Mechanical Properties and Oxidation Resistance of $\text{Ti}_{1-x}\text{W}_x\text{N}$ Coatings

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Titanium-based hard coatings have been developed by adding different metals to TiN in order to obtain mechanical, tribological, and thermal properties that are superior to those of TiN. In this study, $\text{Ti}_{1-x}\text{W}_x\text{N}$ films were synthesized from $\text{Ti}_{1-x}\text{W}_x$ alloy targets ($x=0, 0.25, 0.35, 0.5, 0.75$, and 1.0) by radio-frequency magnetron sputtering. X-ray diffraction analysis indicated that all of the prepared films were solid solutions with a NaCl-type structure, and their interplanar spacing changed as the W content (x) was varied. The microhardness gradually increased from 21 GPa (at $x=0$) to 28 GPa (at $x=0.66$) and then decreased to 22 GPa (at $x=1.0$). The average coefficient of friction varied between 0.4 and 0.8, and the wear track had a depth below $0.15\text{ }\mu\text{m}$ in the films with $x=0-0.66$. The exothermic peak of differential thermal analysis shifted from $814\text{ }^\circ\text{C}$ (at $x=0$) to $846\text{ }^\circ\text{C}$ (at $x=0.34$) during dynamic oxidation. Correspondingly, the film with $x=0.34$ showed the smallest mass gain during isothermal oxidation at $600-700\text{ }^\circ\text{C}$, and its resistance against oxidation was better than that exhibited by TiN (at $x=0$). The surface properties in terms of microstructure, microhardness, tribological properties, and oxidation resistance were also characterized as functions of the W content.

Keywords : $\text{Ti}_{1-x}\text{W}_x\text{N}$, Microstructure, Microhardness, Coefficient of Friction, Oxidation Resistance

1. Introduction

TiN has been widely used as a protective coating on cutting tools, forming tools, and dies because of its hardness and resistance against wear, corrosion, and oxidation. Over the last few decades, ternary Ti-based nitrides such as $\text{Ti}_{1-x}\text{Al}_x\text{N}$, $\text{Ti}_{1-x}\text{Cr}_x\text{N}$, $\text{Ti}_{1-x}\text{Zr}_x\text{N}$, $\text{Ti}_{1-x}\text{Si}_x\text{N}$, and $\text{Ti}_{1-x}\text{Ni}_x\text{N}$ have been developed by incorporating foreign metals into the basic TiN structure to bring about microstructural transitions that would lead to improvements in the physical and chemical properties. For instance, the microhardness of $\text{Ti}_{1-x}\text{Al}_x\text{N}$ ⁽¹⁾ gradually increases from 20 to 32 GPa between $x=0$ and 0.6 , while its NaCl-type cubic structure remains unchanged. Corresponding to the transformation or the precipitation of ZnS-type wurtzite structure beyond $x=0.6$, the microhardness rapidly decreases to 14 GPa. In other instances, $\text{Ti}_{1-x}\text{Cr}_x\text{N}$ ⁽²⁾ and $\text{Ti}_{1-x}\text{Zr}_x\text{N}$ ⁽³⁾ exhibit higher corrosion resistance and thermal stability, respectively, than those of TiN. Furthermore, in the case of $\text{Ti}_{1-x}\text{Si}_x\text{N}$ ⁽⁴⁾ and $\text{Ti}_{1-x}\text{Ni}_x\text{N}$ ⁽⁵⁾, the maximum hardness is obtained by preventing plastic deformation and the propagation of dislocations when the polycrystalline TiN transforms into a nanocomposite comprising nanocrystallites and amorphous phases at certain x values.

Tungsten has been recognized as a key element in various tooling materials such as cemented carbide, cermet, and high-speed steel. Adding tungsten to these materials is an effective way to improve material strength, wear resistance and heat resistance. Therefore, it can be expected that the surface properties of TiN are enhanced by doping tungsten as well. To harden TiN, $\text{Ti}_{1-x}\text{W}_x\text{N}$ is prepared from various $\text{Ti}_{1-x}\text{W}_x$ alloy targets under a N_2 -Ar atmosphere at different N_2/Ar partial pressures. Shaginyajin et al.⁽⁶⁾ reported that the microhardness of $\text{Ti}_{1-x}\text{W}_x\text{N}$ deposited from a $\text{Ti}_{0.3}\text{-W}_{0.7}$ target was dependent on the nitrogen concentration, crystal structure, morphology, and residual stress. Silva et al.^(7, 8) prepared several $\text{Ti}_{1-x}\text{W}_x\text{N}$ films from a $\text{Ti}_{0.5}\text{-W}_{0.5}$ target, and they

showed that the hardness, coefficient of friction, and coefficient of wear of the films vary because the nitrogen content affected the ratio of Ti to W.

However, a comprehensive study of the microstructure, mechanical properties, and thermal properties of $\text{Ti}_{1-x}\text{W}_x\text{N}$ with different x values has not been reported to date. In this study, we deposited $\text{Ti}_{1-x}\text{W}_x\text{N}$ films from $\text{Ti}_{1-x}\text{W}_x$ ($0 \leq x \leq 1.0$) alloy targets using radio-frequency (RF) magnetron sputtering in mixed N_2 -Ar discharges. After deposition, the crystal structure, interplanar spacing, microhardness, tribological properties, and oxidation resistance of the films were analyzed as functions of the W content. The impact of W atoms on the surface properties of TiN is presented here in the context of its use as a wear-resistant coating.

2. Experimental method

$\text{Ti}_{1-x}\text{W}_x\text{N}$ films were deposited on polished (111)-oriented Si wafers and stainless-steel substrates by RF magnetron sputtering, using $\text{Ti}_{1-x}\text{W}_x$ alloy targets with $x=0, 0.25, 0.35, 0.5, 0.75$, and 1.0 . The films were deposited on the Si wafers for X-ray analysis, hardness evaluations and the measurements of friction coefficient, whereas the films were deposited on the stainless-steel substrates for the oxidation tests. These films were synthesized under a mixed gas atmosphere of pure N_2 and pure Ar at a total pressure of 1.0 Pa and a N_2 partial pressure of 0.1 Pa . The power density of the targets was 10.6 W/cm^2 , and the deposition temperature was $250\text{ }^\circ\text{C}$. The substrate negative-bias voltage and the target-to-substrate distance were fixed at -50 V and 45 mm , respectively, for all the deposition processes. The films' thickness was adjusted in the range of $1.0-3.0\text{ }\mu\text{m}$ to prevent them from peeling off. The thicknesses of $x=0-0.66$, $x=0.84$ and $x=1.0$ were $3.0, 2.0$ and $1.0\text{ }\mu\text{m}$, respectively.

The metal composition of the films was measured using energy-dispersive X-ray fluorescence (EDXRF; Shimadzu Raynu EDX-800HS) analysis after calibration with a standard Al specimen (99.99% purity). The nitrogen content of the films was measured

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using energy-dispersive X-ray analysis (EDX; Oxford Instruments X-Max80). The films' crystal structures and interplanar spacing of (111) plane were evaluated by X-ray diffraction (XRD; Shimadzu XRD-7000) using Cu K α radiation at 40 kV and 30 mA in $\theta/2\theta$ mode. The peaks of the XRD patterns were identified by International Center for Diffraction Data (ICDD).

The microhardness of the films was measured with a conventional micro-Vickers-hardness tester (Mitutoyo HM-221) under a load of 29.4×10^{-3} N, and the indentation depths for $X=0-0.84$ and $X=1.0$ were 9-15% and 36% of the films' thickness, respectively. The friction tests were performed with a ball-on-disc tribometer (Rhesca FPR-2100) under dry conditions at room temperature. A SiC ball with diameter of 4.8 mm was used, and the mode for rotational motion at a radius of 2.0 mm and speed of 300 rpm was selected with a load of 5.0 N. The surface roughness of the as-deposited state and wear depth after the friction test were determined using a surface-roughness tester (Mitutoyo SJ-301).

The dynamic oxidation and isothermal oxidation tests were conducted with a differential thermal analyzer (DTA; Shimadzu DTA-50) and a thermogravimetric analyzer (TGA; Shimadzu TGA-51H), respectively. To eliminate the effect of the substrate material on the DTA and the TGA measurements, the films were chemically removed from the stainless-steel substrates using a dilute solution of hydrochloric acid. After filtering and cleaning, the films were reduced to powders. For the dynamic oxidation test, each powder was placed in a platinum crucible and heated from room temperature to 1000 °C in air at a heating rate of 15 °C/min. Al $_2$ O $_3$ blocks were used for the inert standard sample in the DTA measurements. For the isothermal oxidation tests, the mass gain of each powder was recorded as a function of time during isothermal oxidation at 600-700 °C. In order to examine the oxidation behavior of the coatings, the as-deposited Ti $_{1-x}$ W $_x$ N ($0 \leq X \leq 1.0$) films on Si wafers were first annealed at 600-700 °C for 1 h in an ambient atmosphere. The surface morphologies of the annealed films were then observed using scanning electron microscopy (SEM; Hitachi SU-1500).

3. Results and discussion

3.1 Chemical composition and microstructure of Ti $_{1-x}$ W $_x$ N films

The metal composition was measured by EDXRF, and the W

Fig. 1 XRD patterns of Ti $_{1-x}$ W $_x$ N films on Si wafers in as-deposited state. The prefix c- refers to Ti $_{1-x}$ W $_x$ N with a cubic structure.

content was calculated from the atomic concentrations of Ti and W. The Ti $_{1-x}$ W $_x$ N films had W content of $X=0, 0.34, 0.47, 0.66, 0.84$, and 1.0 . The nitrogen content obtained by EDX was 48-54 at% in the Ti $_{1-x}$ W $_x$ N films, which can be regarded as stoichiometric nitride. **Fig. 1** shows XRD patterns of the Ti $_{1-x}$ W $_x$ N films with the expected peak positions for TiN (ICDD No. 00-006-0642) and WN (ICDD No. 03-065-2898). Here, the prefix "c-" in c-TiN and c-WN refers to the cubic structure of the metastable nitrides. The XRD spectrum of TiN ($X=0$) indicates the presence of a cubic (NaCl-type) polycrystalline microstructure with (111) preferred orientation. The relatively strong (111) peak and the small broad (200) peak were identified in the XRD pattern of Ti $_{1-x}$ W $_x$ N with $X=0.34$, where the (111) peak appears at a lower diffraction angle, while the NaCl-like structure of the film remained unchanged. The both peaks with $X=0.66$ are closer to those of c-TiN, and the (200) peak with $X > 0.84$ moved toward c-WN. It was determined from the XRD results that the Ti $_{1-x}$ W $_x$ N films exhibited the microstructure of a NaCl-type solid solution, with some Ti atoms replaced by W atoms.

The shifting of the diffraction angles in the XRD patterns indicates lattice shrinkage or expansion in TiN. **Fig. 2** shows the interplanar spacing of (111) plane for the Ti $_{1-x}$ W $_x$ N films with X values ranging from 0 to 1.0. The interplanar spacing increased from 0.243 nm ($X=0$) to 0.248 nm ($X=0.34$), and it subsequently decreased to 0.245 nm ($X=1.0$). NaCl-type structure is comprised of ion binding between metallic element and light element. These changes in the interplanar spacing likely arose from differences in the ionic radii of Ti and W atoms; for example, the radii of Ti $^{2+}$ (86 pm), Ti $^{3+}$ (67 pm), Ti $^{4+}$ (42 pm), W $^{4+}$ (66 pm), W $^{5+}$ (62 pm), and W $^{6+}$ (42 pm) vary quite widely⁹⁾.

3.2 Microhardness and coefficient of friction of Ti $_{1-x}$ W $_x$ N films

The plot of microhardness versus X is shown in **Fig. 2**. The microhardness increased from 21 GPa at $X=0$ to 28 GPa at $X=0.66$ due to solid-solution hardening, and then it gradually decreased to 22 GPa at $X=1.0$. Similar hardening effects resulting from alloying of TiN with foreign metals and changes in hardness with variations in the Al, Cr, and Zr concentrations were reported in our earlier research¹⁰⁾. Additionally, the microhardness at $X=1.0$ was slightly lower than the hardness with 24-28 GPa revealed elsewhere¹¹⁾ because the substrate influenced the film's microhardness with increasing the indentation depth versus the films' thickness up to 36%.

Fig. 2 Changes in interplanar spacing of (111) plane and microhardness for Ti $_{1-x}$ W $_x$ N films versus W content.

Fig. 3 shows the coefficients of friction of the $\text{Ti}_{1-x}\text{W}_x\text{N}$ films deposited on the Si wafers. The average surface roughness of the as-deposited films was 0.01–0.02 μm . For the films with $X = 0$ –0.66, the average frictional coefficients at the steady state were 0.4–0.8. For the films with $X = 0.84$ and 1.0, a drop in the respective frictional coefficients, which are similar to those of the Si wafer, was observed between the initial and steady states after the coatings on the substrates were exposed to wear. The measured wear depth after the friction tests of the films with an X value between 0 and 0.66 was 0.10–0.15 μm , whereas the wear track in films with $X = 0.84$ and 1.0 had a depth of up to 1.20 μm .

3.3 Dynamic and isothermal oxidation of $\text{Ti}_{1-x}\text{W}_x\text{N}$ films

Fig. 4 shows DTA results of the $\text{Ti}_{1-x}\text{W}_x\text{N}$ films during dynamic oxidation between room temperature and 1000 $^{\circ}\text{C}$. The first small DTA peak was recorded at around 345 $^{\circ}\text{C}$, the temperature at which the exothermic reactions occurred through the recovery process and recrystallization^{12), 13)}. In general, the recovery process is strongly correlated with the relaxation of deposition-induced lattice defects and residual stress at an elevated temperature. The DTA signal intensity of TiN ($X = 0$) increased as the temperature increased above 400 $^{\circ}\text{C}$, and the second exothermic DTA peak emerged at 814 $^{\circ}\text{C}$. Milošev et al.¹⁴⁾ revealed by

X-ray photoelectron spectroscopy that TiN changes to $\text{Ti}(\text{N},\text{O})$ at 450 $^{\circ}\text{C}$ and then transforms to TiO_2 at 600 $^{\circ}\text{C}$. Polyakova et al.¹⁵⁾ reported that the DTA peak of TiN during dynamic oxidation appears at 790 $^{\circ}\text{C}$, which closely agrees with our results. The exothermic DTA peak of $\text{Ti}_{1-x}\text{W}_x\text{N}$ with $X = 0.34$ moved to 846 $^{\circ}\text{C}$, which indicates that its oxidation response was sustained at a higher temperature than that observed for TiN. For the $\text{Ti}_{1-x}\text{W}_x\text{N}$ films with $X \geq 0.47$, the DTA peak position shifted from 744 to 648 $^{\circ}\text{C}$.

Fig. 5 (a) presents the TGA results of the $\text{Ti}_{1-x}\text{W}_x\text{N}$ films during isothermal oxidation at 600 $^{\circ}\text{C}$. The TGA curves indicate that the oxidation reaction proceeded parabolically, and the oxidation behavior changed drastically with time and the W content (X). The measured mass gain of TiN ($X = 0$) was 9%, which was similar to the value at $X = 0.47$, and the film with $X = 0.34$ exhibited a considerably lower mass gain of 3% than that exhibited by TiN. As X increased from 0.66 to 0.84, a mass gain of more than 10% was observed. For the WN films ($X = 1.0$), rapid oxidation started at the onset of the TGA measurements; this oxidation behavior is similar to that of tungsten¹⁶⁾. This drop in oxidation resistance resulted from the release of nitrogen from WN to outward owing to thermal diffusion.

The TGA results of the $\text{Ti}_{1-x}\text{W}_x\text{N}$ films during isothermal oxidation at 700 $^{\circ}\text{C}$ are presented in **Fig. 5** (b). The mass gain decreased from 18% at $X = 0$ to less than 10% at $X = 0.34$ when the TGA measurements were completed. The rapid process of oxidation was observed with increasing X at values above 0.47,

Fig. 3 Coefficient of friction of $\text{Ti}_{1-x}\text{W}_x\text{N}$ films as a function of sliding distance.

Fig. 4 DTA analysis of $\text{Ti}_{1-x}\text{W}_x\text{N}$ films during dynamic oxidation from room temperature to 1000 $^{\circ}\text{C}$.

Fig. 5 TGA analysis of $\text{Ti}_{1-x}\text{W}_x\text{N}$ films during isothermal oxidation at (a) 600 $^{\circ}\text{C}$ and (b) 700 $^{\circ}\text{C}$.

Fig. 6 Surface micrographs obtained after atmospheric annealing of $\text{Ti}_{1-x}\text{W}_x\text{N}$ films at 700 °C for 1 h.

and the final mass gain was 15% to 20%. Although the oxidation of $\text{Ti}_{1-x}\text{W}_x\text{N}$ films with $X=0.66$ proceed slowly than that of $X=0.84$ at 600 °C, the mass gain with $X=0.66$ was higher compared to that exhibited by $X=0.84$ at 700 °C. This reverse phenomenon of their oxidation behaviors was caused by the formation of pores and cracks as discussed in **Fig. 6**. According to the thermochemical data reported by Barin et al.¹⁷⁾, the values of standard free energy for the formation of metal oxides per mole of oxygen at 600 and 700 °C are −852 and −835 kJ, respectively, for Ti_2O_3 ; −786 and −768 kJ, respectively, for TiO_2 ; and −413 and −397 kJ, respectively, for WO_3 . The higher free energy values for the formation of WO_3 suggest that its initial formation progressed slowly, and the incorporation of W atoms into TiN would enhance this initial oxidation resistance.

Fig. 6 shows the SEM micrographs obtained after atmospheric annealing of the $\text{Ti}_{1-x}\text{W}_x\text{N}$ films at 700 °C. The appearance of oxidation products and scales in the micrographs confirm the DTA and TGA results. In addition, the surface micrographs indicate that several defects, such as pores and cracks, were formed in the oxide films with increasing X values. Similar phenomena and trends were observed in the films that were subjected to atmospheric annealing at 600 °C. Because oxygen diffused into the film through these defects, the films with $X=0.47$ –1.0 had similar or higher mass gains than TiN (**Fig. 5** (a) and (b)). Based on TGA results and SEM observation, $\text{Ti}_{1-x}\text{W}_x\text{N}$ films $X=0.34$ exhibits superior oxidation resistance owing to delaying its initial oxidation and the fewer defects.

4. Conclusions

$\text{Ti}_{1-x}\text{W}_x\text{N}$ films with $X=0$ –1.0 were synthesized by RF mag-

netron sputtering, and their microstructure, microhardness, coefficient of friction, and oxidation behavior were studied. All the films were solid solutions with a cubic structure, and their interplanar spacing increased from 0.243 nm (at $X=0$) to 0.248 nm (at $X=0.34$), and then decreased to 0.245 nm (at $X=1.0$). The microhardness changed with the W content, and a maximum hardness of 28 GPa was obtained at $X=0.66$. The average coefficient of friction ranged between 0.4 and 0.8, and the minimum wear depth was 0.10 μm. During isothermal oxidation at 600 and 700 °C, a minimum mass gain of approximately 3% and 10%, respectively, were observed for the films with $X=0.34$. Our results suggest that the incorporation of W atoms into TiN effectively enhanced the surface properties, such as microhardness and oxidation resistance, of the material.

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