reasonable to believe that the formation of a TiN phase with equiaxed grains probably requires deposition temperatures higher than 500°C.

4.2. TiN Film Deposited on 316L Stainless-steel at 500°C

When the substrate material contains very little C, (e.g, 316L contains less than 0.04% C by weight), our results reveal that N can diffuse out of the TiN phase into the α-Ti phase and cause the formation of the δ'-TiN. According to the latest Ti-N phase diagram, the δ'-TiN exists as a stable phase with an atomic N concentration of 38% and a C_c-(Si_2Th) type tetragonal crystal structure [17]. In the micrograph, there is no evidence of any form of chemical interaction between coating and substrate atoms. However, the austenitic structure of the 316L stainless steel appears to have been partially transformed into martensite structure (denoted by an arrow) as can be seen in Figure 2. This could very well be due to high residual stresses that exist in ion-plated films. In short, when substrate is poor in C atoms, the growth morphology of the grains within the underlayer is dominated by the infusion of N from the overlayer TiN phase. The growth behavior of the grains within the TiN phase though is largely controlled by the reaction thermodynamics and diffusion kinetics of the Ti and N atoms.

4.3. TiN Film Deposited on 440C Stainless-steel at 500^{0}C

In the absence of the underlayer α-Ti, the growth behavior of the TiN grains is again controlled by the reaction thermodynamics and diffusion kinetics of the Ti and N adatoms. Even though the substrate steel contained about 1% C by weight, there is no physical evidence on the influence of substrate and/or its chemical composition on the growth characteristics of the TiN film.

4.4. Proposed Model and Concluding Remarks

Based upon the experimental observations presented above, the following mechanistic model is presented to describe the growth modes of films formed on various surfaces at different temperatures (see Figure 4).

Under situations where bulk diffusion rates are low (e.g., deposition at 100^{0}C), the growth modes of the films are controlled by the surface diffusion capability of the adatoms. Owing to a continuous energetic bombardment, Ti adatoms can diffuse large distances and result in a Stranski-Krastanov type layer+island growth mode when there are no impeding effects from other atomic species. When N atoms are introduced into the system, Ti adatoms react with N and result in the formation of the TiN grains whose growth behavior is largely controlled by the kinetic constraints. Under situations where bulk diffusion rates are also high (e.g.,

500^0C), growth modes of the grains within various phases are controlled by the combined effects of both surface and bulk diffusion capabilities of the participating atomic and/or molecular species as illustrated in Figure 4. In general, the size and the shape of grains within various crystalline phases at different temperatures are subject to thermodynamic and kinetic constraints imposed upon the atoms that constitute these grains.

An in-depth knowledge of the atomistic processes that control the extent of solid state interactions at or near the interfaces as well as within the solid films, and how these interactions affect the general film properties, may be of potential importance when developing novel coatings with improved properties. Based on the results of this study, one may predict the nature and the extent of solid state interactions at or near the interfaces for a given deposition condition, and establish model relationships between interface and performance characteristics of the resultant coating-substrate systems. By using a similar approach, prior to the deposition of TiN or TiC, one can plasma nitride and/or carburize the steel substrates to a small extent as an initial step, followed by the deposition of a thin underlayer of Ti, Hf, Zr etc., for achieving graded interfaces with dual-phase structures, e.g., α-Ti+TiC at moderate deposition temperatures. Hence, the danger of softening the substrate steels and creating large internal stresses may be minimized. A few studies in the recent literature have demonstrated that film adhesion relates strongly to the chemical characteristics of the interfaces between hard coatings and steel substrates [18-20].

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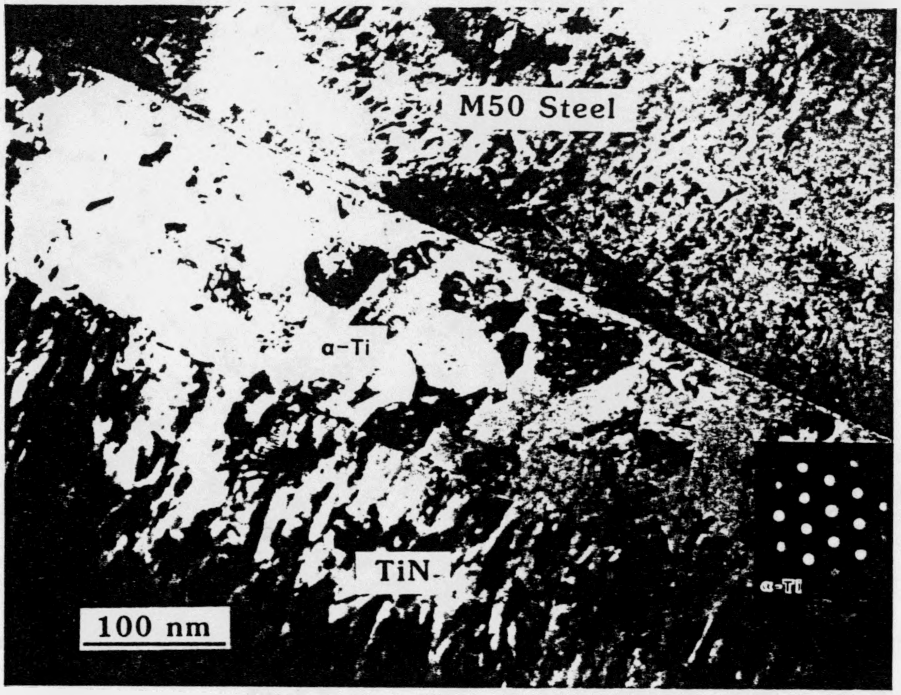
FIGURE CAPTIONS:

Fig. 1. XTEM micrographs of the interfacial regions of the TiN films ion plated at a) 100, b)300 and c)500°C on M50 steel substrates with an α-Ti underlayer.

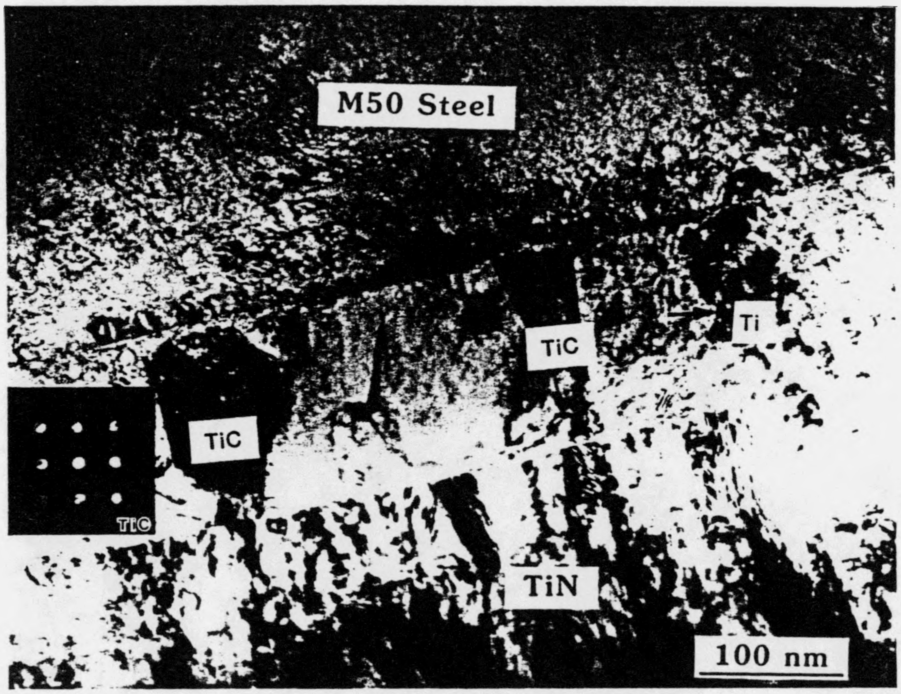
Fig. 2. An XTEM micrograph of the interfacial region of the TiN film ion plated at 500°C on a 316L stainless steel substrate with an α-Ti underlayer.

Fig. 3. An XTEM micrograph of the interfacial region of the TiN film ion plated at 500°C on a 440C stainless steel substrate without an α-Ti underlayer.

Figure 4. A schematic illustration of the mechanistic model that explains the growth modes of films on top of various phases.

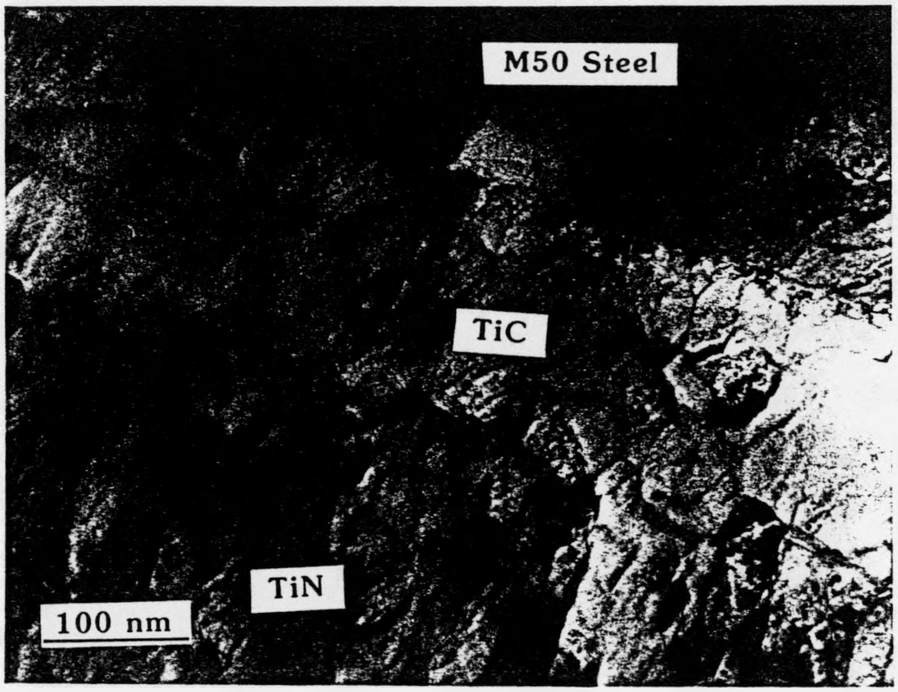


(a)



(b)

Fig. 1



(c)

Fig. 1

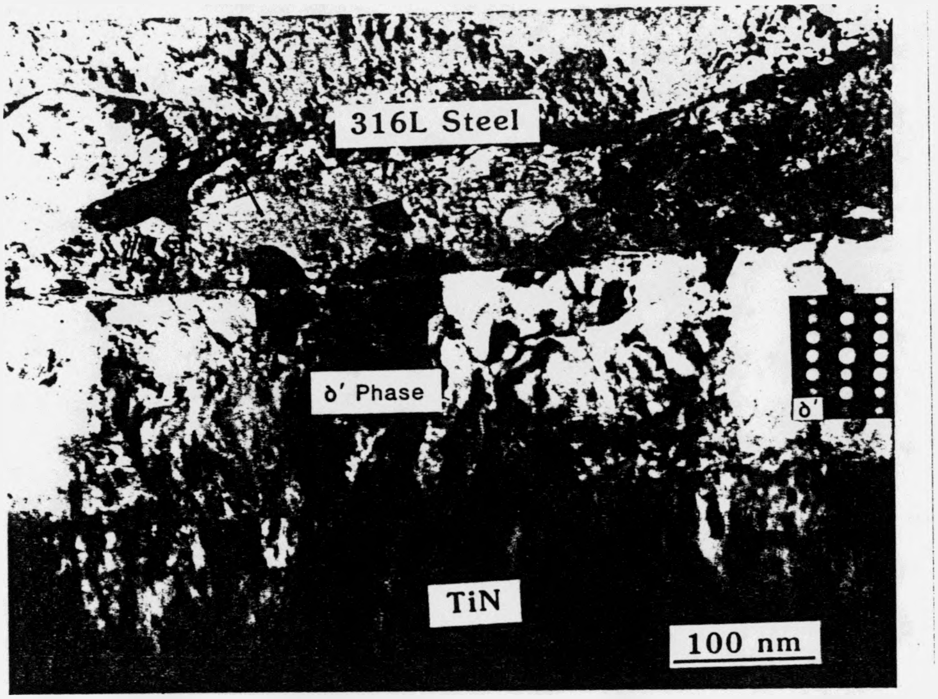


Fig. 2

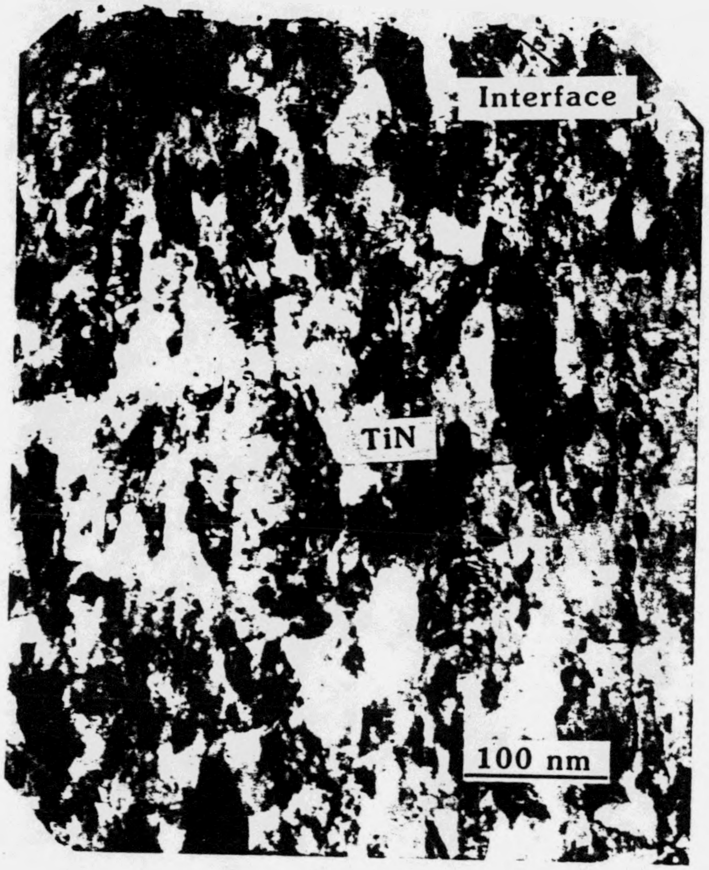


Fig. 3

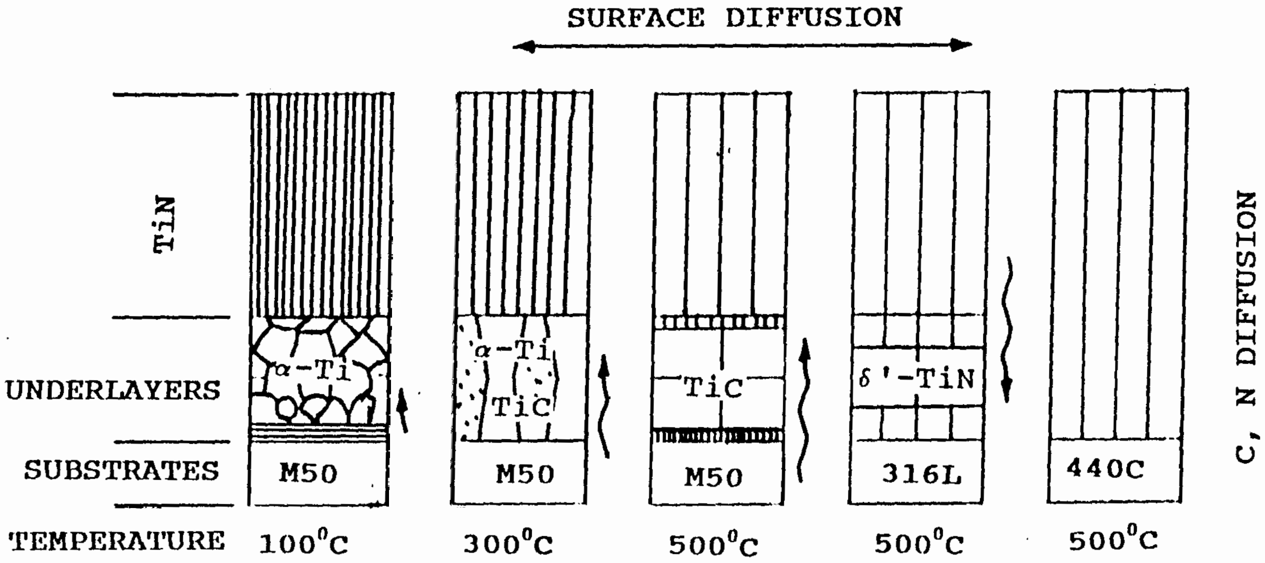

SURFACE DIFFUSION
TiN
UNDERLAYERS
SUBSTRATES
TEMPERATURE
α-Ti
α-Ti
TiC
TiC
δ'-TiN
M50
M50
M50
316L
440C
100°C
300°C
500°C
500°C
500°C
C, N DIFFUSION

Fig. 4