High Dose Nitrogen Implantationof PVD Titanium Nitride Coatings

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Abstract – Cemented carbide samples coated with TiN in a standard commercial PVD process were implanted with the 90 keV nitrogen ions. The dose rate varied within (1.35–9.0) μA·cm^{-2} and the implanted dose varied within (3.6–13.4)·10^{17} cm^{-2}.

Transmission electron microscopy, Auger electron spectroscopy, scanning electron microscopy, optical micro-measuring 3-d station and nanoindentation were used in the investigation.

All samples show TiN exfoliation. This results in a loss of the nitrogen implanted zone, and a consequent loss of the wear-resistance properties. There is concomitant uptake of post-implantation oxygen which is believed to form an amorphous TiO_2 component in the surface leading to the well-established low frictional properties. This uptake decreases as the dose rate increases and would also lead to a loss of the wear-resistance properties. The results confirm that a dose 3·10^{17} cm^{-2} is optimal provided that the dose rate does not exceed the present industrial standard.

1. Introduction

Ion implantation is a standard procedure for improving the wear resistance of tool steels and coated cutting tools at an industrial level using nitrogen [1] or metal ions [2, 3]. As summarized in [4, 5], the effects of implantation are twofold: an implanted zone (termed the IZ) is generated where the ions come to rest directly beneath the surface, with a hardened implantation affected zone (termed the IAZ) extending below it; this is often termed the long range effect. Cutting tools may be coated with TiN and its homologues as made by chemical vapour deposition (CVD) or physical vapour deposition (PVD) methods. The former type of coating is nearly free of residual stress (it is generally slightly tensile, 0–0.3 GPa) whilst the latter has a high residual compressive stress (order of 6 GPa). As summarized previously [6, 7] implanting TiN made by CVD with lower mass ions such as nitrogen, carbon or Ti-Ni dual implants increases its hardness and wear resistance but with little change in residual stress. Increasing the implantation energy beyond a certain threshold causes a rapid increase in the compressive residual stress which can lead to failure by exceeding the tensile strength-a condition termed over-implantation. TiN made by PVD is already under high compressive residual stress and is therefore generally implanted only with lower mass ions either metal or nitrogen.

It has been found that the effect of nitrogen implantation is optimal at 3·10^{17} ions cm^{-2} implanted with a typical ion current (dose rate) of 3.17 μA·cm^{-2} [1] at an energy of typically 90 keV; lower doses have little effect, but higher doses (in contrast to metal ion implantation) lead to a softening of the surface. The mechanisms were examined by Bull et al. [8] where previous work was also reviewed in some detail (and is therefore not repeated here). The present work is an extension to the higher ranges of implantation dose and dose rate to understand the mechanism of this loss of wear resistance. It constitutes the latest in a series of studies carried out by the authors [8–10] to understand the mechanism of nitrogen implantation in TiN.

2. Experimental procedure

The samples were commercially cemented carbide substrates which were coated with approximately 3 μm TiN in a standard commercial PVD process by Balzers, Germany. The samples were implanted with nitrogen at 90 keV with a N_2^+ to N^+ ratio of 1.6:1 in a cryo-pumped commercial-size ion beam assisted deposition (IBAD) unit with ion implantation capabilities. The base pressure was in the range (2.67÷5.3)·10^{-5} Pa. This implantation system was used (in place of the diffusion pumped system used in the earlier study [10]) to ensure that effectively all the oxygen was removed from the system such that any oxygen recorded in the surface subsequent to implantation would only be that still remaining from the unimplanted virgin surface of the TiN coating (and possibly some oxygen absorption by a damaged surface on exposure to atmosphere following processing); it should be added that this system is used for IBAD treatments with reactive materials.

The implantation was carried out under conditions typical of industrial usage, but at higher rates and to higher doses. A 3×3 matrix of samples, low-to-high current densities (dose rates) low-to-high doses, was made as per the data given in Table 1. As the majority of N_2^+ ions under 90 keV break on impact into two at 45 keV, the ion range and damage parameters were calculated from Transport of Ions in Matter (TRIM) program [11] and were therefore made for 45 and 90 keV N^+. These are, respectively: ion range R_p=62 and 119 nm; ΔR_p=24 and 35 nm; damage range X_d=40 and 101 nm; ΔX_d=20 and 45 nm. The total profile is thus that from the 45 keV majority component skewed to higher values by the 90 keV component, as shown in our previous study [10]. It should be mentioned that the current industrial practice [2] of nitrogen ion implantation is completed in 1 h so that the time scales required by the present samples would make them non-viable commercially.

Table I. Implantation current density (dose rate) (μA·cm^{-2}) and implanted dose (10^{17} ions·cm^{-2}) in the present 3×3 sample matrix: (dose rate-dose)

1.44–3.6	1.78–8.9	1.35–13.4
4.55–3.8	5.45–9.1	4.01–13.4
7.8–3.9	9.0–9.0	6.7–13.4

The samples were studied as follows:

The samples were then cut in half by electro-spark machining to form two rectangular sections 6×12 mm^2: The coated and implanted surface sections of these half-samples were slit by electro-spark machining to depths of, respectively:

– 300 μm for preparing thin foils parallel to the surface for study by transmission electron microscopy (TEM),
– 2 mm for study by Auger electron spectroscopy (AES) and the optical 3-d imaging mentioned above.

3. Results and discussion

The results of nanoindentation

– At the medium and highest dose rates, the hardness profile is the same for all doses.
– At the lowest dose rate the hardness decreases as the dose increases.

The effect of dose rate at a given dose is as follows:

– At the lowest dose, the dose rate has no effect.
– At the medium dose, the lowest dose rate gives the lowest hardness and shows the largest variability.
– At the highest dose, the highest and lowest dose rates give low hardness.

Transmission electron microscopy

Electron microscopy studies were carried out with thin foils some 150–180 nm thick, cut parallel to the sample surface, as in previous work [3, 4, 6, 8]. Shown in Figs. 1–3 are the (a) bright field micrographs, (b) selected area diffraction (SAD) patterns, and (c) dark field micrographs, respectively, for the sample subset implanted with the lowest dose, and at the dose rates in the range 1.44–7.8 μA·cm^{-2} (left-hand column in Table 1). The minimum grain size which could be detected is estimated to be about 5 nm.

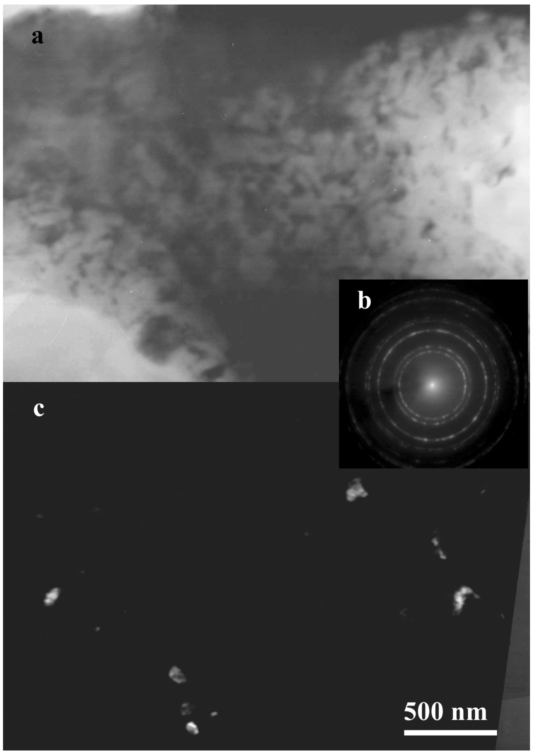

Fig. 1. The bright field image (a), selected area diffraction pattern (b), and dark field image (c) of the TiN coating implanted at a dose rate of 1.44 μA·cm^{-2}

Amorphous material is found in the IZ, but crystalline material is always present; the IZ becomes increasingly amorphous as the ion implanted dose increases. The mean grain size was not changed by the implantation process; it remains constant through the columnar coating down to the substrate interface. The extinction contours indicate a high level of residual compressive stress which is usual in TiN made by PVD methods, as noted above. The number of these contours falls with increasing dose rate, indicating a concomitant decrease in residual stress.

The lattice parameters are changed by the implantation process. The data taken from the micrographs in Figs. 1–3 are 0.4228 nm, 0.4258 nm and 0.4178 nm, respectively. The extent to which these changes are caused by compositional or stress changes is not clear at this time.

Auger electron spectroscopy

The results for the sample subset implanted with the lowest dose (i.e., corresponding to the samples shown in Figs. 1–3, and the left-hand column in Table 1) are shown in Fig. 4. It is apparent that extensive oxygen contamination is present. This is believed to have come from two sources:

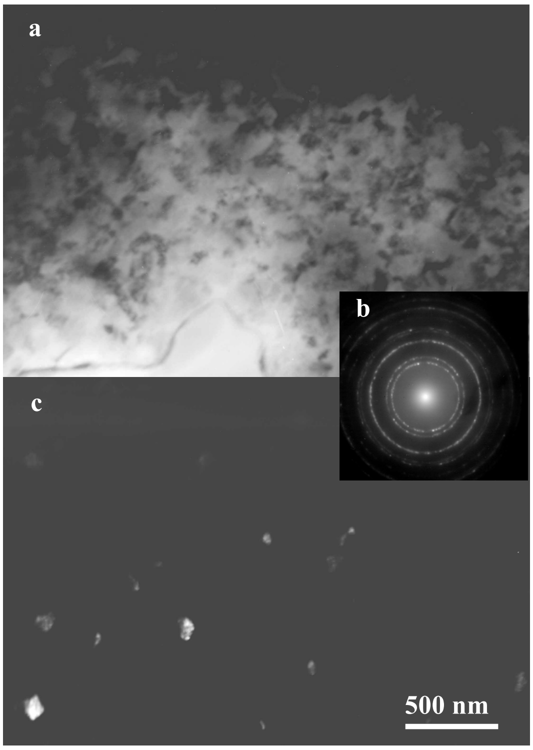

Fig. 2. The bright field image (a), selected area diffraction pattern (b), and dark field image (c) of the TiN coating implanted at a dose rate of 4.55 $\mu A \cdot cm^{-2}$

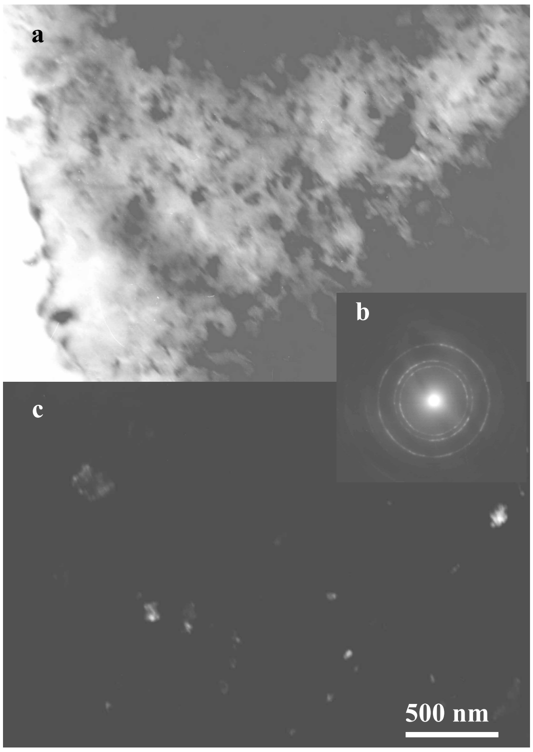

Fig. 3. The bright field image (a), selected area diffraction pattern (b), and dark field image (c) of the TiN coating implanted at a dose rate of 7.8 $\mu A \cdot cm^{-2}$

- A small part, possibly some 4 %, has probably been incorporated during the implantation process itself; such incorporation is common in nitrogen ion implantation as found from past experience with other systems.

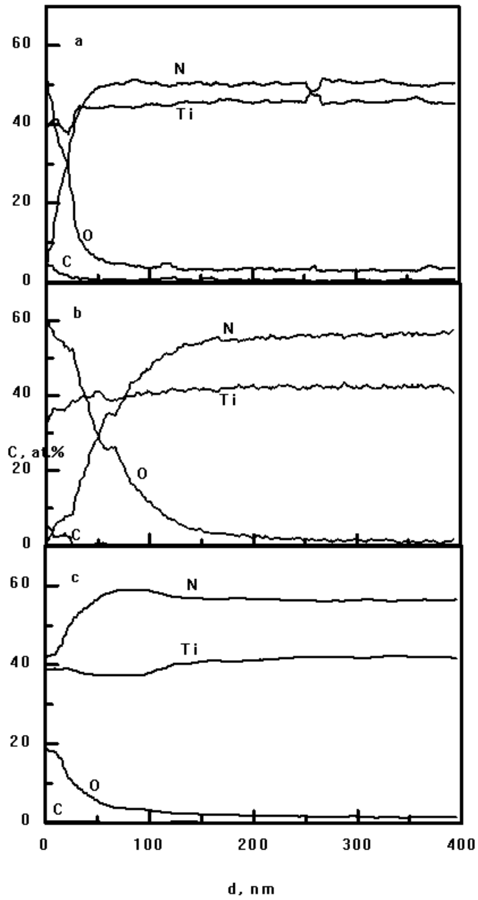

Fig. 4. The AES profiles for the sample subset implanted with increasing dose rate at the lowest dose studied (i.e., the sample subset in the left-hand column of Table 1 and corresponding to those shown in Figs. 1—3)

- In view of the precautions taken to exclude oxygen from the system when implanting the samples, the majority of the oxygen is believed to have been absorbed by the extensively damaged, reactive surface left after the surface exfoliation, on its exposure to atmospheric air after opening the chamber. Whilst this cannot be established experimentally, it is supported by the observation (Fig. 4) that the oxygen level is lower (as is the carbon level) in samples implanted at higher dose rates where the exfoliation and surface damage would be expected to be greater. The carbon present is considered to be the remnant of the native Ti(N,C,O) film typical of TiN coated samples [8].

The TiN coatings deposited by the Balzers process are generally somewhat hypo-stoichiometric. As a first approximation however, taking the AES data to be semi-quantitative on the ordinate axis with an actual nitrogen content in the bulk TiN to be 50 %, the nitrogen 'hump' in the sample implanted at the highest dose rate (Fig. 4, *c*) corresponds to $TiN_{1.07}$ which is just above the maximum equilibrium solid solution $TiN_{1.05}$ and may possibly indicate that some nitrogen is retained at grain boundaries or as bubbles in this sample. It would thus appear that, in general, the major amount of nitrogen which was intended to be implanted in the TiN has indeed been lost through exfoliation accompanying the implantation process.

4. Discussion

Amorphization

As discussed previously [10], bonding in TiN is essentially metallic and metallic materials cannot be readily amorphized unless a metalloid such as boron is present. Even extremely rapid cooling (10^9 K s^{-1}) from the liquid state after intense ion beam treatment leaves a crystalline surface [12]. It is well established that some multi-component alloy systems such as the La-base or Zr-Al-Ni-Cu [15] alloys can be retained in an amorphous condition but the conditions for this are well established [16] and would not include crystallographically simple cases such as TiN.

In general, metallic materials under ion bombardment are more likely to undergo recrystallization and grain refinement [8]. This is supported by the present TEM micrographs which show that crystalline material is present throughout the IZ material still remaining on the sample after exfoliation.

X-ray amorphous material

The present samples contain a high concentration of oxygen incorporated into the surface by post-implantation oxidation (Fig. 4) and which can form TiO_2, a material which is readily amorphized by an ion beam. This would lead to the low frictional properties which have been reported for implanted TiN [1], and also clarify the loss of X-ray intensity in the surface regions of such samples [9]. It is remarkable that the sample implanted at the lowest dose rate has retained the largest amount of oxygen. If the low frictional properties are indeed caused by the presence of amorphized TiO_2 then the wear behaviour will fall as the dose rate increases, as is indeed observed.

5. Conclusions

The present 3×3 matrix of samples, nitrogen ion implanted at a series of low-to-high dose rates and low-to-high doses, all show surface exfoliation. This results in a loss of the nitrogen implanted IZ, and a consequent reduction in the wear-resistant properties. The condition is one of over-implantation, reminiscent of that observed in metal ion implantation.

There is a concomitant uptake of post-implantation oxygen which is believed to form an amorphous TiO_2 component in the surface leading to the well-established low frictional properties. This uptake decreases as the dose rate is increased and would also lead to a loss of such properties.

The work confirms that a dose of $3\cdot10^{17}$ ions cm^{-2} appears optimal provided that the dose rate does not exceed the present industrial standard.

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