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Determination of interfacial fracture energies of Ni films on titanium and stainless steel substrates by peel test ①

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[Abstract] The interfacial fracture energy G, which includes the effect of residual stress, was deduced for Ni films on titanium and stainless steel substrates based on the energy-balance argument and the numerical method for the work expenditure G_{db} of Moidu et al. The estimated interfacial fracture energies G are independent of the film thickness, the peel angle and the residual stress. The value of G for Ni films on a stainless steel substrate is about 5.47~ 6.08 N/m for various peel angles θ, while 5.33~ 6.72 N/m for Ni films on titanium substrate with various film thickness h. The effect of the residual stress on the peel strength P/b was also discussed.

[Key words] peel test; interfacial fracture energy; work expenditure; residual stress
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1 INTRODUCTION

Thin films are widely used in micro-electronic devices and structural components. The adhesion strength of thin films to substrates is of major concern because of thin-film-coated structure failure due to interfacial debonding. The intrinsic adhesion between two materials is associated with the inter-atomic or intermolecular forces, of which the quantitative assessment remains still as a challenge[1]. The peel test is a mechanical test that has been extensively used to measure adhesion strength. However, serious plastic deformation and high bending angle occur at the crack tip during peeling, with the result that the peel strength does not truly represent the interfacial fracture energy. The measured peel strength includes not only the debonding force of the interface but also the force necessary for the plastic deformation of the film. It is of interest to predict the plastic dissipation and thereby to extract the fracture energy from the measured peel strength for a given film/substrate system and configuration.

The effect of film plasticity was first considered in detail by Chen and Falvin[2], who presented an approximated solution for the peel stress in the presence of film plastic deformation. Since then several theoretical analyses of film plasticity and approximate numerical methods to estimate film plastic dissipation of the peel test appeared in the Ref. [3~ 6]. Recently, Kim et al[7], Moidu et al[8,9] and Kinloch et al[10] analyzed the plastic deformation of strips assumed to be made of elastic perfectly plastic material and bilinear hardening material, the authors modeled the attached part of film as elastic-plastic beam on an elastic foundation, and calculated the energy dissipated during peel test in a more detail. Especially, Kinloch et al[10] presented a simple and effective method to calculate the work expenditure during peeling. Moidu et al[9] follow the approach of Kinloch et al[10] and carry out some improvements in the method.

The peel tests of flexible polymer strips on metallic substrates and thicker metallic films on polymer substrates were investigated[5,7~ 13], however, few papers are concerned with peel tests of thin metallic films on metallic substrates, especially with the effect of residual stress on the interfacial fracture energy. In the present work, an expression including the effect of residual stress on the interfacial fracture energy is proposed according to the energy-balance argument. Besides, the influence of residual stress on the external work is also involved in the expression. The numerical method of Moidu et al[9] is employed to evaluate the values of the interfacial fracture energy for Ni films on stainless steel substrate for various peel angles and Ni films on Titanium substrate with various film thickness. The effects of peel angle, film thickness and residual stress on the interfacial fracture energy are discussed.

2 THEORETICAL CONSIDERATIONS

2.1 Basic concepts

The interfacial fracture energy G may be derived from an energy-balance argument[10], such as that

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$$G = \frac{1}{b}\left[\frac{\mathrm{d}U_{ext}}{\mathrm{d}a} - \frac{\mathrm{d}U_s}{\mathrm{d}a} - \frac{\mathrm{d}U_{dt}}{\mathrm{d}a} - \frac{\mathrm{d}U_{db}}{\mathrm{d}a}\right] \quad (1)$$

where $\mathrm{d}U_{ext}$ is the external work, $\mathrm{d}U_s$ the stored strain energy in the peeling arm, $\mathrm{d}U_{dt}$ the energy dissipated during tensile deformation of the peeling arm, $\mathrm{d}U_{db}$ the energy dissipated due to bending of the peeling arm near the peel front, b the width of film on substrate, and $\mathrm{d}a$ the debonding length. In fact there exists residual stress in thin film due to the differences of thermal expansion coefficient, as well as other physical properties, etc. So, the effect of residual stress on the interfacial fracture energy must be taken into consideration. Moreover, the change of the kinetic energy should also be considered during peeling. Let $\mathrm{d}U_{rs}$ be the stored strain energy of film on the substrate and $\mathrm{d}U_k$ the kinetic energy of film/substrate system, then Eqn. (1) can be modified as

$$G = \frac{1}{b}\left[\frac{\mathrm{d}U_{ext}}{\mathrm{d}a} - \frac{\mathrm{d}U_s}{\mathrm{d}a} - \frac{\mathrm{d}U_{dt}}{\mathrm{d}a} - \frac{\mathrm{d}U_{db}}{\mathrm{d}a} + \frac{\mathrm{d}U_{rs}}{\mathrm{d}a} - \frac{\mathrm{d}U_k}{\mathrm{d}a}\right] \quad (2)$$

The value of G reflects the energy to break the interfacial bonding forces and the energy dissipated locally ahead of the peel front in the plastic or visco-elastic zone at the crack tip.

For the calculation of $\mathrm{d}U_{ext}$, the strains in the thin film induced by the residual stress must also be taken into account. Thus, the expression for $\mathrm{d}U_{ext}$ presented in Ref. [10] can be improved as

$$\mathrm{d}U_{ext} = P\mathrm{d}a[(1-\varepsilon_{rl}) - \cos\theta + (1-\varepsilon_{rt})\varepsilon_a] \quad (3)$$

Simultaneously, the stored strain energy in the peeling arm $\mathrm{d}U_s$ and the energy dissipated during tensile deformation of the peeling arm $\mathrm{d}U_{dt}$ can be expressed as

$$\mathrm{d}(U_s + U_{dt}) = b(1-\varepsilon_{rt})h\mathrm{d}a\int_0^{\varepsilon_a}\sigma\mathrm{d}\varepsilon \quad (4)$$

where h is the thickness of the peeling arm, which is peeled in a steady state under a constant load P at a certain peel angle of θ, as shown in Fig. 1(a), ε_a is the tensile strain in the stretched peel arm after separation, ε_{rl} and ε_{rt} are the longitudinal strain and transverses strain in the film on substrate induced by residual stress, respectively.

Furthermore, we may ignore $\mathrm{d}U_k$ for slow peeling and if the peeling arm is considered to have a relatively large tensile stiffness, say, have a relatively large elastic modulus E, then we obtain the following equation from Eqn. (2):

$$G = \frac{P}{b}(1-\cos\theta) - \frac{\mathrm{d}U_{db}}{b\mathrm{d}a} + \frac{\mathrm{d}U_{rs}}{b\mathrm{d}a} \quad (5)$$

where

$$\frac{\mathrm{d}U_{db}}{b\mathrm{d}a} = G_{db}, \quad \frac{\mathrm{d}U_{rs}}{b\mathrm{d}a} = G_{rs} \quad (6)$$

where G_{db} is the work expenditure per unit advance of the interfacial crack for per unit width of the film, G_{rs} is the stored strain energy per unit area of film on the substrate.

If the longitudinal component of the residual tensile stress is σ_{rl}, while the transverse one is σ_{rt}, for elastic material it also yields

$$G_{rs} = \left[\frac{1}{2}\varepsilon_{rl}\sigma_{rl} + \frac{1}{2}\varepsilon_{rt}\sigma_{rt}\right]h = \frac{h}{2E}(\sigma_{rl}^2 + \sigma_{rt}^2 - 2\nu\sigma_{rl}\sigma_{rt}) \quad (7)$$

where E and ν are elastic modulus and Possion's ratio of the film, respectively.

From Eqn. (6), an alternative representation of Eqn. (5) is

$$G = \frac{P}{b}(1-\cos\theta) - G_{db} + G_{rs} \quad (8)$$

If the plastic bending of the peeling arm is too small to induce significant effect, the terms concerning plastic bending can be ignored, then

$$G = \frac{P}{b}(1-\cos\theta) + G_{rs} \quad (9)$$

Under condition of the residual stress free or residual stress ignorable in the film, it gives

$$G = \frac{P}{b}(1-\cos\theta) \quad (10)$$

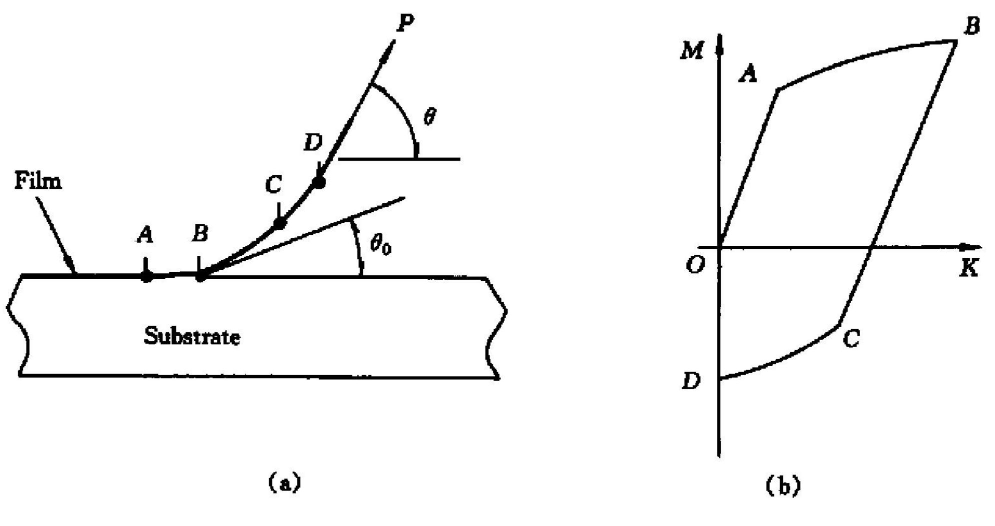

Fig. 1 Deformation of peeling arm
(a) —Configuration of steady-state peeling; (b) —Moment-curvature relation

2.2 Procedure to estimate G_{db}

For the existence of plastic bending in the peeling arm during peeling, the determination of the interfacial fracture energy G needs firstly to evaluate the work expenditure G_{db}, as shown in Eqn. (8).

According to the analysis of deformation of peeling arm, we can derived the work expenditure G_{db}. Fig. 1(a) shows the configuration of the deforming film in a steady-state peel test[9, 10], the corresponding moment-curvature (M — K) diagram is shown in Fig. 1(b). The deformation process of the film undergoes the follow stages: (a) elastic loading (O — A), (b) plastic loading (A — B), (c) elastic unloading (B — C) and (d) reverse plastic loading (C — D). Under certain conditions the point C and D coincide, i. e., the reverse plastic bending stage is absent. Fig. 2 shows the corresponding stress distribution in film cross section for various stage of bending for a bilinear hardening material film[9]. The work expenditure G_{db} within the film in steady-state peeling is given by the area enclosed by O — A — B — C — D — O (see Fig. 1(b)), i. e.

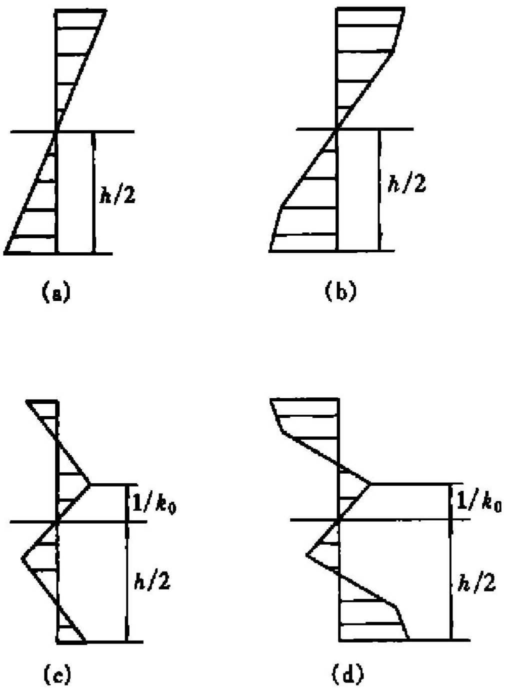

Fig. 2 Stress distribution in film cross-section for various stages of bending
(a) —Elastic loading; (b) —Plastic loading;
(c) —Elastic unloading; (d) —Reverse plastic loading

$$G_{db} = \frac{1}{b}\int M\,dK \qquad (11)$$

The moment-curvature relationship may be obtain by knowing the stress distribution of the film cross-section, and the following equation

$$M = \int_{-h/2}^{h/2} b\sigma z\,dz \qquad (12)$$

where σ is the bending stress at depth z (z is 0 at the neutral axis and it equals $h/2$ at the film surface).

For a bilinear hardening material (see Fig. 3, $\alpha > 0$), Moidu et al[9] used the approach similar to that of Kinloch et al[10], but adopted different stress distribution, the boundary condition and the curvature of C point (see Fig. 1(a)). They derived final expression for the film work expenditure as:

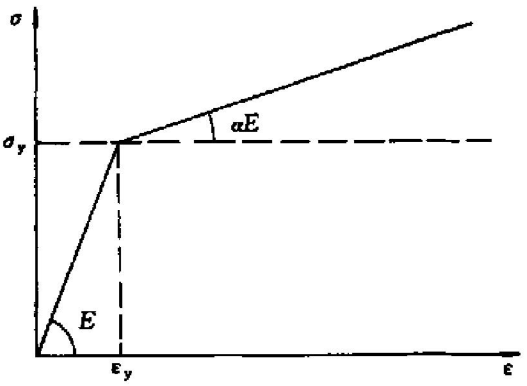

Fig. 3 Stress —strain curve of bilinear material

$$G_{db} = 0 \quad (k_0 \leqslant 1) \qquad (13)$$

$$\frac{G_{db}}{M_0 K_e} = (1-\alpha)\left[\frac{k_0^2}{3} + \frac{2}{3k_0} - 1\right] \qquad (14a)$$

$$\frac{P}{bM_0K_e}[1-\cos(\theta-\theta_0)] = \frac{k_0^2}{3}$$

$$\left(1 < k_0 \leqslant 1 + \frac{1}{1-\alpha}\right) \qquad (14b)$$

$$\frac{G_{db}}{M_0 K_e} = f_1(k_0, \alpha) \qquad (15a)$$

$$\frac{P}{bM_0K_e}[1-\cos(\theta-\theta_0)] = f_2(k_0, \alpha)$$

$$\left(k_0 \geqslant 1 + \frac{1}{1-\alpha}\right) \qquad (15b)$$

where

$$f_1(k_0, \alpha) = \frac{1}{3}\alpha(1-\alpha)(2-\alpha)k_0^2 + [2(1-\alpha)^2 - \alpha(1-\alpha)(2-\alpha)]k_0 + \frac{1}{3(1-\alpha)k_0}\cdot \{2(1-\alpha)^2 - (2-\alpha)^2[(4-\alpha^2) - 6(1-\alpha)]\} + (2-\alpha)^2(1+\alpha) - 4(1-\alpha)(2-\alpha) - (1-\alpha) \qquad (15c)$$

$$f_2(k_0, \alpha) = \frac{1}{3}[1-(1-\alpha)^3]k_0^2 + [2(1-\alpha)^2 - \alpha(1-\alpha)(2-\alpha)]k_0 + \frac{(2-\alpha)^2}{3(1-\alpha)k_0}\cdot [6(1-\alpha) - (4-\alpha^2)] + (2-\alpha)^2(1+\alpha) - 4(1-\alpha)(2-\alpha) \qquad (15d)$$

where α is the work-hardening parameter, as shown in Fig. 3, which can be determined from the shape of the stress versus strain curve for the film material; M_0 is the ultimate plastic moment per unit width; K_e the elastic limit curvature of film; k_0 the ratio of the radius of curvature at onset of plastic yielding to the actual radius of curvature at the peel front; θ_0 the base angle of the film at the root of the interfacial crack.

The terms M_0 and K_e are given by

$$M_0 = \frac{1}{2\sqrt{3}} E \varepsilon_y h^2 \tag{16}$$

$$K_e = \frac{\sqrt{3}}{h} \varepsilon_y \tag{17}$$

where ε_y is the yield strain of the film (see Fig. 3).

The correlation between θ_0 and k_0 is given by[10]

$$\theta_0 = \frac{1}{3}(4\varepsilon_y) k_0 \tag{18}$$

Based on the different range of k_0, which represents the different case of plastic bending deformation of the peeling arms, the expressions of G for numerical calculation are divided into three kinds of cases (see Eqns. (13) ~ (15b)). The first one is that plastic deformation doesn't exist in peel arm during both the initial loading process and the subsequent stretched or unloading process. The second case is when the initial bending of the peeling arm involves plastic deformation, while the unloading and stretching of the arm keeps elastic one still. The third case corresponds to the plastic deformation of both loading and unloading processes of the peeling arm.

Furthermore, one has to decide whether the material behavior falls under "the first case", "the second case" or "the third case"; see Eqn. (13) to Eq. (15b). Using the equations for either "the second case" (Eqns. (14a), (14b)) or "the third case" (Eqns. (15a), (15b)), together with Eqn. (18), the values of k_0 and θ_0 can be determined, which satisfy the pair of equations consistently. The selection of the appropriate "case" can then be made[10].

3 EXPERIMENTAL DETAILS

Ni films were coated on stainless steel substrates to investigate the effect of the peel angle on the interfacial fracture energy, and the ones on titanium substrates to study the effect of the film thickness on the interfacial fracture energy. The substrates were treated with mechanical polishing first, then washing off oil by hot aqueous alkali and surfacial activation by hydrofluoric acid. Consequently, the commercial tape was pasted on some parts of the substrate to prevent the corresponding parts of substrate from coating Ni films. Electroplating technique was employed to fabricate the Ni films, the thickness of which is commanded by "Time Controlling" technique provided the electric current is stable with the relative fluctuation being less than 5%. The temperature of the electroplating solution was controlled at 50~ 55 ℃.

The critical peel load per width (termed as peel strength P/b) corresponding to the onset of the interfacial crack propagation during very slow peeling was determined by naked eyes. The peel strengths for the same thickness of the Ni films on the stainless steel substrate under different angle were measured on different peeling stage of the same sample, the peel angle varied from 40° to 90°, the tested results are reported in Tables 1 and 2. X-ray diffraction was employed to measure the longitudinal and transverse components of the residual tensile stress in Ni films. The results show that the residual stress in Ni films on the stainless steel substrates is neglectful. While the values of the residual stress and the peel strength of the Ni films on the titanium substrates are shown in Table 3. The elastic modulus E, yield stress σ_y, yield strain ε_y and work-hardening parameter α of the Ni film are regarded as the same as those of the bulk Ni material with the same hardness, that is E = 210 GPa, ε_y = 0.28%, σ_y = 500 MPa and α = 0.03.

Table 1 Interfacial fracture energies of Ni films on stainless steel substrates at different peel angles (b = 13 mm, h = 13 μm)

Peel angle θ/(°)	(P/b)/(N·m^{-1})	G/(N·m^{-1})
90	5.95	5.95
75	7.38	5.47
65	9.78	5.65
50	15.38	5.49
40	24.31	5.69

1. All the peel arms don't take place plastic bending during peeling;
2. Residual stresses in the films are zero.

Table 2 Interfacial fracture energies of Ni films on stainless steel substrates at different peel angles (b = 14 mm, h = 10 μm)

Peel angle θ/(°)	(P/b)/(N·m^{-1})	G_{db}/(N·m^{-1})	G/(N·m^{-1})
90	13.42	7.34	6.08
75	17.71	7.06	6.07
65	21.29	6.32	5.97
50	34.86	6.41	6.04
40	47.71	5.13	6.03

1. All the peel arms take place plastic bending during peeling;
2. Residual stresses in the films are zero.

4 RESULTS AND ANALYSES

4.1 Work expenditure G_{db}

In experiments, it was found that plastic bending deformation appears in some specimens during peeling. Such a case occurs during the peeling tests for the interfacial fracture energies of Ni films with the thickness h = 10 μm on stainless steel substrates at different peel angle (see Table 2). Plastic bending deformation also appears in the testing of the interfacial fracture energies of Ni films on titanium substrates for specimens 1 and 2 in Table 3.

The evaluation of G_{db} can be performed according to what has been stated in section 2. By using the model of Moidu et al, the thin film-substrate systems

Table 3 Interfacial fracture energies of Ni films on stainless steel substrates ($\theta = 90°$)

Specimen	Thickness h/μm	(P/b)/(N·m^{-1})	σ_{rt}/MPa	σ_{rl}/MPa	G_{rs}/(N·m^{-1})	G_{db}/(N·m^{-1})	G/(N·m^{-1})
1	7.6	14.44	−24	−116	0.22	9.33	5.33
2	10.7	11.46	−88	−134	0.47	5.21	6.72
3	13.5	5.40	−127	−139	0.80	0	6.20
4	18.3	5.00	−96	−177	1.32	0	6.32
5	22.5	5.20	−103	−132	1.06	0	6.26

Sample 1 and 2 take place plastic bending deformation during peeling.

can be divided into different groups. There are only two systems fall under the "second case", the first one is what appeared in Table 2 with peel angle $\theta = 40°$, the second one happens for the film with the thickness $h = 10.7$ μm in Table 3. While, in Table 2 except peel angle $\theta = 40°$ all the others and in Table 3 the system with the film thickness $h = 7.6$ μm belong to "the third case". All of them in Table 1 and the others in Table 3 are corresponding to "the first case". The results shown in Table 2 and 3 are the corresponding values of this approach.

The local angle θ_0 in Eqns. (14a) to (18) is evaluated self-consistently, which is approximate to 0.5°. The variation of θ_0 with varying film thickness and peel angle is very small. However, the value of θ_0 reported in the literature differs from the value obtained here—say, 0.5°[5, 7~13]. This may be induced by the rather greater stiffness of the film and the substrate used here, while the other researchers concerned only polymers with less stiffness. At the same time the interfacial adhesive strength here is relatively small. Thus, the peeling arms of the Ni films approach to pure-bending elastic-plastic beams.

4.2 Peel strength *P/b*

The measured peel strengths are given in Table 1 ~ 3, which indicate that the peel strength depends on the thickness of the film, the peel angle and the residual stress in the films significantly, which means that the value of the peel strength is not a "material parameter".

The residual stress of films on substrates would reduce the peel strength. The peel strength decreases with the residual strain energy. As to a given residual stress gradient, the total residual strain energy increases with the thickness of the film, which leads to the peel strength decrease with the thickness of the film. Thus, the film could peel off from the substrate automatically as long as the thickness of the film reaches some critical value.

4.3 Interfacial fracture energy *G*

As discussed previously, the value of the interfacial fracture energies G can be evaluated by Eqn. (8) provided relevant terms are well assessed. Shown in Tables 1~ 3 is the interfacial fracture energy for different cases. It can be seen from the tables that the interfacial fracture energy is a "material parameter" which is independent of the thickness of film and peel angle as well as residual stress in the film.

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