ADHESION MEASUREMENT OF FILMS & COATINGS

VOLUME 2

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K.L. Mittal

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Preface

This book documents the proceedings of the Second International Symposium on Adhesion Measurement of Films and Coatings held under the auspices of MST Conferences in Newark, New Jersey, October 25–27, 1999. We labelled it the Second Symposium as the first event on this topic was held in Boston, December 5–7, 1992, under the aegis of Skill Dynamics, an IBM company, the proceedings of which have been properly chronicled [1]. However, for historical reasons it should be recorded that the premier symposium on this topic (with a slight change in title) was held in Philadelphia under the auspices of the American Society for Testing and Materials (ASTM), the proceedings of which were published as STP-640 by the ASTM in 1978. Because of the long hiatus between the ASTM Symposium and the one held in Boston, we deemed it more appropriate to label the Boston event as the First Symposium.

Films and coatings are used for a variety of purposes – functional, decorative, protective, etc. – in a host of applications. Irrespective of the purpose or application of a film or a coating, their adequate adhesion to the underlying substrates is of paramount importance. Concomitantly, the need to develop techniques for quantitative assessment of adhesion of films and coatings is all too obvious.

Since the Boston Symposium in 1992 there has been considerable activity in devising new, more reliable and more efficient ways to measure adhesion of films and coatings. In the opening article in the proceedings volume of the Boston Symposium, yours truly had listed 355 techniques for measuring adhesion of films and coatings. Why are there so many techniques? Apparently, there is no single technique which will apply in every situation or which everyone will be happy with. A more important question is: What do these techniques measure? And the answer is: Practical Adhesion. Quite often the question asked is: What is the best method for adhesion measurement? And the answer is: The best method is the one that simulates the actual usage stress conditions as closely as possible. Concomitantly, the best method will be different, depending on the conditions to which a film–substrate system will be exposed.

As a result of the brisk activity and tremendous interest in the topic of adhesion measurement of films and coatings, we decided to hold this second event. The technical program for this symposium contained a total of 29 papers and many different techniques were discussed. There were very lively and illuminating (not exothermic) discussions, both formally and informally.

Apropos, the third symposium on this topic is planned to be held in Newark, New Jersey, November 5–7, 2001.

Now coming to this volume, it contains a total of 20 papers. It must be recorded here that all manuscripts were rigorously peer reviewed and suitably modified (some twice or thrice) before inclusion in this book. So this book is not merely a collection of unreviewed papers but represents the highest standard of a publication. The topics covered include: measurement and analysis of interface adhesion; relative adhesion measurement for thin film structures; adhesion testing of hard coatings by a variety of techniques; challenges and new directions in scratch adhesion testing of coated substrates; application of scratch test to different films and coatings; evaluation of coating- and substrate adhesion by indentation experiments; measurement of interfacial fracture energy in multifilm applications; laser induced decohesion spectroscopy (LIDS) for measuring adhesion; pulsed laser technique for assessment of adhesion; blade adhesion test; JKR adhesion test; coefficient of thermal expansion measurement; and residual stresses in diamond films.

Yours truly sincerely hopes that this book, along with its predecessor [1], will provide a commentary on the current state of the art anent adhesion measurement of films and coatings and will further provide a fountainhead for new ideas.

Acknowledgements

First, I am thankful to Dr Robert H. Lacombe, my colleague and friend, in helping to organize this symposium by taking care of a myriad of details entailed in such an endeavor. My sincere thanks go to the reviewers for their time and efforts in providing valuable comments which are *sine qua non* to maintain the highest standard of a publication. Without the contribution, interest and enthusiasm of the authors, this book could not be embodied and my thanks to all the contributors. Last, but not least, my appreciation is extended to the staff of VSP for the job well done in producing this book.

K.L. Mittal

[1] K.L. Mittal (ed.), *Adhesion Measurement of Films and Coatings*, VSP, Utrecht, The Netherlands (1995)

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Interface adhesion: Measurement and analysis

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Abstract—A protocol for quantitative adhesion measurements would allow implementation of design codes and durability models for multi-layer devices. The mechanics underlying the adhesion energy is largely complete. Test methods capable of providing the necessary information are at an advanced stage of development, but future innovation and analysis are still needed before a fully-integrated methodology can be prescribed. The status of the test methods is described and related to the overall goal. Models that allow adhesion to be related to the fundamentals of bond rupture and plasticity are examined, inclusive of concepts that inter-relate quantum mechanics results to adhesion measurements made at the continuum level. The additional effort needed to coalesce these models into a predictive tool is discussed.

Keywords: Adhesion measurement; interface toughness; oxide/metal interfaces; adhesion models; adhesion test methods.

1. INTRODUCTION

Two types of measurements are relevant to adhesion [1-4]: (i) the stress at which the interface separates, σ_c, and (ii) the energy dissipated per unit area upon extending a crack along the interface, Γ_i (in J/m^2). The latter has the same role as the fracture toughness in homogeneous materials [5-7]. The former includes effects of defects and of stress concentrations (especially at free edges) [3] and is thus test specific and inherently stochastic. While both are important, here, the energy density is emphasized, since it is amenable to quantitative comparison with mechanisms and models [2,8-10] and moreover, in principle, the measurements can be used explicitly in design codes and durability models for multi-layer systems. That is, a methodology similar to fracture mechanics-based design of structural components [5-7] could be used subject to the construct of the appropriate numerical code [11]. This prospect can only be realized if the test methods yield quantitative measures of Γ_i. Accordingly, the emphasis of this brief overview is on a pathway toward a quantitative design strategy applicable to multi-layer systems.

Since the likelihood of establishing a successful strategy would be enhanced if a mechanistic basis is established, a complementary theme is the development of

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mechanism-based models. Much of the quantitative information about mechanisms has been gained from metal/oxide interfaces [2]. A summary of this information (Fig.1) provides a perspective. Clean interfaces devoid of reaction products are inherently tough and ductile. Such high adhesion is realized even though the metals are polycrystalline and non-epitaxial. When failure occurs, it does so either by brittle cracking in the oxide or by ductile fracture in the metal. Only measurements for Al/Al_2O_3 indicate *consistently* tough, ductile interfaces. Broad ranges have been cited for most other interfaces, because of embrittling effects of contaminants and segregants. Stress corrosion due to the presence of moisture in the test environment exacerbates weakening in some cases.

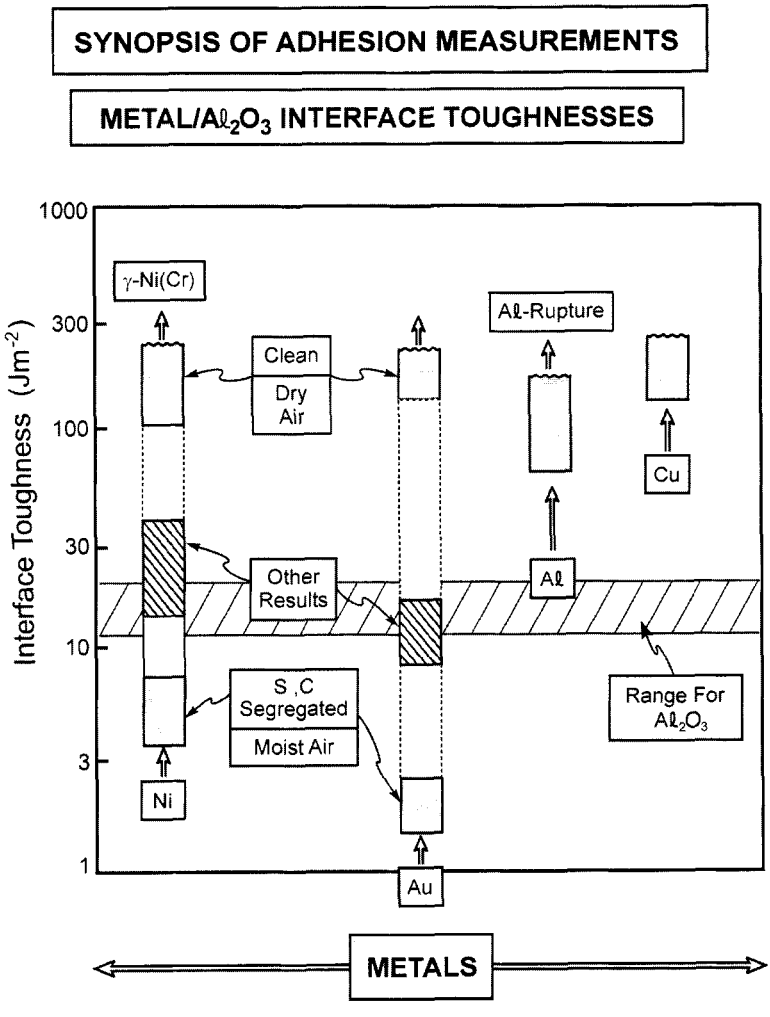


Figure 1. The range of toughness found between various metals and Al_2O_3. Note that many results reside in discrete domains that depend on "cleanliness".

Two fundamentally important factors cause cracks at interfaces to differ from those in homogeneous materials [4]. (i) The elastic property mismatch causes the energy release rate, G, and the mode mixity angle, ψ, to differ at the same loading. These differences are fundamentally related to the first Dundurs' parameter:

$$\alpha_D = \frac{\overline{E}_1 - \overline{E}_2}{\overline{E}_1 + \overline{E}_2} \tag{1}$$

where $\overline{E}$ is the plane strain Young's modulus. The subscripts 1 and 2 refer to the two adjoining materials. (ii) Mixed mode cracks ($\psi \neq 0$) may extend along interfaces. Accordingly, the fracture toughness must be specified as a function of ψ. A useful phenomenological relation is [4]:

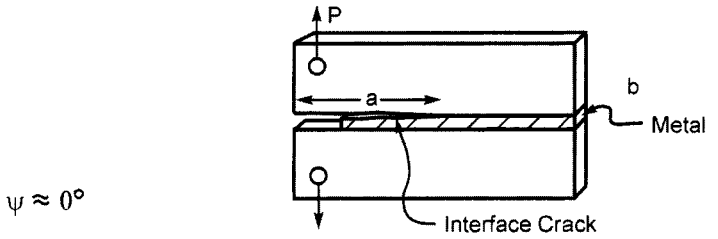
$$\Gamma_i / \Gamma_i^o = 1 + \tan^2(1-\lambda)\psi \tag{2}$$

where Γ_i^o is the mode I toughness and λ is a mixity parameter that reflects the role of the interface non-planarity, as well as the plasticity in the adjoining materials. There is no mixed mode effect if $\lambda = 1$, but a strong dependence when λ is small. Interface adhesion is only meaningful when addressed with specific reference to λ.

With this background the overview is laid out as follows. The basic philosophy of quantitative adhesion measurement is addressed. The merits of specific test methods for thin films are discussed. Some adhesion results are reviewed and related to mechanisms.

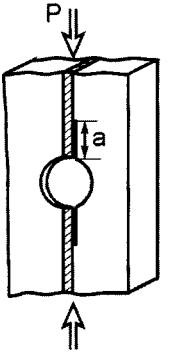
2. MEASUREMENT PHILOSOPHY

Measuring interface adhesion is more challenging than the corresponding measurements on their homogeneous counterparts. There are two main issues. The geometrical configurations encompassing interfaces of practical interest often constrain specimen design. Large-scale inelastic/plastic deformations limit options, because of the vastly different thermo-mechanical properties of the adjoining materials. For interfaces made by diffusion bonding or brazing [2,12-17], many different configurations are available (Fig. 2) [1,2, 18-24]. The main restriction is that residual stresses often exist and these must be taken into account in determining the energy release rate, G, and mode mixity angle, ψ. Among these configurations, those that exhibit stable crack growth are preferred [21,22], wherein G *decreases* with increase in interface crack length, a, at specified load, P (or remains invariant with crack length). Such configurations greatly facilitate the introduction of well-defined pre-cracks before conducting the adhesion measurement. For mode I, the Double Cantilever Drilled Compression (DCDC) specimen [21] has this feature. It has been used to test metal/oxide and polymer/inorganic interfaces (Fig.2b). For mixed-mode loading, bending configu-



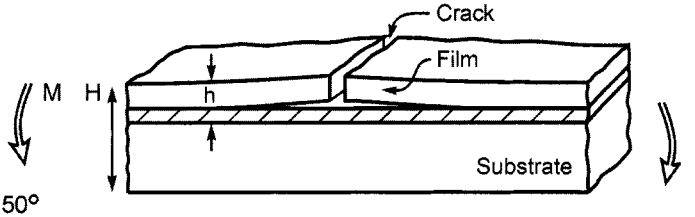
$\psi \approx 0°$

a) Double Cantilever Beam



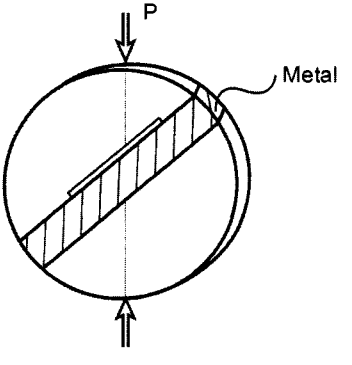
$\psi \approx 0°$

b) Double Cantilever Drilled Compression



$\psi \approx 50°$

c) Mixed Mode Flexure



$0 \leqslant \psi \leqslant 90°$

d) Brazil Specimen

Figure 2. Test configurations used to measure the interface toughness on bonded bi-material systems.

rations are applicable (Fig.2c) [22]. In both cases, when one of the constituents is transparent, optical imaging may be used to monitor crack growth and study the mechanisms [12,15].

When one of the constituents is a thin film or coating, few quantitative methods exist. There are two basic approaches.

(i) Loads are applied to the film and the displacements are measured as the interface de-adheres. Such methods are exemplified by the peel test (Fig. 3) [25,26].

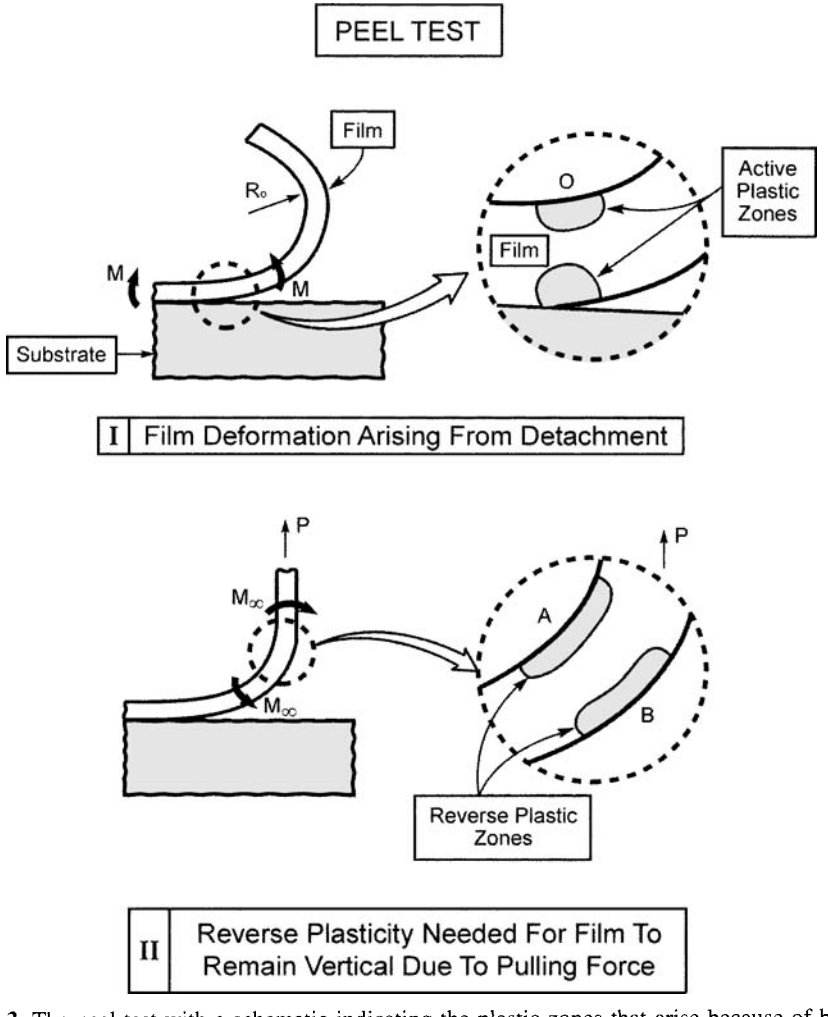


Figure 3. The peel test with a schematic indicating the plastic zones that arise because of bending (near-tip and reverse), which complicate interpretation of the measurements. In step I, film curvature arises because of the moment M near the tip that causes delamination, with consequent plasticity. In step II, the straightening of the film required by the applied loading is demonstrated, along with the zones of reverse yielding.

This test (and others like it) has the advantage of testing simplicity, but the interpretation is complex. The problem is that the work done is not solely governed by the energy expended around the crack (Fig.3). Deconvoluting the measurements in a manner that isolates the adhesion is challenging[26].

(ii) Residual strains are introduced by various means and the extent of the interface delamination caused by these strains is measured. There are at least three variants. (a) When the *substrate is ductile*, strain can be introduced into the film by deforming the substrate: multi-strain [19] and impression tests [23,24,27] exemplify this approach (Fig.4). In such tests, the strains can be imposed precisely and measured accurately. The precision is limited by the ability to detect and measure the dimensions of the interface delamination. (b) For films on *brittle substrate,* a strain energy density sufficient to de-adhere the interface can be induced by depositing an adherent overlayer. This layer must have sufficient intrinsic strain and thickness to achieve the critical strain energy density. This approach has been referred to as the superlayer test[20] (Fig.5). (c) Alternatively, localized strains can be generated by indenting or scratching the film [18]. Quantification requires calibration of the strains induced in the film.

There have been several reviews of thin film adhesion measurement [28-32]. The differing purpose of the following section is to provide perspective on the subset of tests that have the intrinsic prospect of measuring $\Gamma_i(\psi)$ with the precision needed to use the results for design and durability purposes. Other tests will continue to be used for quality control since they are straightforward to implement.

3. THIN FILM ADHESION MEASUREMENT METHODS

3.1. Peel tests

These tests have been applied primarily to flexible films. The test has the attribute that the peeling force is measured in a steady-state condition, wherein the shape of the strip remains invariant with displacement. This force is used as a measure of interfacial quality. The responses may be explored through the parameter [25],

$$\eta = 6EP/\sigma_o^2 h \tag{3}$$

where P denotes the applied force per unit width of the strip, E its Young's modulus, h its thickness and σ_o is the yield strength of the film. When $\eta << 1$, the film deforms elastically and the peel force P becomes a direct measure of the interfacial fracture resistance: $\Gamma_i \equiv P$. However, the minimum film thickness h^* needed to assure elastic peeling (obtained from (3) by equating η to unity), is typically quite large, and given by:

$$h^* = 6E\Gamma_i/\sigma_o^2 \tag{4}$$

For example, to be in the elastic range, Cu films having $\sigma_o \approx 100MPa$ and $\Gamma_i \approx 100Jm^{-2}$, require that $h^* \geq 1cm$. Thinner films deform plastically, whereupon a large scale yielding analysis is needed to interpret the measurements.

Then, the problem is that the work done by the peel force is not solely governed by the energy expended around the crack, for the following reason [26] (Fig.3). As the strip peels, it experiences a bending moment that induces yielding not only around the crack front but also on the upper surface. Such deformations cause the film to curl. Moreover, the reaction force induced by interface bonding requires that the film be bent back as the crack extends. This is realized through an opposite bending moment that causes reverse yielding. The yield zones *O* (near-tip bending), *A* and *B* (reverse bending) comprise redundant plastic work which convolutes with the interfacial work of rupture. De-convoluting the measurements in a manner that isolates the adhesion energy is required and, often, is not possible.

3.2. Microscratch and impression tests (Fig.4b)

These tests are variants on the same basic idea. That is, forces imposed through an indentation introduce a residual stress field that, in turn, causes the interface to delaminate. Measurements of the force and the size of the induced delamination permit estimates to be made of the interface toughness[23,24,27].The difference between the two methods relates to the scale of the indentation and the nature of the substrate. *Impression tests* are used with ductile substrates having well-established stress/strain characteristics. The indenter is pushed through the film into the substrate to an extent sufficient to assure that the indentation force is dominated by the substrate. In such cases, the strain distribution induced in the film can be determined with precision by using a finite element analysis: whereupon, the energy release rate and the mode mixity can be determined as a function of the delamination size. Consequently, provided that the latter can be measured, $\Gamma_i(\psi)$ can be determined, explicitly.

The Microscratch method confines the impression to the film [18]. It may thus be used with both brittle and ductile substrates. However, the constitutive properties of the film are rarely known with any accuracy and, moreover, the deformation fields are quite complex. Consequently, the strains in the film and the energy release rate can only be approximated. As analyses of the test improve, the approximations become less restrictive, but to the authors' knowledge, significant uncertainties still remain. Nevertheless, given the relative simplicity of the test, further efforts at improving the analysis are clearly warranted.

3.3. The blister test

This test is commonly used for thin polymeric films spun onto a substrate having a circular or square perforation [33-36]. The blister is created by fluid pressure applied through the perforation. The pressure needed to cause debonding can be explicitly related to Γ_i through the mechanics of a pressurized elastic, circular blister.

The effects of residual stress can be readily included. When applicable, this test provides measurements amenable to usage in design. The limitations include the inability to measure Γ_i for adherent interfaces that cause the film to yield.

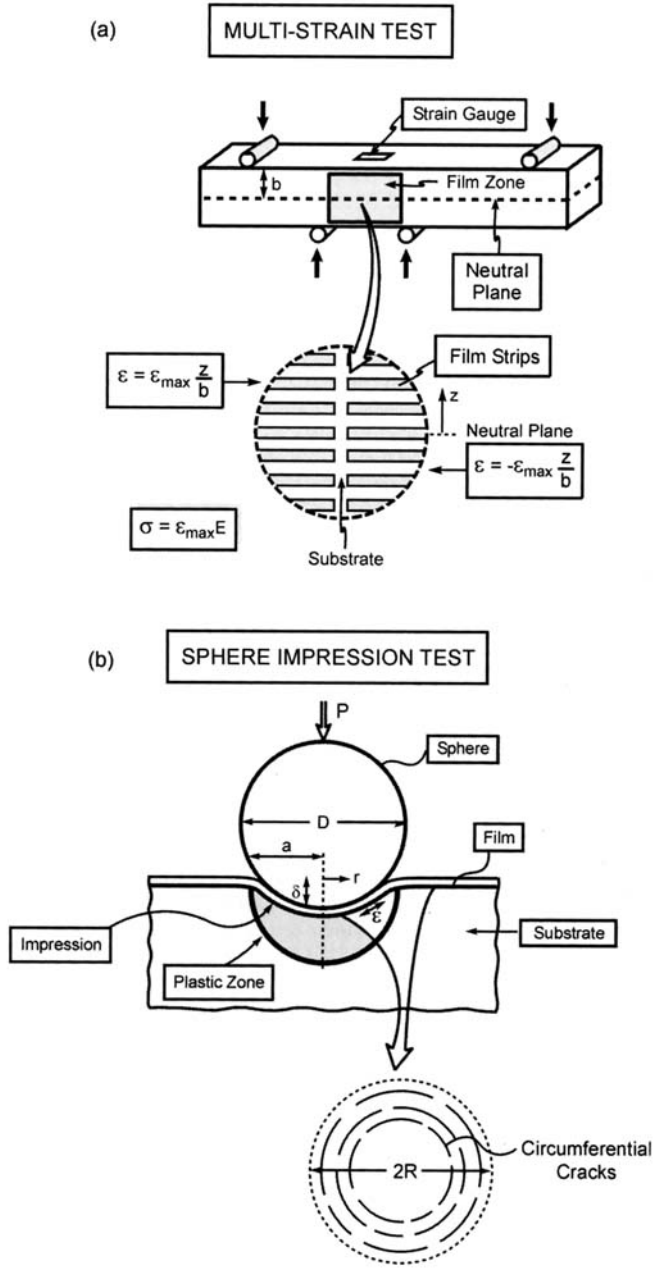


Figure 4. Tests used to measure the toughness of interfaces between thin films and a ductile substrate: (a) multi-strain test, (b) sphere impression test.

3.4. The superlayer test (Fig. 5)

This test allows a steady-state loading of a thin film system at the mode mixities relevant to system failure [20]. The approach involves the use of a residual stress that duplicates the problem of interest. Since, for typical thin films and representative residual stresses, the induced energy release rate is below the fracture toughness of most interfaces having practical interest, a procedure that substantially increases G is required. Deposition of a superlayer increases the effective film thickness and also elevates the residual stress. Implementation of this test requires micro-machining by photolithography, wherein the film of interest is deposited in the usual manner onto the substrate. Thereafter, the superlayer is electron beam evaporated onto the film. Subsequent lift-off defines the geometry. The film is patterned to form narrow strips. A through-cut is made in the bi-layer by either etching or milling. When the strips delaminate after severing, the energy release rate exceeds the debond energy, $G_{ss} > \Gamma_i$. However, the debond arrests before reaching the end of the strip. The length of the remnant ligament is a measure of the adhesion energy (Fig. 5) [2].

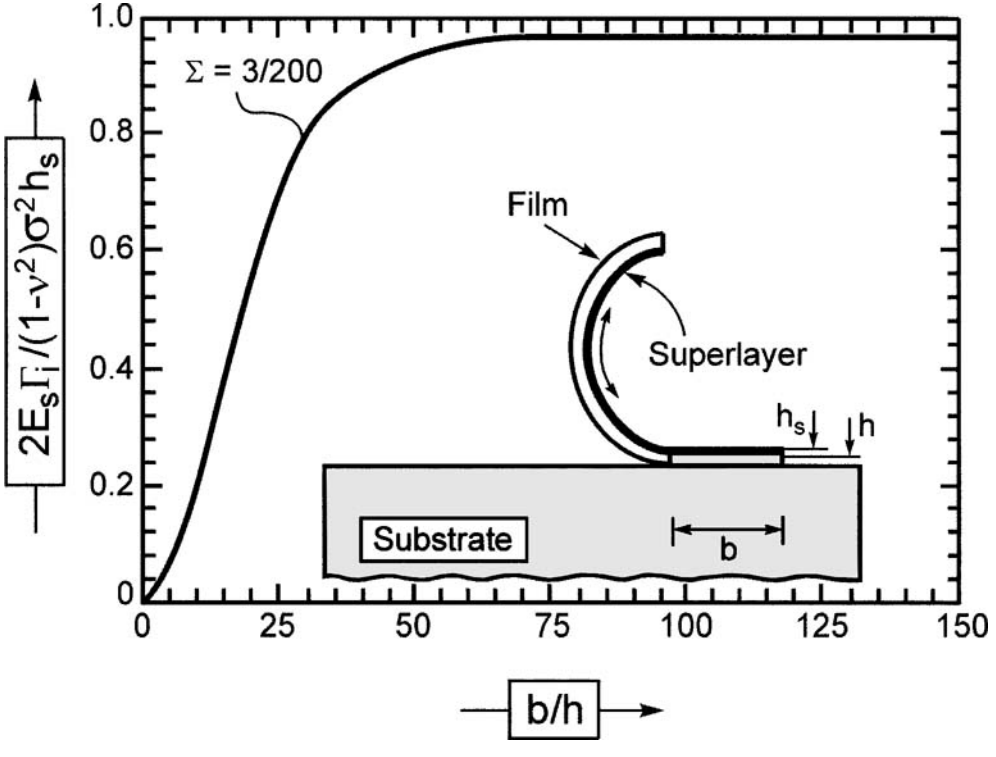


Figure 5. Superlayer method for measuring the interface adhesion between thin films and brittle substrates. Also shown is the energy release rate as a function of the length of the remnant ligament.

3.5. The multistrain test

This test requires a ductile template in the form of a beam that can be deformed after the films have been deposited [19,37] (Fig. 4a). Stainless steel has been used for this purpose. One surface is polished to an optical finish and a thin layer of polyimide spun onto this surface. The film is then deposited onto the polyimide and patterned into strips, parallel to the long axis of the beam, with a gap at the center. The beam is subjected to bending, with the coated surface on the side. As bending occurs, each strip experiences a different strain: zero at the neutral axis and a maximum adjacent to the tensile surface. There is a corresponding variation in the strain energy. Upon testing, those strips located near the tensile surface are most susceptible to de-adhesion, while those closer to the neutral plane remain attached. Accordingly, in tests that exhibit delamination, a critical strain at which it occurs can be identified. Then, if the film behaves elastically and its Young's modulus is known, the steady-state energy release rate and the interface toughness can be obtained with acceptable accuracy. However, adherent films do not de-adhere in this test, limiting its range of utility.

4. INTERFACE RUPTURE MODELS

A complementary goal of interface adhesion investigations is the development of mechanism-based models that provide understanding of the issues that control Γ_i [2]. The inherent challenge is to provide a connection between quantum level results for the salient bond rupture parameters [2,38-40] (the work-of-adhesion, W_{ad}, and the bond strength, $\hat{\sigma}$) and the practical, or engineering, adhesion energy, Γ_i, through models of plastic deformation that incorporate length scale effects (Fig. 6) [2,41-43]. This section examines the current status. Approaches have been attempted that address this challenge at two limits. These limits and a transition between them are reviewed.

In one limit, designated as the Suo, Shih and Varias (SSV) model[9], the interface cracks are assumed to be atomically-sharp and surrounded by an elastic enclave, having height D above the interface. Outside the elastic zone, plastic deformation is allowed to develop, characterized by a yield strength, σ_o and strain hardening coefficient N. Because the tip is surrounded by an elastic region the stresses are singular. Accordingly, bond rupture only requires that the energy release rate attain the work-of-adhesion. This criterion fully prescribes the model, with the understanding that D is a fitting parameter. The primary dependencies of Γ_i/W_{ad} are on D/R_o and N, where R_o is the plastic zone size, defined as [2,9,40]:

$$R_o = (1/3\pi)EW_{ad}/\sigma_o^2 \tag{5}$$

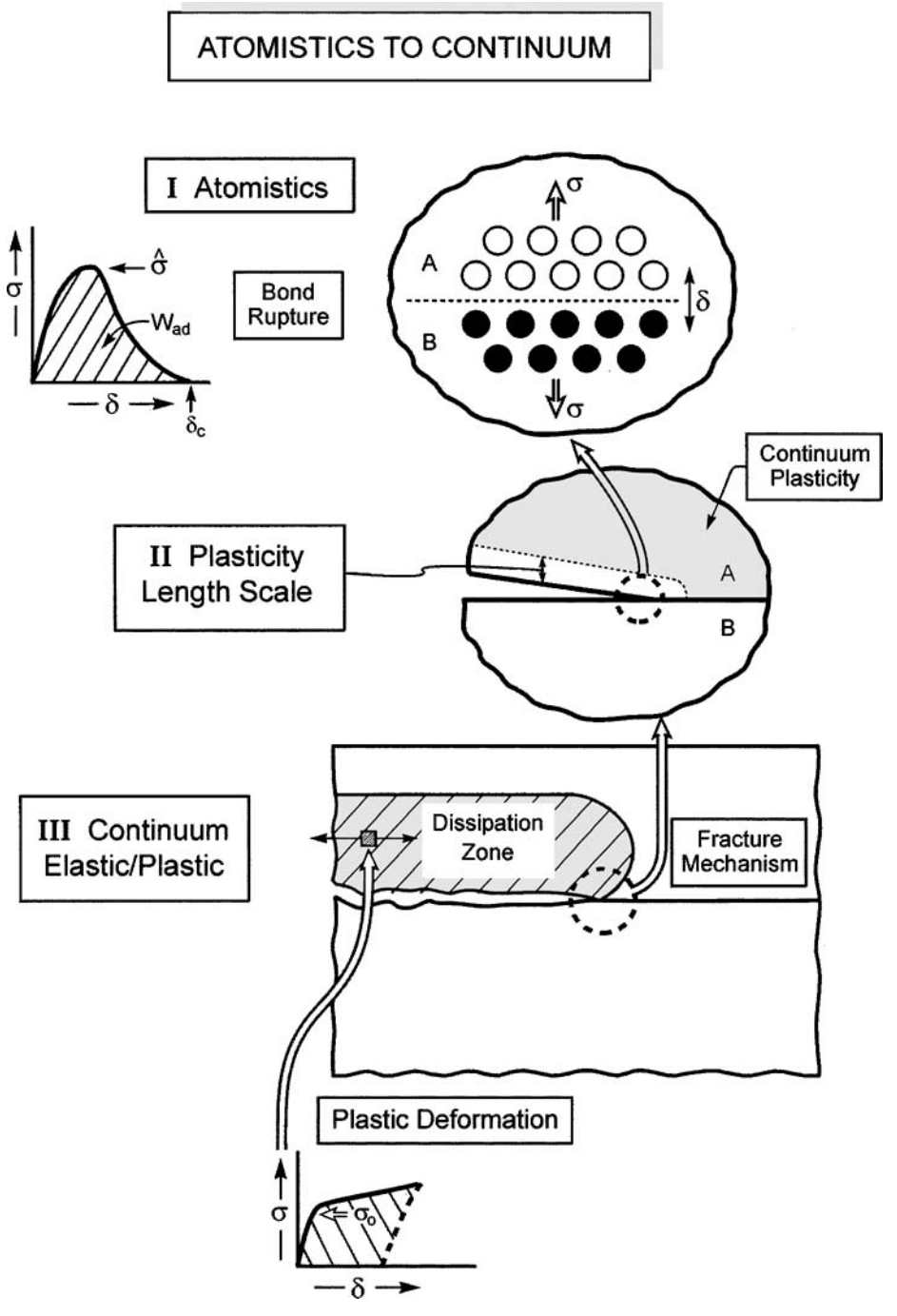


Figure 6. A schematic illustrating the zones of inelastic deformation that occur around interface cracks, with associated length scales.