Property Evaluation of Vapor-Deposited TiN Film by the Analysis of Elastic Waves*

(1st Report, Nondestructive Evaluation of Elastic Properties by Laser Surface Acoustic Waves)

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The elastic properties of TiN films deposited on stainless steel SUS317J2 by three physical vapor deposition methods were estimated from the velocity dispersion of laser surface acoustic waves (SAWs) in the frequency range of 30 to 60 MHz. The velocity dispersion of Rayleigh waves was obtained by the scanning interference fringes (SIF) system and was used to estimate the elastic stiffness of the films. Depending on the deposition method, Young's moduli of TiN films were found to increase in the order of activation reaction method (ARE) → hollow cathode discharge (HCD) → arc ion discharge (AID) method. The attenuation of SAWs was the highest for AID film due to the poor quality of the film.

Key Words: Nondestructive Evaluation, Titanium Nitride, Elastic Properties, Laser Surface Acoustic Waves, Scanning Interference Fringes, Physical Vapor Deposition

1. Introduction

Titanium nitride (TiN) and titanium nitridecarbide Ti(C, N) are widely used as hard-facing films of machining tool and wear components due to their excellent wear resistance⁽¹⁾. We have in the past^{(2),(3)} examined the feasibility of using TiN and Ti(C, N) as hard-facing coating of let-down valve components in a coal-liquefaction process which suffers from serious slurry erosion. Stainless steel SUS317J2 (25Cr-13Ni-0.8Mo-0.05C-Fe) with Vickers hardness of 320 was used as the substrate metal for the let-down valve,

because of its superior corrosion resistance and machinability. However, its hardness is lower than that of superhard alloys such as Co-WC, which is often used as machining tool. Wear resistance of hard-facing coatings depends significantly on the characteristics of both the film and substrate metal because the film tends to exfoliate from the deformed soft substrate metal.

Since the physical and mechanical properties of TiN and Ti(C, N) films deposited by PVD and CVD can be controlled by selecting substrate and vapor deposition conditions, the properties of these films should be evaluated in a nondestructive way. However, to our knowledge, there is no widely accepted method for evaluating the properties of films with thickness of 4 - 5 micrometers. Accurate evaluation of the elastic stiffness and Poisson's ratio of thin films is important particularly in the measurement of residual stress by the X-ray method and also in the calculation of the adhesion strength of the film. The ultrasonic spectroscopic method has recently enabled the measurement of elastic stiffness of thin films; however, it requires a liquid couplant for transmitting and receiving ultrasonics^{(4),(5)}. Since the ultrasonic waves are

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measured for specimen set in water, wave attenuation in the film, which provides information on pinholes (or pores), can hardly be measured.

On the other hand, surface acoustic wave (SAW) has often been used for estimating the elastic properties of thin films because it reveals the characteristic dispersion of velocity and attenuation depending on both elastic properties and thickness of the film^{(6),(7)}. In order to measure such properties of thin films, a wide frequency band SAW system is required.

We have developed a noble laser SAW system with wide frequency band up to 110 MHz. With this, we measured the velocity and attenuation dispersion of TiN and Ti(C, N) films deposited by three PVD methods. Among the SAWs, the velocity dispersion of the Rayleigh wave can be accurately computed from the given elastic properties, density and thickness of the film. The properties were estimated by the inverse processing of the measured velocity dispersion of the Rayleigh wave.

In general, the physical and mechanical properties of the film are influenced by the quality of the film, which is, in turn, affected by grain size, preferential orientation, porosity, impurity and residual stress. The SAW system with limited frequency band cannot measure all these microproperties. Therefore, in this paper, we mainly discuss the effect of porosity (or cavity) and inclusion in the films on the dispersion of velocity and attenuation. We also discuss the correlation between the properties estimated from SAW and the fracture strength of films estimated by the source simulation of acoustic emission (AE). In the present paper, we introduce a newly developed wide-band laser SAW system, the elastic properties of TiN and Ti(C, N) films estimated from the velocity dispersion of the Rayleigh wave, and porosity and inclusion in the films estimated from the attenuation dispersion.

2. Specimen

We used TiN and Ti(C, N) films deposited on SUS317J2 steel by activation reaction evaporation (ARE), arc ion discharge (AID) and hollow cathode discharge (HCD) methods. The specimens are, as shown in Table 1, expressed as ARE-N, AID-N, HCD-N and ARE-CN. The symbols -N and -CN imply TiN and Ti(C, N), respectively. However, Ti(C, N) film was deposited only by the ARE method. The films were deposited at 350°C by a professional company. The films were deposited by the following procedure to improve their adhesion strength: 1) deposition of metallic titanium film of 0.1 µm thickness by ion bombardment; 2) deposition of TiN or Ti(C, N) of 2 µm thickness by one of the above three methods; 3) deposition of metallic titanium of 0.1 µm thickness by

Table 1 Four kinds of TiN, Ti(C, N) coatings deposited on SUS317J2 steel

No.	Sample name	Deposition method	Deposited film	Vickers hardness Hv	Porosity %
1	ARE-CN	Activated Reactive Evaporation	Ti(C,N)	2600	6.65
2	AID-N	Arc Ion Discharge	TiN	2150	31.2
3	HCD-N	Hollow Cathode Discharge	TiN	1750	7.14
4	ARE-N	Activated Rective Evaporation	TiN	1100	5.30

Fig. 1 Surface topograph of AID-N and HCD-N films by laser microscopy

ion bombardment; and 4) deposition of 2-µm-thick TiC or Ti(C, N). Thus each film consists of the following four layers: substrate metal/metallic Ti/bottom TiN/metallicTi/top TiN.

The craters, pores and splashed particles in the film were measured using a laser microscope. Since the craters and splashed particles could not be separately measured using the laser microscope, these are treated as the defects in this research because the craters are often caused by fallingoff of the splashed particles and vacancies exist along the splashed particles⁽⁸⁾. In Fig. 1, typical laser microscopic photographs of AID-N and HCD-N films are shown. The AID-N film shows large defects in particular, in-plane porosity reaches 31.2%. In contrast, the defects in the HCD film are generally small and the porosity is estimated to be 5.30%. The higher porosity of the AID-N film is assumed to be due to the heavy bombardment by titanium ions.

Figure 2 shows the relationship between Vickers hardness (Hv) and applied load. Accurate hardness measurement of TiN film was extremely difficult due to the presence of the metallic titanium layer. For instance, the diagonal distance of indentation at 0.049 N is about 2 µm, which is exactly the thickness of the top TiN layer; however, it is influenced significantly by reading error. At a larger load, the difference in hardness between the films becomes unclear due to the effect of the substrate metal. We used the hardness

Fig. 2 Dependence of Vickers hardness on applied load

determined by a load of 0.245 N, in which the diagonal distance is between 3.5 and 4 μm . The hardness of the AID film scatters significantly due to a high degree of porosity, but is shown in the figure as average hardness of 15 measurements. The hardness of the AID film is the highest among the films studied in spite of its high porosity. This is assumed to be due to the compressive residual stress induced by the shot-peening effect of ion bombardment. The hardness of the AID film was reported to be measured as higher value due to the elastic recovery of indentation after unloading⁽³⁾. The same result was reported, by Mizuguchi et al.⁽⁹⁾, for the TiN film deposited on stainless steel by the AID method.

Although the hardness as well as the velocity of the Rayleigh wave is affected by residual stresses and intrinsic stresses⁽¹⁰⁾ induced by particle inbedding, it is at present almost impossible to measure true film properties, that are not influenced by residual stress.

3. Laser SAW System and Velocity Dispersion

In order to measure the velocity dispersion over a wide frequency band, we developed a new laser SAW system (scanning interference fringe at phase velocity, abbreviated as the SIF system), in which two laser beams with different wave numbers were scanned at the velocity of the Rayleigh wave⁽¹¹⁾. The system is illustrated in Fig. 3. Two laser beams of Q-switched Nd-YAG with frequencies of $\omega_1/2\pi$ and $\omega_2/2\pi$ were focused on the film surface at angles θ_1 and θ_2 to produce scanning interference fringes. The dispersion of the phase velocity and the attenuation of the Rayleigh wave were measured by changing the frequency difference $\omega_d/2\pi = (\omega_1/2\pi - \omega_2/2\pi)$ using a frequency-variable Bragg cell (30–110 MHz). The positions of both the mirrors and the Bragg cells were precisely controlled using computer-controlled stages. The transmitted Rayleigh waves were measured by an optical knife edge system with an avalanche photodiode detector for which an argon ion laser,

Fig. 3 Schematic illustration of scanning interference fringes

Fig. 4 Phase velocity dispersion of pure aluminum measured by the SIF system

chopped by an optical modulator, was used as the probe laser.

The phase velocity of the SAW generated by this method is given by⁽¹²⁾

$$V_{\text{SIF}} = \omega/k_f \quad (1)$$

where ω is the angular frequency determined by the spectral analysis of the monitored SAW. k_f denotes the wave number of the interference fringe and is given by

$$k_f = 2k \sin[(\theta_1 + \theta_2)/2] \quad (2)$$

Since the phase velocity is significantly affected by the accuracy of small angle of incidence, θ_1 and θ_2 , the angles are measured using a pure aluminum plate as the reference material. Figure 4 shows the phase velocity dispersion of pure aluminum in the frequency range from 30 to 110 MHz. The error in the phase velocity is estimated to be less than 1%. The dispersion of the SAW can be determined simultaneously with the phase velocity by changing the SAW propagation distance.

4. Results and Discussion

We measured the phase velocity of the Rayleigh

wave in the frequency range from 30 to 60 MHz. In Fig. 5 are illustrated the typical detected wave (a) and its power spectrum at 50 MHz (b) for the AID-N film. The detected wave is the average of 20 measurements and shows a S/N ratio higher than 20 dB. The velocity dispersion was determined from the frequency of the maximum peak of (b), and is shown in Fig. 6.

The phase velocity increases with frequency because the Rayleigh wave velocity of TiN film is higher than that of the substrate metal. The velocity dispersion changes significantly depending on the deposition method. For instance, the velocity at 50 MHz is highest for the AID-N film, and is almost 120 m/s higher than that of the ARE-N film. Data scatter of the ARE-N film, which has the highest porosity, is large compared to that of other films. In contrast, the ARE-CN film showed the highest velocity and its data scatter is the smallest.

We estimate the elastic properties of TiN films from these velocity dispersions using the matrix transfer method of Adler et al.⁽¹³⁾. The properties of film are determined such that the computed dispersion for

Fig. 5 Example of monitored SAW (a) and its power spectrum (b)

Fig. 6 Phase velocity dispersion of the Rayleigh wave for four kinds of TiN and Ti(C, N) films.

a 5-layer structure of SUS/0.1 μm Ti/2 μm TiN/0.1 μm Ti/2 μm TiN agrees with the experimental dispersion. Computation was performed under three assumptions: 1) TiN is an isotropic elastic material; 2) both elastic properties and density change stepwise at each interface; 3) each layer is mechanically continuous, or the stresses and strains across the interface are continuous. Assumption 3) is valid because the TiN film showed excellent adhesion under compressive loading. Assumption 1) might be incorrect because the TiN film is considered to grow epitaxially and usually shows preferential orientation. However, it is almost impossible to measure the orientation dependence of the phase velocity dispersion by the laser SAW system due to the limited spatial resolution of the system. We assume here that TiN is an isotropic elastic material. Under these assumptions, we have to determine Young's modulus E , Poisson's ratio ν and density ρ of TiN and titanium metal, given the thickness of each layer. However, the estimation of three unknown properties is likely to lead us to overestimation. Thus we used Poisson's ratio estimated by the strain gauge method. Shown in the Fig. 6 are the experimental Poisson's ratio (0.26–0.29), which seems to be slightly larger than that reported for bulk TiN (0.236)⁽¹⁴⁾. Poisson's ratio of the SiC film deposited by CVD is reported to be 0.35–0.36⁽¹⁵⁾, and is larger than that of bulk SiC. We also examined the effect of Poisson's ratio on the phase velocity dispersion by computer simulation, and found that the change in Poisson's ratio from 0.2 to 0.29 increased the phase velocity by only 5 m/s. This velocity change is within the experimental error of phase velocities in Fig. 6. Next we computed the phase velocity dispersion of the TiN film using Poisson's ratio in the figure and a density of 5 210 kg/m³⁽¹⁶⁾. Young's modulus, Poisson's ratio and density are taken to be 196 GPa, 0.27 and 8 000 kg/m³ for SUS317J2 steel, and 115 MPa, 0.37 and 4 540 kg/m³ for metallic titanium, respectively. The solid lines in Fig. 6 are the computed velocity dispersions using the given Young's modulus. Young's modulus of porous AID-N film is estimated to be 370 GPa, and is higher by 155 GPa than that (215 GPa) of the ARE-N film. We examine the propriety of the estimated Young's modulus, by referring to published data. For instance, Ito et al.⁽¹⁰⁾ estimated polycrystalline TiN's modulus to be 470 GPa using the Hill's isotropic elastic theory. They also measured the velocity dispersion using an ultrasonic spectra-microscope and found it to be 510 GPa for 1.3- and 3.5- μm -thick TiN films and 370 GPa for 7.1- μm -thick TiN film. For residual stress measurement by X-ray method, Young's modulus of 250 GPa is often used⁽¹⁵⁾, however, this value appears to be smaller than the

reported value (370, 510 GPa) by Ito et al. Young's modulus for ARE-N estimated by us is slightly smaller than that estimated by Ito et al.⁽¹⁰⁾, but is close to their data.

The higher modulus for the AID-N film, in spite of its poor film quality, is considered to be due to the extremely high compressive stresses, almost ultimate tensile strength (3 GPa), induced by ion bombardment⁽⁹⁾. Although there are no experimental data showing the relationship between the Rayleigh wave velocity and residual stresses, Toda et al.⁽¹⁷⁾ reported that the SH wave velocity increases by about 50 m/s with 1 GPa compressive stress. If this relationship were to hold for the Rayleigh wave, the Rayleigh wave velocity would decrease by 150 m/s with 3 GPa compressive stress, leading to a higher Young's modulus. The elastic properties estimated from SAW velocity dispersion are significantly influenced by residual stresses in the film; however there seem to be no fundamental data to support this statement.

Furthermore, we examined the relationship between hardness and Young's modulus, since Tanaka et al.⁽¹⁸⁾ reported a linear relationship between them for Si_3N_4 , SiC and Al_2O_3 ceramics. Figure 7 shows the relationship between hardness and Young's modulus. Data are very close to the line given by Tanaka et al.⁽¹⁸⁾

We also examined wave attenuation and film quality. Since the Rayleigh wave velocity of the TiN film is faster than that of the substrate metal, SAW becomes the leaky wave at frequencies higher than the cut-off frequency at which the Rayleigh wave velocity in the film exceeds the shear wave velocity of the substrate metal. The cut-off frequency for the TiN film was computed to be at around 90 MHz. However, we cannot detect the Rayleigh wave at frequencies higher than 65 MHz. The absence of a Rayleigh wave above 65 MHz appears to be due to not the cut-off frequency but wave attenuation in austenitic stainless steel. Stainless steel is known to be a

highly attenuative material⁽¹⁹⁾. Then we measured wave attenuation by changing both the frequency and SAW propagation distance. Figure 8 shows enveloped SAWs at 50 MHz for the AID-N film (left) and those at 60 MHz for SUS317J2 steel (right) as the propagation distance is changed from 0.54 to 0.63 mm. No SAW could be observed at propagation distances longer than 0.63 mm for the AID-N film. In the case of the substrate metal, in addition to the larger attenuation, a second peak was observed at propagation distances of 0.59 and 0.63 mm. The wavelength of SAW at frequency range from 50 to 60 MHz is 45 to 50 μm and is almost 10 times the thickness of TiN film. These wavelength of SAW is close to the large grain size of the substrate metal. Since the SAW propagates through both the surface TiN film and the substrate metal, the second peak observed in Fig. 8(b) is considered to be due to the interference of grain boundary scattering. Wave scattering by average grain size (20–30 μm) of the substrate metal becomes more pronounced at higher frequencies, finally resulting in no SAW.

Figure 9 shows the wave attenuation of films and substrate metal in the frequency range from 30 to 55 MHz. The wave attenuation increases with increasing frequency in the power range of 3.6 to 4. This frequency dependence agrees with that of Rayleigh

Fig. 8 Effect of propagation distance on the enveloped SAW at 50 MHz for the AID-N film (a) and at 60 MHz for SUS317J2 (b)

Fig. 7 Relationship between Vickers hardness and Young's modulus

Fig. 9 Attenuation dispersion of the Rayleigh wave

scattering. Higher attenuation of the AID-N film by almost 20 to 30 dB than that of the other films is due to the scattering by craters and splashed particles in the film. On the other hand, attenuation difference was hardly observed between HCD-N and ARE-N films. This implies that the quality of these two films cannot be diagnosed by wave attenuation.

5. Conclusion

We estimated the elastic constants of TiN films deposited by three vapor deposition methods from the velocity dispersion of laser SAW. Film quality was also estimated from wave attenuation in the frequency range from 30 to 60 MHz. The results are summarized below.

1) We developed a new laser SAW system (SIF system) in which the interference of two laser beams with different frequencies was scanned at the phase velocity of SAW. This system measures the phase velocity dispersion within 1% error as well as wave attenuation in the frequency range from 30 to 110 MHz. This system also enables non-contact and non-destructive evaluation of materials without the need for a liquid couplant.

2) Young's moduli, estimated in such a way that the computed velocity dispersions agree with the measured ones, were found to be 370 GPa for the AID-TiN film, 305 GPa for the HCD-TiN film and 215 GPa for the ARE-TiN film. A linear relationship between estimated Young's moduli and Vickers hardness was found for the TiN and Ti(C, N) films.

3) No SAW was detected at frequencies higher than 65 MHz for the 4.3- μ m-thick TiN film deposited on SUS317J2 steel. This appears to be due to wave attenuation and scattering by grain boundaries in the substrate metal, and also by craters and splashed particles in the TiN film, rather than the cut-off frequency (90 MHz) of the SAW. The wave attenuation of all TiN films increased from 3.6 to 4.0 power of the frequency; however, the wave attenuation of the AID-N film with a number of pores and splashed particles is almost 20 dB higher than that of the other two TiN films.

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