Advanced indentation technique for strength evaluation of hard thin films

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Abstract

A new hybrid technique for studying the fracture mechanism and strength of hard thin film is developed. The technique utilizes acoustic emission (AE) data, corrosion potential fluctuation (CPF) data and finite element method (FEM) for Vickers indentation test. This method was applied to TiN film deposited by PVD method on four metallic substrates of austenitic stainless steel, carbon steel, forging steel and pure iron. We detected both the AE and CPF from equidistant ripple cracks or step-wise terraces produced outside of the indentation during loading in a buffer solution (H₃PO₄, pH 6.86). Characteristic potential fluctuations, termed as a RD-type CPF (rapid drop to active potential and gradual recovery) and strong AEs were simultaneously produced by Mode-I ripple cracks of the film. They were produced by film bending during the penetration of the pyramidal indenter. The number of ripple cracks observed during indentation agreed well with that of RD-type CPF. Detailed analysis indicated the generation of ripple cracks at a constant distance \( L_c \). The value of \( L_c \) can be predicted by the RD-type CPF timing and the penetration rate of the indenter. Bending strength of the film was estimated by FEM using the \( L_c \) value. Intrinsic strength of the TiN film, determined by subtraction of residual stress, was measured as 0.9–1.4 GPa. These values are almost constant independent of the substrate material and consistent with the reported strength of 1.2 GPa.

Keywords: Indentation; Finite element method; Acoustic emission; Corrosion potential fluctuation; Fracture strength of film

1. Introduction

Hard ceramic thin films are brittle and often suffer cracking and exfoliation. Evaluation of fracture strength of the hard thin films is important for practical applications. Various evaluation methods such as scratch and tensile loading have been utilized so far. As the ceramic film deposited on a steel substrate has compressive residual stresses higher than the strength of the substrate, it is generally difficult to induce film fracture by tensile test and determine the intrinsic fracture strength of the film [1]. Indentation method, however, makes the evaluation of film strength possible, since it produces tensile stresses larger than the residual compressive stress. It becomes a good method to understand the contact fracture characteristic, which shows strong dependency on the substrate materials. Indentation test, however, requires an advanced system to monitor what is happening in a small contact region. Acoustic emission (AE) can be a powerful tool to monitor the fracture process and mode of the film.

We previously monitored AEs during micro-indentation tests on TiN films deposited onto an austenitic stainless steel plate [2–4]. Fracture process and mode of the film fracture were successfully revealed by radiation pattern analysis of Lamb wave AEs. A technical challenge for application of the AE technique to the indentation test is that the detection of fine AE signals is often hindered by contact noise. Separation of contact noise and AE signals is needed for correct interpretation of the fracture process, but this is often difficult.

Another powerful tool for monitoring the fracture process of an indented film is corrosion potential fluctuation (CPF). The CPF can monitor the initiation of localized corrosion [5] of substrate metal induced by local fracture of the film when the sample is in a selected corrodant. Non-conductive diamond indenter is suitable for corrosion potential monitoring of conductive TiN film. Here the corrodant must be a solution to produce a non-Faradic reaction of the substrate metal. Local anodic current due to anodic dissolution of the substrate metal is expected to produce a rapid drop of corrosion potential to active potential (named as the RD type CPF). CPF method can be a monitoring technique of micro-cracks more sensitive than the AE. It makes a significant contribution for separating the AE signals from contact noise. Time delay between the occurrences of an AE signals and a corresponding CPF will give us another interesting information on film fracture
process. Our previous research on the TiN on Type AISI304 revealed that the film suffered Mode-I ripple cracks due to tensile stress developed by film bending. If we can determine the distance of the ripple crack by AE and/or CPF methods, we can estimate the fracture strength of the film by FEM analysis.

In this study, we propose a new indentation technique to evaluate the intrinsic strength of hard surface film deposited on soft substrate metals. In order to study the fracture behavior of the PVD-TiN films deposited on four types of soft metallic substrates, we simultaneously monitored AE and CPF during micro-Vickers indentation test in a neutral buffer solution. Next we estimated the fracture process of the TiN films by FEM using the AE and CPF data.

2. Material and experimental procedure

The hard films tested are TiN with the thickness of a few micrometers. The TiN films were deposited by hollow cathode discharge method onto four types of ductile metals, namely, metastable austenitic stainless steel (AISI304), plain carbon steel (SS400), forging steel (YXR33) and commercial pure iron (Fe). For AISI304 substrate has a middle thin layer was formed before the TiN films were deposited, to improve their adherability to the substrate. These samples are designated as TiN/Ti/AISI304, TiN/SS400, TiN/YXR33, and TiN/Fe hereafter. Film thickness, specimen size and mechanical properties of film and substrate are shown in Table 1 [7]. Table 2 shows the elasto-plastic properties of substrates estimated by dual indentation method [8,9].

We performed micro-indentation test using an electromagnetic servo-testing machine equipped with a Vickers indenter and two eddy current sensors. This machine can measure relationship between indentation force, \( F \), and indentation depth, \( h \), or \( F-h \) curves with high resolution. All tests were performed with loading rate, \( dF/ds \), of 10 mN/s, maximum indentation force, \( F_{\text{max}} \), 20 N and holding time, \( t_v \), of 60 s at room temperature.

We monitored AEs using four resonant type small sensors (Type PICO: PAC, center frequency at 450 kHz). They were mounted on the film surface to monitor the Lamb AE wave. We also used a wide band sensor (WD: PAC) mounted on the bottom surface of the specimen, as shown in Fig. 1. Output of the WD sensor was used as trigger signal. Outputs of the sensors were amplified to 60 dB by preamplifiers (PAC), and digitized by an A/D converter (GAGE Applied, Inc.) and fed to a personal computer. AEs are digitized at an interval of 40 ns with 2048 points. The threshold value for channel 1 (trigger channel) was set at 25 mV.

We also monitored CPF by film fracture in a neutral phosphate buffer solution (\( \text{H}_3\text{PO}_4 \), pH 6.84). A plastic cell of 20 mm diameter was glued on the specimen surface. This cell is connected to another cell with a reference electrode of Ag/AgCl. Output of the electrode was digitized by a digital voltmeter (RE6871E: ADVANTEST) at resolution of 1 \( \mu \)V and time interval of 59 ms.

| Film/substrate | TiN/Ti/AISI304 | TiN/SS400 | TiN/YXR | TiN/Fe |
|----------------|---------------|-----------|---------|--------|
| Film thickness (\( \mu \)m) | 4 | 4 | 3.5 | 1 |
| Specimen shape (mm) | 30'\times30'\times2' | 30'\times30'\times2' | 30'\times30'\times2' | 30'\times30'\times2' |
| Hardness, HV | 2100/760/260 | 2200/180 | 2100/340 | 2320/90 |
| Young's modulus, \( E \) (GPa) | 350/150/196 | 360/204 | 353/202 | 347/198 |

Fig. 1. Experimental setup for micro-Vickers indentation test with AE and corrosion potential monitoring.
3. Result and discussion

3.1. AE monitoring and ripple crack

Fig. 2 shows the $F-h$ curves and cumulative AE counts. Total AE counts changed depending on the substrate metals, but all events were detected during the loading. Fig. 3 shows typical AE waveforms detected during loading on TiN/Ti/AISI304. It is noted that polarities of the first $S_0$ mode Lamb waves are positive, indicating the Mode-I fracture [6]. Open triangles in Fig. 2a shows the AE timing from the Mode-I fracture. Most AEs were produced by the Mode-I crack with opening vector in the direction parallel to the film surface. Mode-I film cracking occurred frequently during the loading only for TiN/Ti/AISI304. Other specimens produced weak AEs whose fracture type could not be classified. No clear relationship observed between the cumulative AE counts and hardness of the substrate. Specimen of AISI304 (Hv-260) and pure iron (90) substrate produced AEs more than 200 counts, but specimens of YXR33 (340) and SS400 (180) substrate produced AEs less than 150. This is because many contact noises are included, but the weak amplitude makes the classification difficult. We needed another information to classify them.

Fig. 4 shows surface microphotographs of contact region. There observed a number of steps in the pyramidal indentation of four samples. These steps are film cracks, called ripple cracks. It is noted that the distance between the cracks is different depending on the substrates. AEs detected during the loading appear to come from this type of crack. In Fig. 5, contour map of stress in the radial direction, $\sigma_r$, by FEM is shown for TiN/Ti/AISI304. It shows that large tensile stress ($\sigma_r$ region) developed outside the contact region where the film cracks were produced. When the cracks move under the indenter with increasing the penetration depth, they close their opening due to the compressive stress in $\sigma_\theta$ and $\sigma_\phi$ region. As the tensile stress in $\sigma_r$ region is higher than the tensile strength of the film, the crack is produced by tensile stress.
under the bending of the film. A number of Mode-I ripple crack are produced outside the contact point continuously with the progress of the indentation. All FEM calculations for other substrate materials exhibited the similar stress distribution.

Fig. 6 shows the number of ripple cracks observed by SEM in the contact region as a function of distance from the center of indent, \( r \). The four types of open symbols (\( \bigcirc, \bigtriangleup, \Delta, \Box \)) indicated the number of film crack observed by SEM. The cracks were counted for \( r \) value far from 20 \( \mu \)m since cracks near the center of contact region was too small and unclear to be counted. Here, the crack numbers were measured on four pyramidal planes. The lines in the figure express linear-regression lines for all specimens. The reciprocal of the slope of these lines designates the distance of the ripple cracks, \( L_c \). The values of \( L_c \) for TiN/Ti/AISI304, TiN/SS400, TiN/YXR and TiN/Fe were measured as 5.0, 5.2, 2.9, and 1.3 \( \mu \)m.

### 3.2. Film fracture analysis using AE and CPF

Fig. 7 shows changes of corrosion potential and cumulative AE counts as a function of loading time for four samples. Change in the indentation force is also shown by dashed line. The corrosion potential started to show frequent small fluctuation when AE count increased rapidly during loading. However, no potential fluctuation was observed during unloading for all samples. Fig. 8 shows timing of AE (triangle) and RD-type potential fluctuations in magnified time scale. It is noted that small CPFs do not necessarily accompany AEs but large RD-type CPFs occurred at or slightly after AE generation. Similar behavior was observed over the entire

Fig. 4. Micrograph of contact region.

Fig. 5. Contour map of radial stresses computed by 2D-FEM model for TiN/Ti/AISI304.

Fig. 6. Cumulative number of ripple cracks as a function of \( r \).

\[
N = \alpha \times r + \beta
\]

| Material       | \( \alpha \) | \( \beta \) | \( L_c(\mu\text{m}) \) |
|----------------|------------|------------|------------------------|
| TiN/Ti/AISI304 | 0.20       | 1.92       | 5.0                    |
| TiN/SS400      | 0.19       | 0.20       | 5.3                    |
| TiN/YXR        | 0.35       | 6.79       | 2.9                    |
| TiN/Fe         | 0.76       | 20.44      | 1.3                    |
loading time. This strongly suggests that the RD-type CPFs are caused by the local anodic current of substrate metals due to relatively large film fractures at the outside of contact region. No AE at weak CPF suggests that the crack volume of film fracture is too small to produce strong AE. Indeed, we observed some small sub-cracks crossing or connecting the parallel ripple cracks, as shown in Fig. 4. CPF is more sensitive to small film fracture than the AE, but the important information for the fracture strength estimation of the TiN film is the frequency (distance) of parallel ripple cracks rather than the small sub-cracks. Thus we counted only the large CPFs associated with strong AEs. The large CPFs showed the rate of potential shift ($\Delta E/\Delta t$), of which the rates were greater than 0.4 mV/s. Cumulative counts of the large CPFs are shown as a function of $r$ by solid symbols and approximated by four lines in Fig. 6. These lines agree well with the ripple cracks by SEM. It is new
3.3. FEM for film fracture strength

Axially symmetric structural models for FEM were created for all specimens using a commercially available FEM code, MARC (K-7) in conjunction with MENTAT III (ver.3.3.0). FEM calculations were performed assuming that the film is elastic perfect plastic body and the substrate elastic plastic body approximated by piecewise linear curve including work hardening. Material properties used are shown in Tables 1 and 2. Diamond indenter of a conical pyramid with a top angle of 136° is regarded as a rigid material. This angle is the angle of two pyramidal faces of Vickers indenter. As the calculated stress distribution by two-dimensional models for Vickers indenter was in good agreement with that of three-dimensional models in our previous research [3], thus two-dimensional model was adopted in this study.

In the model, we first induced a crack in the film at \( r = 41-42 \mu m \) at which the ripple crack initiated at constant distance. Fig. 9 shows the distribution of \( \sigma_r \) along distance from the center of indent, \( r \) as a function of four penetration depths, \( h \). Indentation produces the maximum tensile stresses as shown by open circles. They increased with an increase of the penetration and their location shifted to the outside.

In order to study the propriety of \( \sigma_r \) distribution when the film cracking occurs, we calculated \( \sigma_r \) distribution using another model with second simulated crack at the location of \( L_c \) from the first crack. It was revealed that the film cracking released the tensile stress. This implies that the film crack occurs when the stress reaches the fracture strength of film. Dotted line in Fig. 9 indicates the position of the simulated crack, and dashed line the second crack. Here the location of second crack occurs at the location from data of Fig. 6, i.e at 5.0 mm from the first crack for TiN/Ti/AISI304, 5.2 m for TiN/SS400, 2.9 mm for TiN/YXR33 and 1.3 mm for TiN/Fe. The maximum stress at the position of the second crack corresponds to the fracture strength of TiN film, \( \sigma_f \). These values were shown in Table 3.

It should be noted that these calculations did not consider the effect of residual stress in the films. Thus, we measured the residual stresses by X-ray method and estimated the intrinsic strength \( \sigma_{f,\text{film}} \) of the film. Residual stresses are shown in the second column of Table 3. The intrinsic strengths of films, obtained by subtracting the residual compressive stress from the fracture strength \( \sigma_f \), are shown on the bottom column. They are estimated as 0.9–1.4 GPa, independent of substrate materials. The value of \( \sigma_{f,\text{film}} \) was reported as 1.2 GPa in TiN/Ti by tensile loading test [10]. Tensile test can measure

| Film/substrate | TiN/Ti/SS304 | TiN/SS400 | TiN/YXR33 | TiN/Fe |
|----------------|-------------|-----------|------------|-------|
| Fracture strength, \( \sigma_f \) (GPa) | 5.5         | 3.0       | 2.9        | 3.6   |
| Residual stress, \( \sigma \) (GPa)    | -4.6        | -2.0      | -1.5        | -2.2  |
| Residual strength, \( \sigma \) (GPa)  | 0.9         | 1.0       | 1.4         | 1.4   |

Fig. 9. Distribution of radial stress computed by 2D-FEM model with a simulated crack.

finding that the number of ripple cracks can be measured by CPFs and AE in real time.
the film strength since the residual stress of the TiN on Ti is less than \(-1\) GPa. However, the TiN film deposited on soft metals of our research has large compressive stress. Therefore, the present indentation technique can be a useful method for fracture strength evaluation of hard film deposited on soft metal.

4. Conclusion

We utilized advanced Vickers indentation test with acoustic emission (AE) and corrosion potential fluctuation (CPF) system to study the fracture process of TiN film deposited on four soft substrate metals. FEM analysis based on the measured data can estimate the fracture strength of TiN film. Results are summarized below.

1. Vickers indentation on the samples in neutral buffer solution produces a number of ripple cracks in the TiN film. AEs and CPFs detected during loading are found to be from Mode-I ripple crack and subsequent anodic current increase of the substrate metals, respectively. Spacing of the ripple cracks can be estimated by generation rate of large potential shift associated with strong AE. Fracture process of the film in limited narrow region can be studied by AE and CPF method.

2. FEM analysis predicted that ripple crack is produced by large tensile stresses due to the film bending. These ripple cracks were found to initiate at a certain distance, \(L_c\), which could be predicted from the generation rate of large CPF. We estimated the fracture strength of the films using the \(L_c\) value. Intrinsic strength of TiN films, obtained by subtracting the residual compressive stress from the fracture strength of the film, was estimated as 0.9–1.4 GPa.

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