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Characterization of Compositionally Graded Ti(C,N) Films Deposited by Plasma-Enhanced Chemical Vapor Deposition

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Compositionally graded Ti(C,N) films were prepared on high speed tool steel substrates by pulsed dc plasma-enhanced chemical vapor deposition (PECVD) at 823 K using gas mixtures of $TiCl_4$, N_2, CH_4, H_2 and Ar. The films were formed by continuously increasing the $CH_4/(CH_4+N_2)$ ratio with remaining other parameters constant. We studied structural, compositional and mechanical properties of the films. Fracture cross-sections of the films showed columnar structures. X-ray diffraction analysis showed that the films had the NaCl structure with a preferred orientation of 200, like TiN films by PECVD. Glow discharge optical emission spectroscopy analysis revealed that carbon and nitrogen contents in the films changed continuously. The hardness of the films was 3400 Hv(0.05N). Scratch tests demonstrated that the adhesion of the films was higher than that of single-layer $Ti(C_{0.9},N_{0.1})$ films by PECVD. Furthermore, the films had superior tribological characteristics compared with those of single-layer TiN films by PECVD.

Key words: PECVD, Ti(C,N), compositionally graded films, characterization, tribology

1. INTRODUCTION

Plasma-enhanced chemical vapor deposition (PECVD) process has been widely applied to surface modification for metal moulds because its good throwing power, i.e., the ability to coat irregularly shaped objects, even at low coating temperature[1-5]. Many papers have reported the preparation of monolithic films such as TiN, Ti(C,N) and TiC by PECVD[6-10]. Generally, TiN films have good adhesion for steel substrates, but those hardness and wear resistance are lower than Ti(C,N) and TiC films. On the other hand, Ti(C,N) and TiC films have high hardness and wear resistance, but those adhesion for steel substrates are inferior to that of TiN films. Consequently, it is expected that compositionally graded Ti(C,N) films have superior adhesion and wear resistance. Contrary to physical vapor deposition (PVD) process, PECVD process is entirely based on gaseous materials. Accordingly, the process facilitates the production of compositionally graded films. Very little work is currently available in the published literature on compositionally graded Ti(C,N) films by PECVD. This paper describes on the preparation of compositionally graded Ti(C,N) films by pulsed dc PECVD, and their structural, compositional and mechanical properties of the films.

2. EXPERIMENTAL

Fig.1 shows a schematic diagram of the pulsed dc PECVD apparatus used. The apparatus consisted of a reaction chamber, an external heater, a vacuum system, a rotation system of a working table, a pulsed dc power supply, a gas supply system and a computer control system. The effective dimensions of workpieces treated in this apparatus are 460 mm in diameter and 800 mm in height. The specimens used were JIS (Japanese Industrial Standards) SKH51 (high speed tool steel). They were heat-treated in a vacuum furnace before the deposition. The size of the SKH51 specimens was 12.7 mm square and 4.7 mm thickness. Their Vickers hardness (Hv) was 750. The deposition conditions of compositionally graded Ti(C,N) films are shown in Table Ⅰ. Compositionally graded Ti(C,N) films were deposited on high speed tool steel substrates at a temperature of 823 K using gas mixtures of $TiCl_4$, N_2, CH_4, H_2 and Ar. The films were formed by continuously increasing the $CH_4/(CH_4+N_2)$ ratio with remaining other parameters constant. The flow control of those gases was performed using mass flow controllers with computer. Single-layer TiN films (2.1 μm in thickness) and single-layer $Ti(C_{0.9}N_{0.1})$ films (1.9 μm in thickness) by the pulsed dc PECVD

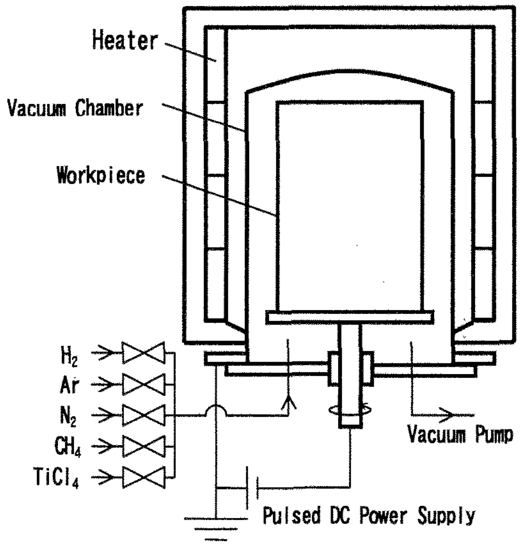

Fig.1 Schematic diagram of the pulsed dc PECVD apparatus.

Table I

Deposition conditions of compositionally graded Ti(C,N) films.

Deposition temperature (K)		823
Deposition time (min)		180
Pressure (Pa)		270
Discharge voltage (V)		700
Frequency (kHz)		20
Duty cycle (%)		10-50
Flow rate of gas (cm^3/min)	H_2	2000
	Ar	270
	N_2	500→190
	CH_4	0→140
	$TiCl_4$	60

were used in order to compare with the compositionally graded Ti(C,N) films.

The cross-sectional morphologies of the compositionally graded Ti(C,N) films were examined by scanning electron microscopy (SEM). Energy-dispersive X-ray spectroscopy (EDX) was used to analyze elements in the films. Glow discharge optical emission spectroscopy (GDOS) was used to examine the depth profiles of the elements in the films. X-ray diffraction (XRD) analysis was used to determine the lattice parameters of the films. Since $Ti(C_x,N_y)$ follows Vegard's law[11] , the compositions of the films are determined from the lattice parameters. Hardness of the films was measured using a micro Vickers indenter on the polished surface of the films. Adhesion of the films was investigated using scratch tester (made by CSEM). During scratch testing, the sliding speed was 10 mm/min and the loading rate was 100 N/min. Friction and wear properties were evaluated with a ball-on-disk type tribometer (made by CSEM). Surface roughness of all disk specimens was unified to be lower than Ra: 0.01 μm, Ry: 0.1 μm by polishing with diamond paste. The testing conditions were as follows: ball, SiC, 6.35 mm in diameter, 2400 Hv; load, 10 N; sliding speed, 400 mm/s; sliding distance, 500~5000 m; relative humidity, 60 %; temperature, 298 K; unlubricated condition.

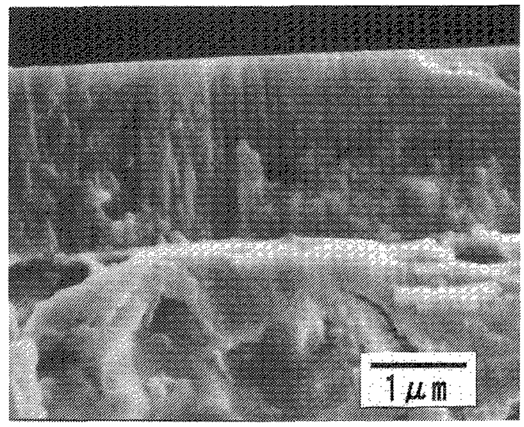

Fig.2 Cross-sectional SEM image of the compositionally graded Ti(C,N) film deposited by PECVD on a SKH51 substrate.

3. RESULTS AND DISCUSSION

3.1 Cross-sectional morphology

Fig.2 shows a cross-sectional SEM image of the compositionally graded Ti(C,N) film deposited by the pulsed dc PECVD on a SKH51 substrate. The thickness of the film was 2.0 μm. Fracture cross-sections of the compositionally graded Ti(C,N) films showed columnar structures and the width of the columnar was narrower than that of the TiN films by PECVD.

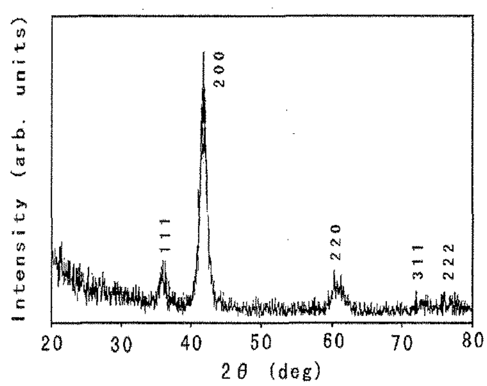

Fig.3 XRD pattern of the compositionally graded Ti(C,N) film.

3.2 Compositional and structural analysis

EDX analysis showed that the chlorine content in the compositionally graded Ti(C,N) films was 1.13 at%. Fig.3 shows the XRD pattern of the compositionally graded Ti(C,N) film. The film showed the same preferred orientation of 200 as the TiN film by

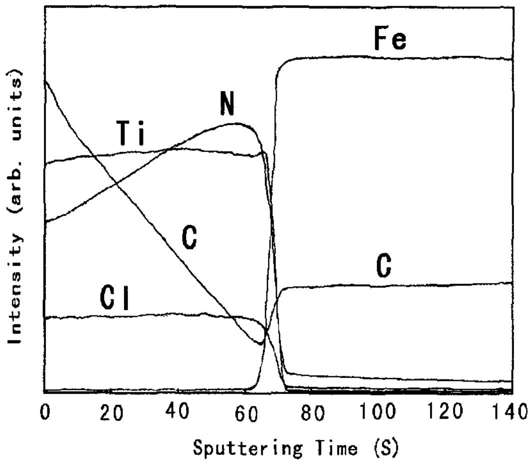

Fig.4 GDOS concentration depth profiles for each element for the compositionally graded Ti(C,N) film deposited by PECVD on a SKH51 substrate.

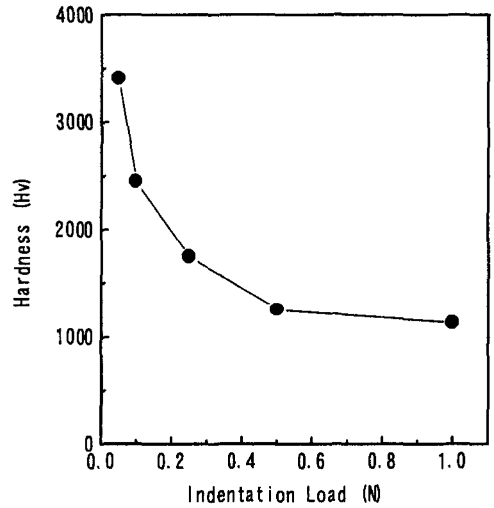

Fig.5 Vickers hardness of the compositionally graded Ti(C,N) film deposited by PECVD on a SKH51 substrate as a function of the indentation load.

PECVD. This diffraction pattern corresponds to the diffraction at the upper Ti(C,N) film, because an incident angle was set at 0.5° in this XRD analysis. This film has the same NaCl structure as TiN film by PECVD. The lattice parameter for the film was 0.432 nm, which was bigger than that of TiN films by PECVD (0.427nm). Since $Ti(C_x,N_y)$ follows Vegard's law, the chemical formula of the upper layer can be written as $Ti(C_{0.9},N_{0.1})$.

Fig.4 shows GDOS concentration depth profiles for each element for the compositionally graded Ti(C,N) film. The carbon concentration decreased gradually from its surface toward the substrate. On the contrary, the nitrogen concentration increased gradually from its surface toward the substrate. Compositionally graded Ti(C,N) films were, thus, confirmed to be successfully formed. There was no concentration of chlorine at the interface of the film and the substrate.

3.3 Hardness

Fig.5 shows Vickers hardness of the compositionally graded Ti(C,N) film as a function of the indentation load. The surface hardness decreases with increasing indentation load, because it is influenced by the hardness of the substrate. At the indentation load of 0.05 N, the hardness of the film was 3400 Hv. The hardness was higher than that of TiN films by PECVD (2250Hv).

3.4 Adhesion

The film adhesion was measured by the scratch tester. Table II shows scratch test results obtained for the single-layer TiN film, the single-layer $Ti(C_{0.9},N_{0.1})$ film and the compositionally graded Ti(C,N) film. The critical load was detected by acoustic emission. The values for the single-layer TiN film is the highest of all, the single-layer $Ti(C_{0.9},N_{0.1})$ film is the lowest of all. The values for the compositionally graded Ti(C,N) film are slightly lower than that of the TiN single-layer film. Thus, we conclude that the compositionally graded design of the films results in the enhanced adhesion of the films to the substrates.

Table II
Scratch test results obtained for the single-layer TiN film, the single-layer $Ti(C_{0.9},N_{0.1})$ film and the compositionally graded Ti(C,N) film.

Specimen	Critical load (N)
Single-layer TiN film	45
Single-layer $Ti(C_{0.9},N_{0.1})$ film	23
Compositionally graded Ti(C,N) film	40

3.5 Tribological properties

Friction coefficients were determined by a ball-on-disk tribometer. Fig.6 shows relations between the friction coefficient and the sliding distance for the compositionally graded Ti(C,N) film, the TiN film by PECVD and the uncoated specimen. When the sliding distance is in the neighborhood of 500m, the friction coefficients for the compositionally graded Ti(C,N) film, the TiN film and the uncoated specimen were 0.11, 0.47 and 0.61 respectively. Namely, the friction coefficient for the compositionally graded Ti(C,N) film is the lowest of all the specimens tested in this investigation.

Table Ⅲ
Wear volumes of balls, wear widths of disks and wear factors of disks for each specimen.
(ball: SiC, load: 10 N, sliding speed: 100 mm/s, sliding distance: 500 m)

Specimen	Wear volume of ball (mm^3)	Wear width of disk (mm)	Wear factor of disk (mm^3/Nm)
Uncoated	3.71×10^{-3}	0.65	------------
Single-layer TiN film	2.32×10^{-4}	0.42	1.30×10^{-7}
Compositionally graded Ti(C,N) film	5.13×10^{-5}	0.21	4.38×10^{-9}

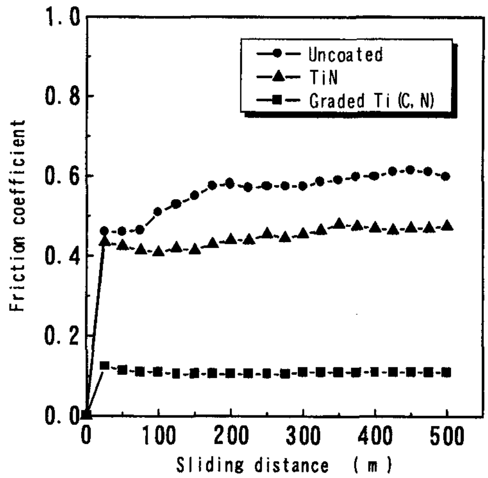

Fig.6 Relation between the friction coefficient and the sliding distance for the compositionally graded Ti(C,N) film, the TiN film and the uncoated specimen.
(ball: SiC, load: 10 N, sliding speed: 100 mm/s)

Table Ⅲ shows wear volumes of balls, wear widths of disks and wear factors of disks for each specimen. The wear width of disks coated by the compositionally graded Ti(C,N) film is the smallest of all the specimens tested. Also, wear factor of the film is 4.38 $\times10^{-9}$mm/Nm, and this value is lower than that of TiN film. Furthermore, the wear volume of a ball for the compositionally graded Ti(C,N) film is the smallest of all the specimens tested. The reduced ball wear signifies that the film is less aggressive to the counterpart material. Therefore, the compositionally graded Ti(C,N) films have superior wear resistance and lubrication.

Next, durability of each film was investigated. Durability of a film was defined as the sliding distance required for the film to achieve a friction coefficient value identical to these evident in an uncoated specimen. The durability of the TiN film was 800 m. On the other hand, that of the compositionally graded Ti(C,N) film was 5000 m. Therefore, the compositionally graded Ti(C,N) film had about six times higher durability than the TiN film.

The compositionally grade Ti(C,N) films produced in this study significantly enhanced the durability in comparison to single-layer TiN films, opening a prospective for industrial application.

4. CONCLUSIONS

The following conclusions can be drawn from these tests.

(1) The compositionally graded Ti(C,N) films were prepared successfully by pulsed dc PECVD on steel substrates.
(2) Fracture cross-sections of the films showed columnar structures.
(3) The films had the NaCl structure with a preferred orientation of 200, like TiN films by PECVD.
(4) The carbon and nitrogen contents in the films changed continuously.
(5) The hardness of the films was 3400 Hv(0.05N).
(6) The adhesion of the film was higher than that of the single-layer $Ti(C_{0.9},N_{0.1})$ film by PECVD.
(7) The films had superior tribological properties compared to TiN films by PECVD and uncoated steel specimens.
(8) The compositionally graded Ti(C,N) films prepared by PECVD are suitable for coatings on metal moulds.

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