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Elastic modulus of TiN film investigated with Kroner model and X-ray diffraction①

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[Abstract] The four-point bending method was applied to measure X-ray elastic constants(XEC) of (422) and (331) planes of TiN coating. Elastic Modulus and XECs of all the crystal planes were calculated by Kroner method. The results from the calculation and the experiment were compared. It is concluded that the XECs values of same film prepared by different techniques scatter a little because of the effects of stoichiometric proportion and microstructure of films.

[Key words] elastic constants; four-point bending; X-ray diffraction; titanium nitride
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1 INTRODUCTION

Hard coatings, e.g. TiN, deposited on tools or machine parts, can improve the wear and corrosion resistance[1,2], and in some cases, reduce the friction coefficient, thus the service life can be greatly improved. However, these coatings are subject to high internal stresses due to the substantial difference in thermal expansion, elastic constant, plasticity etc, between hard coating and metal substrate. Additionally the growth process of the film can also provide contribution to the internal stress level of the coating. High internal stress results in weak bonding strength between the substrate and the coating as well as the low fracture toughness of the coating itself. Over the past decades internal stress became an important issue in study and optimization of thin film processing. For a thin film with a few microns in thickness, X-ray diffraction techniques are valuable means to determine strain by measuring the changes in lattice spacing. However only when the elastic constants are known, can the internal stress be obtained from the gathered strain data.

The elastic modulus is a constant which is not sensitive to the structure or composition. For a bulk material, this constant can be tested by conventional mechanical method using a standard specimen. However, a few microns-thick film deposited on a substrate is not able to meet the needs of conventional mechanical testing. Furthermore, the elastic modulus of the thin film may not be equal to that of the bulk material for its special dimension when the grain size of the film is in a nano scale. Practically, for some films, there are no corresponding bulk materials to be tested.

The data of elastic modulus in the literature are scattered in a broad range. For TiN film, an X-ray elastic constant of the (422) crystal plane, 250 GPa, (the bulk modulus) was used by some Japanese researchers[3,4], but in other publications, 640 GPa was employed[5]. In other words, with the same X-ray measurement, the reported values of residual stress may differ more than two times.

Because of the selective feature of X-ray diffraction profiles, the lattice strain was obtained from a certain (*hkl*) plane, and the elastic modulus was associated with this plane[6]. Once the elastic modulus value of (*hkl*) plane is known, the X-ray elastic constant can be easily calculated. The elastic moduli measured from different (*hkl*) planes are not consistent with each other. Perry[7] measured the elastic moduli from different (*hkl*) planes of TiN by X-ray diffraction and obtained the real value through regression. If the data from the different planes are scattered due to the characteristics of the films, such as strong preferential orientation involved, the experimental data may be insufficient for regression.

In this study, the four-point bending method is applied to measure the elastic constant of selected planes. A theoretical analysis is also performed to compare the results from Kroner calculation and the experiment.

2 EXPERIMENT AND THEORETICAL CALCULATION

2.1 Samples

The substrate material was M2 high speed steel with a size of 100 mm × 15 mm × 2 mm.

Sample 1 and sample 2 were TiN films coated by plasma chemical vapor deposition (PCVD) and physi-

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cal vapor deposition (PVD) methods at Xi'an Jiaotong University. PCVD was supplied with direct current power and $TiCl_4$ was used as precursor. Multi-arc ion plating was used in PVD process. The thickness of each sample was around 3 μm.

Sample 3 and sample 4 were TiN films coated by PVD method on both sides of the substrates at Limburgs Universitair Centrum, the thickness of the two samples was 3 μm and 5 μm, respectively.

2.2 Experimental method

The four-point bending method was applied to measure TiN X-ray elastic constants of (422) and (331) planes.

X-ray diffraction measurement was performed with D/max-3A diffractometer and MSF-Ⅱ X-ray stress analyzer.

The traditional equation of X-ray diffraction analysis is

$$\varepsilon_{\varphi,\psi} = \frac{1}{2}S_2 \cdot \sigma_\varphi \cdot \sin^2\psi + S_1(\sigma_1 + \sigma_2) \quad (1)$$

$$\frac{1}{2}S_2 = \frac{1+\nu}{E}, \quad S_1 = -\frac{\nu}{E}$$

where $S_2/2$ and S_1 are X-ray elastic constants; σ_1 and σ_2 are principle stresses; σ_φ is the stress along φ direction. The Eqn. (1) can also be rewritten as

$$\sigma = -\frac{E}{2(1+\nu)} \cdot \cot\theta_0 \cdot \frac{\pi}{180} \cdot \frac{\partial(2\theta)}{\partial(\sin^2\psi)} \quad (2)$$

$$\sigma = MK \quad (3)$$

$$M = \frac{\partial(2\theta)}{\partial(\sin^2\psi)},$$

$$K = -\frac{E}{2(1+\nu)} \cdot \cot\theta_0 \cdot \frac{\pi}{180} \quad (4)$$

where θ and θ_0 are the diffraction angles of the (*hkl*) plane with and without strains, respectively; σ is the stress to be calculated; M is the slope of 2θ—$\sin^2\psi$ curve and K is known as X-ray stress constant.

When the samples are under uniaxial loading, Eqn. (3) becomes

$$\sigma_{app} = -\sigma_r + \sigma = -\sigma_r + MK \quad (5)$$

where σ is the total stress; σ_r is the residual stress and σ_{app} is the applied stress.

When the total stress is in the elastic range, the residual stress can not be relaxed, and σ_r is a constant. If σ_{app} is plotted with M and K, σ_r can be obtained.

According to Ref. [8], the film and the substrate are regarded as a double-layered beam in order to calculate the stress in the film. The following Eqn. (6) is used:

$$\sigma_{app} = \frac{3k_1 P[nH + (n-2)h]}{B[H + (n-1)h]^3} \quad (6)$$

where P is the applied load; k_1 is the length of the unequal bending moment zone; B is the width of the sample; H is the thickness of the sample; h is the thickness of the film; n is the ratio of E_f to E_s; E_f and E_s are the mechanical elastic constants of the film and the substrate, respectively. The mechanical elastic constant of TiN is 640 GPa[7] which is widely accepted.

2.3 Theoretical calculation

The elastic constant of (*hkl*) plane for a single crystal can be easily found in the handbook. But this value differs from that of a grain in aggregate environment since the grain is constrained by the surrounding grains. There are different models to calculate the elastic constant of (*hkl*) plane in the polycrystal using the data of single crystal. The equal stress Reuss model and the equal strain Vogit model are often used for rough estimation. Apparently each grain is in a state of equal stress or equal strain won't be true in reality. These two states can only be taken as the upper and lower limits of the elastic constant. Hill model takes arithmetic average of the Reuss and Vogit values and is close to the experimental result. The arithmetic average value can't be employed for further calculation since no physical meaning involved. Kroner model[9, 10], as a self-consistent model, has been widely accepted for theoretical analysis. For thin film, Kroner model assumes that all grains without orientation dependence are in spherical or elliptical shape, which may deviate from the columnar structure of the deposited film with texture. But for an approximation, this model is the best one for elastic constant calculation. Otherwise, this model assumes that the strain of the ellipsoid is related to the macro elastic constant.

$$\varepsilon_g = (S + u_g)\sigma_m \quad (7)$$

where ε_g denotes the strain of one crystal in the material; σ_m denotes average stress; S is the macro compliance to be calculated; u_g shows the deviation between the macro and the micro elastic constants:

$$u_g = [E(C_g - C) + I]^{-1} - I \quad (8)$$

where C is the stiffness and $C = S^{-1}$, E is defined by[11]

$$E_{ijkl} = \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} D_{jl}^{-1} x_i x_k \mathrm{d}\varphi \quad (9)$$

In Eqn. (9)

$$\boldsymbol{x} = \begin{vmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\varphi \end{vmatrix}$$

When u is average value of all grains, based on the definition,

$$u_g = 0 \quad (10)$$

S or C can be obtained by iterative calculation if the Eqn. (9) is regarded as the limit condition. The $C_{(1)}$ value, which is assumed as the result of the Hill model[12], and by Eqn. (7) it gives $u_{g(1)}$ as

$$u_{g(1)} = [E(C_g - C_{(1)}) + I]^{-1} - I \quad (11)$$

The next assumption for stiffness is

$$C_{(2)}^{-1} = C_{(1)}^{-1} + u_{g(1)} \quad (12)$$

Successive assumptions can be performed until a satisfactory convergence is obtained.

3 RESULTS

Fig. 1 shows the relationship between the bending load P and the applied strain. Fig. 2 shows the relationship between the slope of the $2\theta-\sin^2\psi$ curve and the applied strain.

According to Eqn. (5) and Eqn. (7), the measured X-ray elastic constants of plane (422) and (331) are summarized as in Table 1 and Table 2.

Table 3 is the XECs of Kroner model which are calculated from the data[13, 14] of single crystal. Table 4 is the elastic moduli of TiN different (hkl) planes.

4 DISCUSSION

Comparing the experimental results in Tables 1 and 2 with the calculated data in Tables 3 and 4, it's found that the deviation of the experimental elastic constants of (422) and (331) with that from the calculation are 9.7% and 8.8%. Tables 1 and 2 show that the maximum deviation for the same plane is 20 GPa. Sue[15] used mechanical deflection and X-ray diffraction to measure X-ray elastic constants of (422) plane of TiN film on the substrate of Ti, Ni and stainless steel, and the value was 411 ±45 GPa. This data is very close to 424.3 GPa in this study.

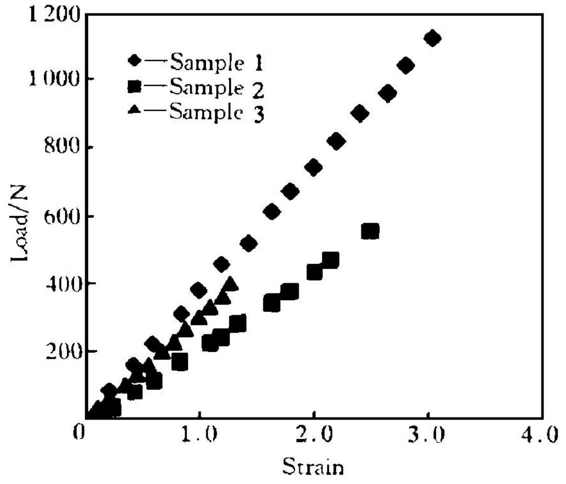

Fig. 1 Relationship between bending load and strain

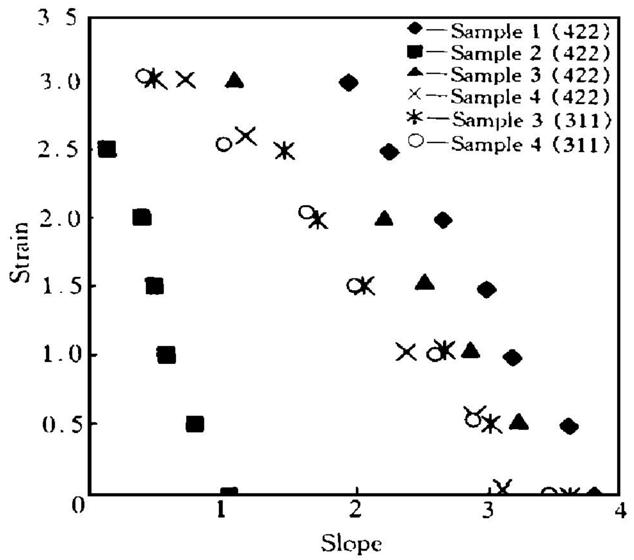

Fig. 2 Relationship between applied strain and slopes of $2\theta-\sin^2\psi$ curves

Table 1 Measured X-ray elastic constants of (422) plane of TiN film

Sample No.	$-S_1$ /(MPa)$^{-1}$	$\frac{1}{2}S_2$ /(MPa)$^{-1}$	E(422) /GPa
2	0.421	2.52	475.6
3	0.431	2.59	463.6
4	0.416	2.49	481.2

Table 2 Measured X-ray elastic constants of (331) plane of TiN film

Sample No.	$-S_1$ /(MPa)$^{-1}$	$\frac{1}{2}S_2$ /(MPa)$^{-1}$	E(331) /GPa
3	0.434	2.61	460.4
4	0.432	2.59	462.8

Table 3 Calculated results of X-ray elastic constants

Plane	$-S_1$	$\frac{1}{2}S_2$	Plane	$-S_1$	$\frac{1}{2}S_2$
(200)	0.420	2.640	(331)	0.495	2.866
(111)	0.512	2.915	(420)	0.464	2.772
(220)	0.489	2.846	(422)	0.489	2.846
(311)	0.463	2.770			

Table 4 Results of elastic modulus by Kroner model

Plane	E/GPa	Plane	E/GPa	Plane	E/GPa
(200)	450.5	(311)	433.5	(420)	433.3
(111)	416.1	(331)	421.8	(422)	424.3
(220)	424.3				

The experimental result of elastic modulus of (422) plane is 463.6 GPa which is a little different from the calculated value (423.4 GPa). This deviation may result from the columnar microstructure of TiN layer. Kroner model is equiaxial grains embedded in the homogeneous substrate. The difference of the equiaxial assumption and the fiber texture structure may result in the difference of X-ray elastic constant. An accurate calculation may use the orientation distribution function (ODF) to correct the effect of the crystal orientation as well as the grains in columnar shape.

Stoichiometric change of a film will result in big change of the constant. Torok and Perry[16] found the value of the elastic constant of TiN prepared by different processes changed from 440 GPa to 610 GPa as the ratio of Ti to N changes from 0.95 to 0.97. In this study the stoichiometry of Ti and N is very close to 1 by PVD method and the elastic constants measured from different PVD films are equal. But for TiN prepared by plasma-CVD method, its stoichiometry of Ti and N deviated from 1 and the elastic modulus of (422) plane is 554.4 GPa. The deposited films are often in a columnar microstructure because of the deposition process. The distribution of the grain and grain boundaries can influence the elastic constant greatly when the film extends along the direction perpendicular to the film surface. If assuming the grains and their boundaries are connected in a parallel way, the effective elastic constant will be

$$\frac{E_e}{E_g}=\frac{\alpha-\alpha\varphi_g}{\alpha+(0.5-\alpha)\varphi_g}+\frac{0.5\alpha\varphi_g}{1-0.5\varphi_g} \quad (13)$$

where E_g is the elastic constant, E_e is the effective elastic constant, φ_g the volume fraction of the grain, $\alpha = E_g/E_b$, E_b the elastic constant of the grain boundary. According to Eqn.(13), the results in Fig. 3 indicate that the density of film affects the elastic constant significantly when the elastic constant of grain is different from that of grain boundary.

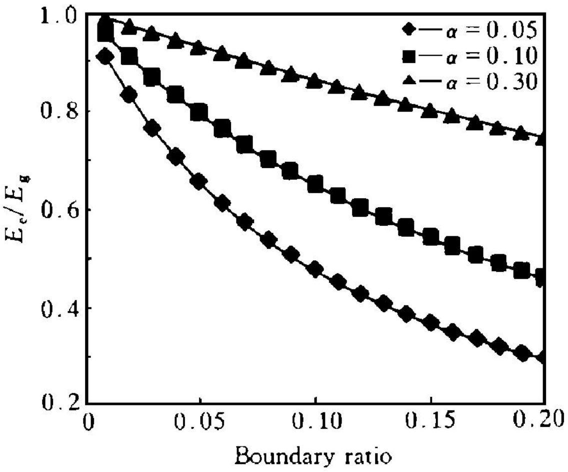

Fig. 3 Effect of boundary ratio of films on elastic constant

Table 5 shows the result after corrected by the method suggested by Ref. [17]. It can be seen that these data are scattered even they are corrected by Kroner method.

Table 5 Data measured by Seemann-Bohlin method after corrected by Kroner method

Sample No.	E(422) /GPa	Sample No.	E(422) /GPa	Sample No.	E(422) /GPa
1	378.6	3	400.9	5	404.5
2	397.1	4	401.5		

From above, it may be concluded that the changes of stoichiometry, microstructure and processing technique result in big change in elastic constant; even though small deviation between the measurement results and the calculated data is involved. The data measured by four-point bending method are in fairly good agreement with the results listed in the literature, and it is a promising method to measure the elastic constant of thin films.

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