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# Influence of aluminum ion implantation on oxidation behavior in air at 500 °C of TiN coatings

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**Abstract**

To study the influence of aluminum implantation on the oxidation behavior of TiN coatings, a metal vacuum vapor arc ion source was used to implant aluminum into TiN-coated AISI 304 steel using an extraction voltage of 40 kV, and with doses ranging from $5 \times 10^{16}$ to $2 \times 10^{17}$ ions/cm$^2$. Weight-gain curves of the as-deposited TiN and Al-implanted TiN samples were measured during oxidation in air at 500 °C for 50 min. A significant improvement was observed in the oxidation behavior of the Al-implanted TiN compared to that of the as-deposited TiN. X-ray photoemission spectroscopy, scanning electron microscopy and glancing angle X-ray diffraction were employed to analyze the valence states of the oxide scale, the surface morphology, and the phase composition of the oxidation layers. Ion implantation leads to the formation of some new phases, most likely (Ti,Al)N or AlN, in the surface top layer. The oxidation rate decreases from $8.2 \times 10^{-8}$ mg$^2$ cm$^{-4}$ s$^{-1}$ for as-deposited TiN to $5.2 \times 10^{-9}$ mg$^2$ cm$^{-4}$ s$^{-1}$ for Al-implanted TiN at dose of $2 \times 10^{17}$ ions/cm$^2$.


*Keywords:* Aluminum ion implantation; TiN coating; Oxidation; MEVVA; Cathodic arc deposition

## 1. Introduction

Transition metal nitride hard coatings have proven to be excellent candidates for improving wear protection, oxidation resistance, and corrosion resistance of machining tools and engineering components. For many applications, coatings are subjected to particularly demanding working conditions, such as elevated temperatures and oxidizing atmospheres. TiN is one of the most popularly used coatings for light-alloy extrusions. To protect the coating from attack by reactive gases, a controlled oxidation process of the coating is highly important.

Ion implantation has often been considered as an additional method to further improve the wear and corrosion resistance of hard coatings on tools or machine parts. Ion implantation has also been examined as a method for improving the surface properties of objects with ceramic protective coatings [1–4]. TiN films deposited by physical vapor deposition (PVD) have been successfully treated by conventional implantation, using a variety of ions such as nitrogen, boron, carbon, argon, nickel, tungsten and chromium [5–8]. The tribological properties, oxidation behavior and hardness of the implanted films have also been studied [6–11]. The ions could be generated by Kaufman [12], metal vapor vacuum arc (MEVVA) [13], Freeman [14], microwave ion sources [15] and plasma source ion implantation (PSII) [16]. Kaufman, Freeman, microwave and plasma ion source use gas or carrier gas to generate ions, while MEVVA can directly generate high density metal ion beam through discharge.

Aizawa et al. [17] used a Freeman ion source with mass analyzer and $AlCl_3$ to generate Al ion beam, the implantation energy was chosen to be constant, 100 keV, to utilize the positive trivalent ions of $Al^{3+}$, and the current density is about 3–5 μA/cm$^2$. It is different to MEVVA technique which is capable of providing almost all the metal ion species with an average current density greater than 120 μA/cm$^2$. The MEVVA ion source provided a pulsed metal-ion beam and the time period of one pulse was 1.2 ms, which was much shorter than an interval (0.3–1.0 s) between the two consecutive pulses. Comparatively, a high dose implantation up to an order of $10^{17}$–$10^{18}$ ions/cm$^2$ can be completed

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within an hour. Three kinds valence of ions are all included, namely $Al^{+}$, $Al^{2+}$ and $Al^{3+}$.

The properties of material depend on its microstructure, composition and processing method. It would be beneficial to develop a procedure for additionally introducing Al into conventional TiN coatings. A direct method for assessing the benefit of any such procedure is to determine the oxide film growth rates during high temperature exposure. The aim of the present work is therefore to study the oxidation behavior of TiN coatings implanted with Al using a MEVVA source implanter. We report and analyze weight-gain curves during oxidation, and give a crystallographic analysis of the as-deposited TiN and Al-implanted TiN samples oxidized in air at 500 °C.

## 2. Experimental procedure

AISI 304 stainless steel samples were machined to a size of $10 \times 15 \times 0.8$ mm. Subsequently, the samples were mechanically ground with 200–800 grade abrasive paper, polished with 1.0 μm diamond paste, ultrasonically degreased in ethanol and acetone, and finally rinsed in deionized water.

A cathodic arc deposition system was used to prepare the TiN coating. The target was made of titanium of 99.9% purity. Prior to deposition, the chamber was evacuated to below $1 \times 10^{-3}$ Pa, and the sample holder was heated to 300 °C. High purity argon gas was introduced to etch the substrate for 10 min using a bias voltage of −600 V. In order to provide better adhesion between the substrate and the coating, a titanium interlayer was then deposited prior to the final TiN coating, using a substrate bias of −300 V for 3 min. High purity nitrogen gas was then introduced and used to deposit titanium nitride, using a bias voltage of −180 V, an arc current of 60 A, and a nitrogen pressure of 0.6 Pa.

The TiN-coated samples were placed on the sample holder in the target chamber of the MEVVA source implanter under a background pressure of $1.0 \times 10^{-3}$ Pa. The implanted area was 12 cm in diameter. The extracted aluminum ions were measured to consist of 38% $Al^{+}$, 51% $Al^{2+}$ and 11% $Al^{3+}$, giving an average charge of approximate 1.7. Implantation ion doses of $5 \times 10^{16}$, $1 \times 10^{17}$ and $2 \times 10^{17}$ ions/cm$^2$ were used, at an extraction voltage of 40 kV and a beam current density of 15 μA/cm$^2$. The maximum temperature of the samples was 150 °C. The temperature was determined by a variety of factors including the extraction voltage, beam current density, implantation time, and the properties of the implanted ions and the base material.

To investigate the high temperature oxidation behavior of the TiN samples, oxidation was carried out in air at 500 °C for 50 min, and weight-gain data were recorded. X-ray photoemission spectroscopy (XPS) was employed to analyze the composition and the valence states of the surface layer of the TiN samples. In addition, glancing angle X-ray diffraction (GAXRD) was used to examine the phase transformation due to the aluminum ion implantation.

## 3. Results and discussion

### 3.1. Weight-gain curves of the TiN samples

Samples implanted with doses of $5 \times 10^{16}$, $1 \times 10^{17}$ or $2 \times 10^{17}$ ions/cm$^2$ were oxidized in air at 500 °C for 50 min. Weight gain per unit surface area vs. exposure time curves were obtained from continuous recording of the sample weight. Fig. 1 shows the oxidation curves at 500 °C in air for Al-implanted TiN with doses ranging from 0 to $2 \times 10^{17}$ ions/cm$^2$.

It is evident that the oxidation weight-gain increases with the exposure time in air, and that the oxidation weight-gain curves for implanted TiN are all lower than that for as-deposited TiN. The results clearly indicate that the oxidation weight-gain rate for Al-implanted specimens decreases with increasing ion dose. Aluminum ion implantation can therefore effectively reduce oxidation of a TiN coating even at a low dose.

According to previous results, during the initial period, the oxidation rate of TiN coatings can be described by a parabolic oxidation equation [18]:

$$\Delta M^2 = 2K_p t,$$

where $\Delta M$ is weight gain per unit area, $K_p$ is the oxidation rate and $t$ is the oxidation time. The parabolic rates for the Al-implanted TiN coatings were calculated as $3.22 \times 10^{-8}$, $2.06 \times 10^{-8}$ and $5.2 \times 10^{-9}$ mg$^2$ cm$^{-4}$ s$^{-1}$ for $5 \times 10^{16}$, $1 \times 10^{17}$ and $2 \times 10^{17}$ ions/cm$^2$, respectively, all of which are lower than the value for the as-deposited TiN coating ($8.2 \times 10^{-8}$ mg$^2$ cm$^{-4}$ s$^{-1}$). It is proposed that the implanted

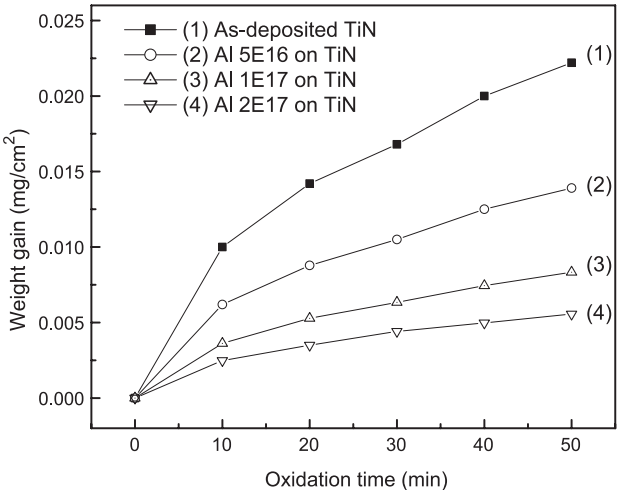


Fig. 1. The air oxidation weight gain of Al-implanted TiN with doses of (1) 0, (2) $5 \times 10^{16}$ ions/cm$^2$, (3) $1 \times 10^{17}$ ions/cm$^2$ and (4) $2 \times 10^{17}$ ions/cm$^2$ at 500 °C.