Effect of Postdeposition Annealing on Structure and Chemistry of the TiN Film/Steel Substrate Interfaces

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EFFECT OF POST-DEPOSITION ANNEALING ON STRUCTURE AND CHEMISTRY OF THE TiN FILM/STEEL SUBSTRATE INTERFACES*

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ABSTRACT

This study deals with solid-state phase transformations occurring at interfaces between a TiN film and an AISI M50 steel substrate during post-deposition annealing at 500 and 1000°C. Cross-sectional transmission electron microscopy (XTEM) was used to investigate the nature of phase transformations at these interfaces. The TiN films were ion plated onto M50 steel with an initial Ti underlayer at 100°C. XTEM and electron-energy-loss spectroscopy of the interfaces indicated that the ion-plated Ti underlayers transformed into a TiC phase during annealing at 500°C and into a Ti(C,N) phase during annealing at 1000°C. In addition, the density of defects within grains was significantly reduced during annealing and the grains themselves became larger.

INTRODUCTION

Chemical and microstructural characteristics of thin films and film substrate interfaces have attracted considerable attention in recent years [1-3] because, these films originate in and intimately bond to the substrate materials across the interfaces. To characterize the interfaces, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), electron energy loss spectroscopy (EELS), and cross-sectional transmission electron microscopy (XTEM) methods have been used extensively [1-4]. From the results of previous investigations, it appears that the nature of adhesion is strongly related to the extent of physicochemical interactions that occur at the film substrate interfaces [4-6]. To achieve good correlation between adhesion strength and physicochemical interactions, it was demonstrated that one must use a combination of analytical tools (e.g., EELS, AES, XTEM) [4].

Because of their increasing importance in the metal-cutting and forming, ball bearing, and electronics industries, TiN coatings and their interfaces have attracted more attention than other coating types. We have examined the effects of deposition temperature and initial Ti underlayers on the nucleation and growth mechanisms of TiN films on tool steel substrates [1-3]. Others have investigated the influence of intermediate layers and various surface pre-treatments on adhesion between TiN films and a variety of steel substrates [4-7].

Among other factors, the deposition of Ti underlayers (typically 0.1 μm thick) was proven to be beneficial to film adhesion and has become a routine practice in industrial TiN coating. It was thought that such an underlayer could act as a glue that holds the TiN film and the underlying substrate together. Another argument was that since Ti is much tougher than TiN, it may help absorb some of the strain energy that may result from mismatches in thermal expansion coefficients and lattice parameters. Recent studies have demonstrated that these initial Ti underlayers may indeed be important in the nucleation and growth modes and thus in the adhesion of TiN coatings to commercial tool steel substrates [4-7]. Using a combination of analytical tools, we demonstrated that both deposition temperature [3] and substrate material [8] play major roles in the chemical state of the Ti underlayers. We found that these initial Ti underlayers transformed partially into a TiC phase during ion plating at 300°C and completely into a TiC phase during ion plating at 500°C [3]. The carbon necessary for the synthesis of the TiC phase comes from the tool steel substrates which are generally rich in C.

Clearly, special emphasis has been placed on determining the effects of various deposition parameters on the structural morphology and chemical characteristics of the films and film substrate interfaces. However, the influence of post-deposition annealing on the chemical and microstructural characteristics of the films and their interfaces has remained relatively unexplored.

TiN coatings are generally subjected to harsh tribological environments often involving high temperatures. For example, during metal cutting and/or forming, the cutting edges of TiN-coated tool bits or inserts may reach quite high temperatures, mainly because of frictional heating. This may in turn increase the activation energy for solid-state diffusion of the atoms in the coating and tool materials and may eventually lead to phase transformations. In this paper, we report the solid-state phase transformations occurring at interfaces between a TiN film and an AISI M50 tool steel substrate during post-deposition annealing at 500 and 1000°C. XTEM was used to investigate the nature of phase transformations at these interfaces. The TiN films were ion plated onto M50 steel with an initial Ti underlayer at 100°C.

EXPERIMENTAL

Substrate Materials

The substrate material in this study was prepared from AISI M50 steel rods (9.5 mm in diameter) by slicing them into 4-mm-thick disks. The chemical composition (in wt.%) of this steel was C: 0.84, Cr: 4.16, Mo: 4.18, V: 0.99, Mn: 0.29, Si: 0.21, S: 0.004, P: 0.005, with the balance being Fe.

One side of each sliced disk was ground and polished progressively to give a final surface finish of approximately 0.05 μm center-line-average. The disks were ultrasonically cleaned in acetone, methanol, and distilled water before being ion plated with TiN.

Ion Plating of TiN

The TiN coatings were deposited on the polished side of the substrate disks in an ion-plating system equipped with a hollow cathode discharge (HCD) electron beam gun that served two important purposes: (a) intensification of glow-discharge plasma around the substrate holder and (b) evaporation of the pure Ti source from a water-cooled crucible. Before ion plating, adsorbed contaminants were removed from the substrate surface by creating an argon glow discharge plasma around the specimens for 10 min. The substrates

were heated to 100°C by radiant heaters. Finally, the HCD gun was energized to evaporate the pure Ti into the argon plasma, which was created and sustained by applying a bias voltage of 100 V negative DC to the substrate holder while chamber pressure was maintained at about 0.11 Pa. A 100-nm thick pure Ti layer was deposited first on the substrate. Nitrogen gas was then admitted into the deposition chamber to synthesize the TiN phase on top of the initial Ti layer. Total thickness of the resultant films was approximately 2 μm. A more detailed description of the ion-plating system and associated procedures can be found in Ref. 9.

Following ion plating, a few of the coated specimens were subjected to post-deposition annealing at 500° and 1000°C for 45 min. A high-vacuum furnace, capable of maintaining a vacuum level of better than 10^{-4} Pa, was used.

Cross-Sectional Transmission Electron Microscopy

Thin foils for XTEM examination were prepared by progressively thinning the cross-sectioned samples with dimpling and ion milling machines. First, the TiN-coated substrates were cut into rectangular slabs, typically 2 x 1 mm. The TiN-coated sides of these slabs were glued together with epoxy and allowed to dry. They were then placed in a 3-mm-diameter stainless steel tube filled with a conductive epoxy. Several disks of 0.5 mm thickness were cut

from this tube and progressively thinned by mechanical grinding. The thickness of the disk center was further reduced with a dimpling machine to about 20 µm. Thinning of the central portion of the samples was continued with an ion beam milling machine that incorporated two ion-beam sources, each operating at 6 kV and an ion current of 2000 µA. A Ta mask was used to avoid preferential milling of either the steel or the TiN side. The Ta mask was positioned to cover at least half of the specimen surface, which was initially milled at an angle of 15° for about 3 h, followed by further milling at a reduced angle of 12.5° for another 3 to 4 h. Our experience has shown that by following these steps, one can successfully obtain a thin foil consisting of both the film and substrate sides of the original samples and is transparent to an electron beam. A more detailed description of the preparation procedures is given in Refs. 1 and 2.

The XTEM examination of the thin foils was conducted in a Philips EM420 analytical electron microscope incorporating a Gatan EELS and an energy-dispersive X-ray (EDAX 9900) data acquisition system. The microscope was operated at 120 kV.

RESULTS AND DISCUSSION

As-Deposited TiN Films

Figure 1a is an XTEM micrograph of the as-deposited TiN film. As is clear from this micrograph, the initially deposited Ti underlayer is unique and is separated from the TiN film and the M50 steel by distinct boundaries. Convergent beam electron diffraction (see pattern in inset of Fig. 1a), together with the EELS spectrum (see Fig. 1b) reveals that the underlayer retains its original crystalline structure, i.e., α-Ti. The presence of some N and C atoms within this layer cannot be ruled out. However, as suggested by the diffraction pattern and the EELS spectrum, the N and C concentrations must have been too low to be detected by EELS and/or to trigger phase changes. According to the Ti-N phase diagram [10], atomic N can dissolve in α-Ti up to about 22 at.% at room temperature without causing phase transformation. Likewise, C can also dissolve in α-Ti as an interstitial species.

As for solid-state interactions between substrate and Ti atoms, we believe that solid-state interdiffusion and chemical reaction rates were inadequate at 100°C. As a result, the initially deposited Ti layer remained chemically undisturbed. However, because of the intense ionic/atomic bombardment, the surface mobility of the Ti atoms was relatively high. Therefore, the Ti atoms could fill in the gaps and low-atomic-density areas and thus suppress columnar

growth. In previous studies, we demonstrated that at higher ion-plating temperatures, e.g., 300 and 500°C, the initial Ti underlayers transformed partially or completely into TiC, depending on deposition temperature [1-4]. The C necessary for phase transformation came from the C-rich tool steel substrates.

Morphologically, the Ti phase consists of large and some small grains. At the top of the substrate surface is a zone about 10 nm thick with no detectable grain boundaries. Based on this observation, we believe that because of the relatively low thermal activation for bulk diffusion and chemical reaction - but also due to a fairly high surface diffusion capability for depositing Ti atoms (mainly because of the continuous ionic/atomic bombardment) - Ti atoms condense first on the surface in a layer-by-layer growth mode, thereby forming a zone with no apparent grain boundaries [3]. However, as the coating thickens, the Ti atoms tend to regroup themselves and form equiaxed grains, as seen in the center of the Ti underlayer (see Fig. 1a). This behavior is known as the Stranski-Krastanov growth mode [11].

As for the TiN film grown atop the Ti underlayer, the grain morphology is the dense columnar type. The boundaries between steel substrate and Ti underlayer, and between Ti underlayer and TiN phase, are rather discrete. Unlike magnetron-sputtered TiN films [2,12], the ion-plated TiN films do not appear to contain intercolumnar pores and/or void networks.

TiN Film Post-Annealed at 500°C

The XTEM micrograph in Fig. 2a shows the microstructure of a TiN film subjected to post-annealing at 500°C. It is clear that marked changes occur in both the chemical and structural states of the films and interfaces during post-annealing.

First, from the convergent beam electron diffraction pattern (inset in Fig. 2a), we found that the initial Ti underlayer had transformed into a phase exhibiting a B1-type NaCl crystal structure. Both TiC and TiN are known to possess this type of crystal structure. Their lattice parameters are also very close, i.e., 4.239 Å for TiN and 4.327 Å for TiC. Therefore based on diffraction pattern alone, it was difficult to ascertain whether the interface was transformed into a TiN or a TiC phase. With the aid of EELS, we found that Ti and C were the most abundant species in this region (see Fig. 2b). Based on these findings, we concluded that the Ti underlayer was transformed into TiC.

Second, as shown in Fig. 2a, the boundaries separating (a) the substrate from the original underlayer and (b) the underlayer from the TiN phase are not as clearly defined as those seen in the as-deposited TiN films. Third, the grains within the underlayer are well-defined and have distinct boundaries. The grains are equiaxed, with sizes in the order of 100 nm. A zone composed of very fine grains (5 to 10 nm across) is also noticeable near the substrate

surface. Finally, although still columnar in nature, the original grain morphology of the TiN phase was somewhat distorted; column diameter becomes larger after post-annealing. Furthermore, the columnar grains shown in Fig. 2a exhibit a lower defect density than that of the original grains.

For the phase transformation during post-annealing at 500°C, we propose the following explanation. We believe that at this relatively high temperature, activation energy for bulk diffusion and chemical reaction increases for the atomic species constituting the coating and substrate materials. In particular, those species with higher diffusion coefficients can migrate with relative ease. Among all the atoms within the film/substrate system, C enjoys the highest diffusion coefficient at 500°C in α-Ti [13]. Therefore, having migrated across the interface, it can accumulate within the underlayer Ti, which incidentally has a high chemical affinity for C. According to a recent paper by Bergner [13], C at 500°C has a diffusion coefficient nearly three orders of magnitude higher than the next candidate atom (N) in the system. The M50 steel consists of 0.85 wt.% C; therefore, we believe that the phase transformation, i.e., the synthesis of TiC, during post-annealing at 500°C was controlled by the C atoms from the steel substrate. In a series of previous studies, we observed that similar phase transformations can also occur at interfaces between Ti underlayers and steel substrates when ion plating was performed at 500°C [1,3].

Diffusion of N from the top layer of TiN into the Ti underlayer is thought to be highly unlikely, because most of the N atoms are already chemically bound to Ti. Thermodynamically, TiN is more stable than TiC and thus cannot be oxidized further by TiC [14]. Nevertheless, the presence of complex phases comprising both N and C atoms, especially near the interphase boundary between TiN and TiC and between TiC and steel cannot be ruled out. The EELS system used in our study had a relatively large beam size (about 40 nm in diameter). This made it difficult to analyze the chemical nature of interphase boundaries at a much finer scale. High-resolution EELS may be helpful in determining the true chemical states of these interfaces.

TiN Film Post-Annealed at 1000°C

The XTEM micrograph in Fig. 3 reveals the extent of solid-state phase transformations at interfaces during post-annealing at 1000°C. Convergent-beam electron diffraction, together with an EELS spectrum (inset) suggested that the initial Ti underlayer had transformed into two phases: TiN and TiC. The presence of other phases incorporating Fe, Cr, or Mo could not be ascertained with EELS, mainly because of the large beam size used.

The grains of the newly formed phases are equiaxed and somewhat smaller than those formed during post-annealing at 500°C. Again, the grains near the M50 substrate are generally smaller than those near the center of the transformed layer. The interface between the

transformed layer and the M50 substrate appears sharp but has a ragged shape.

As is evident from Fig. 3, the columnar nature of the original grains within the TiN phase is preserved even after post-annealing at 1000°C however, the density of defects within the grains is significantly reduced and the columnar grains increase substantially in diameter during post-annealing.

Based on the evidence provided in Fig. 3, we propose the following interpretation for the observed phase transformations at 1000°C. Above 882°C, the α-Ti phase transforms into the ß-Ti phase and the diffusion coefficients of C and N increase dramatically. For example, the diffusion coefficient of N is approximately five orders of magnitude higher in ß-Ti at 1000°C than in α-Ti at 500°C. The diffusion coefficient of C also increases but not as dramatically as that of N. Compared to that in α-Ti at 500°C, the diffusion coefficient of C is nearly three orders of magnitude higher in ß-Ti at 1000°C. Hence, the difference in diffusion coefficient between C and N narrows to about one order of magnitude when the post-annealing temperature is raised to 1000°C. Consequently, along with C, some N atoms can also diffuse into the Ti underlayer at 1000°C and participate in the phase transformation.

We believe that at 1000°C, the extent and nature of the solid-state

phase transformations at interfaces are governed by the solid-state diffusion rates and chemical reaction rates of participating atoms, i.e., C, N, and Ti. Because of their significantly higher diffusion coefficient, C atoms diffuse faster into the Ti underlayer than do N atoms. However, because of a more negative standard heat of reaction with Ti, the N atoms react more readily with Ti than do C atoms (e.g., at 1000°C, the standard heat of reaction for N and Ti to form TiN is about -80,700 cal/mole and for C and Ti to form TiC is about -44,970 cal/mole). Furthermore, there is a distinct possibility that while the Ti atoms may have initially reacted with fast-diffusing C atoms and already turned into TiC, a chemical reaction between N and TiC may have taken place as N atoms become available and TiN may have formed as a result of a secondary phase transformation. At 1000°C, the heat of reaction favors formation of TiN, not TiC. Of course, there are some limiting factors. First, for such a secondary phase transformation to take place, N atoms must be readily available within the underlayer; therefore, there are kinetic constraints. Second, most N atoms are chemically bound to Ti and are not readily available. Thermodynamically, the liberation of N from Ti is thought to be quite difficult. We therefore, believe that the N atoms participating in the phase transformation of the interface region were those of the interstitial solution type, not the reacted type.

Because of the dynamic nature of the kinetic and thermodynamic events at such interfaces during post-deposition annealing, it is

difficult to obtain a clear understanding of the mechanisms involved in the solid-state phase transformations explored in this study. However, the data presented provide some insight and are consistent with the thermodynamic and kinetic constraints imposed on each atomic species at the annealing temperatures used in this study.

CONCLUSIONS

(1) The extent and nature of the solid-state phase transformations at interfaces are subject to particular kinetic and thermodynamic constraints imposed on C, N, and Ti at each post-annealing temperature.

(2) The ion-plated Ti underlayer transforms into a TiC phase during post-annealing at 500°C. The C atoms necessary for phase transformation come from the M50 substrate.

(3) The ion-plated Ti underlayer transforms into TiC and TiN phases during annealing at 1000°C. The N atoms necessary for the synthesis of TiN come from the TiN film.

(4) The density of defects within grains is significantly reduced during post-annealing and the grains become larger.
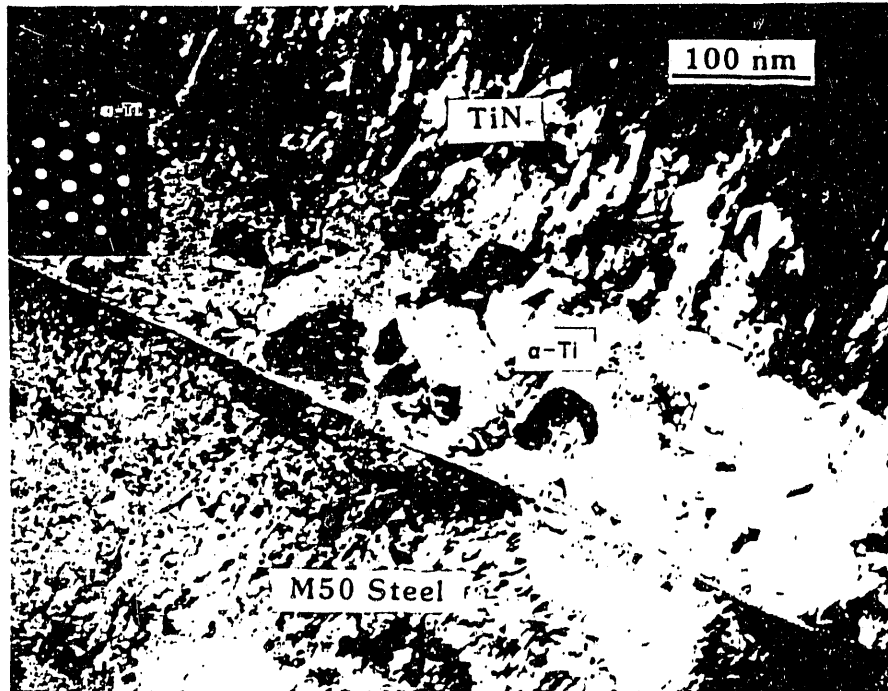
ACKNOWLEDGMENT

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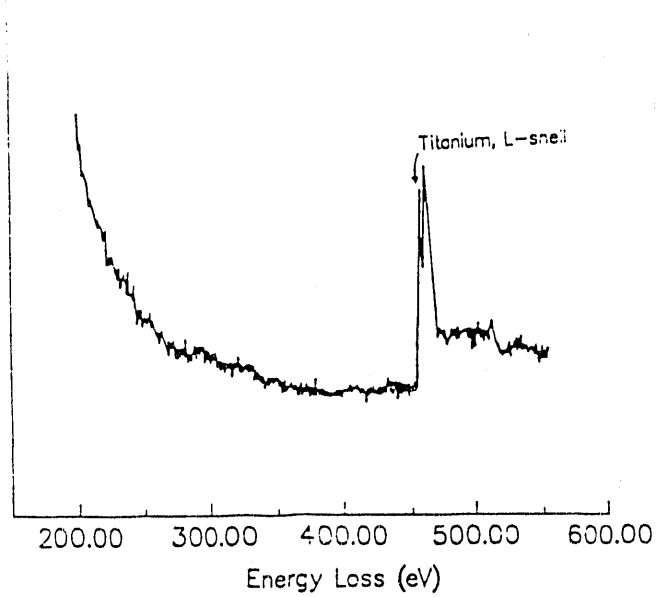
FIGURE CAPTIONS:

Fig. 1. (a) XTEM micrograph (inset shows convergent beam electron diffraction pattern) and (b) EELS spectrum of interfacial region of TiN film ion plated at 100°C on M50 steel substrate with Ti underlayer.

Fig. 2. (a) XTEM micrograph (inset shows convergent beam electron diffraction pattern) and (b) EELS spectrum of interfacial region of TiN following post-annealing at 500°C.

Fig. 3. XTEM micrograph and EELS spectrum of the interfacial region of TiN film following post-annealing at 1000°C.
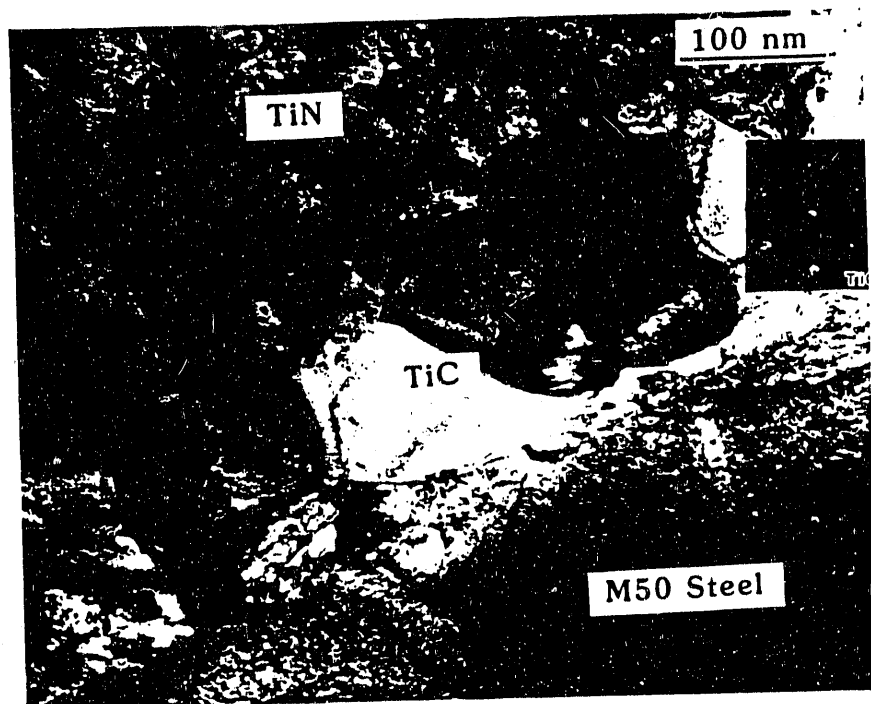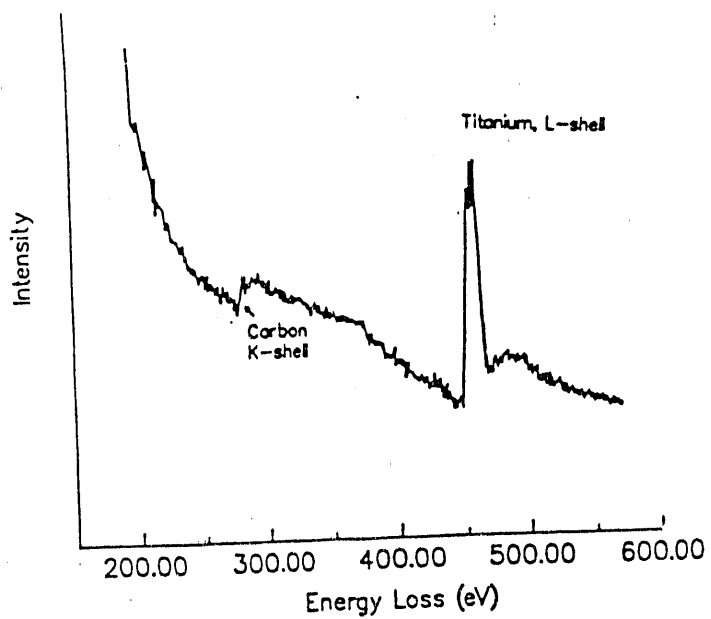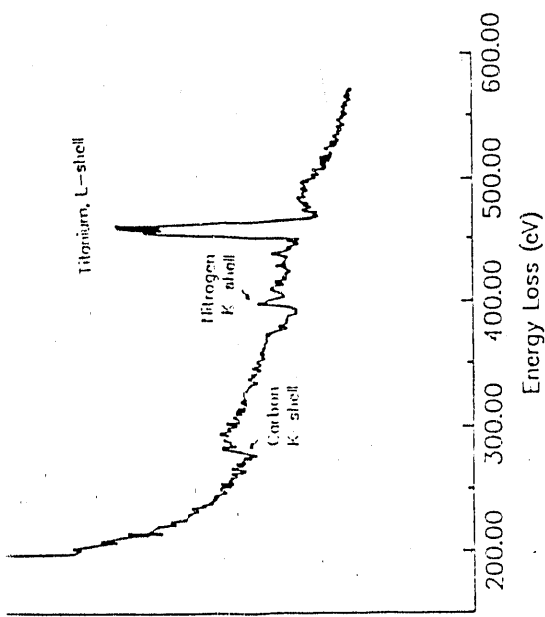
(a)

(b)

Fig. 1

(a)

(b)

Fig. 2

TiN

TiC+TiN

M50 STEEL

100 nm

Titanium, L-shell

Nitrogen
K shell

Carbon
K shell

Intensity

Energy Loss (eV)

200.00   300.00   400.00   500.00   600.00

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