

Scale and Coating Adhesion: A Procedure for Laboratory Tests

Summary

Three techniques (scratch testing, indentation and flexural straining) with appropriate analyses, have been investigated for measurement of adhesion of oxide scales and coatings. Previously published analyses have been simplified to enable the techniques to be used more widely. It is concluded that no single technique is applicable to the full range of industrially-important materials and that the investigator must use judgement in choice of measurement technique and interpretation of the results.

Background

In many engineering applications it is possible to select materials such that the corrosion rate of that material, as measured by scale-growth kinetics, is not life-limiting. Where this is not the case a suitable corrosion-resistant coating can be applied. This approach is perfectly acceptable as long as the oxide scale or coating remains intact. The life-limiting behaviour then becoming the (mechanical) failure of the protective scale or coating. Loss of the coating by spallation is clearly the most damaging failure mode and is in part controlled by adhesion of the oxide or coating to the substrate.

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Introduction

Fracture and spallation of oxide scales has been reviewed in detail by Evans [1] who described mechanisms for failure under both tensile and compressive loading of the scale. Evans successfully quantified a model for oxide spallation by finite element calculations: one important input parameter in this model is the tensile strength of the interface.

The fracture mechanisms of coatings has been considered by Hou and Atkinson [2] who characterised the failures as splitting, delamination and substrate failure near the interface.

There are a large number of tests that can be used to measure adhesion properties and a procedure is required to guide the user to the most suitable test method. The criteria by which tests for scale and coating adhesion must be judged are:-

- generation of a fully-quantifiable output parameter;
- production of a failure mode relevant to service behaviour;
- an output parameter suitable for inclusion in a predictive model;
- suitability for elevated temperature operation.

In this measurement note three types of scale adhesion test are discussed, together with appropriate analysis procedures for each type of test. The tests are applied to oxide scales grown on various alloy systems as well as a series of coating/substrate systems to provide a comprehensive check on the applicability of the different tests to various situations, including the determination of adhesion parameters at high temperature.

Experimental Test Procedures

The adhesion tests considered in this work fall into three categories viz scratch testing, indentation and flexural straining. Each test method has its own requirements, advantages and disadvantages which will be discussed in this section.

Scratch Testing

In this form of test a stylus is traversed across the surface of a flat specimen with either constant or increasing load. The experimental set-up for in-plan scratch testing is shown in [Figure 1](#). Specimen preparation is minimal and the only limitation is that the specimen should be large enough to clamp without interfering with the movement of the stylus parallel to the plane of the traverse table.

The test parameters that must be monitored are the normal (applied) load and horizontal displacement. It is also desirable to monitor cracking events using acoustic emission (AE) and/or the horizontal (frictional) load to aid in the correlation of forces with inspection of the scratch path.

The significant result derived from the scratch test is the critical load for scale failure. This parameter is derived from visual inspection of the scratch track in conjunction with the vertical and horizontal load traces. The derivation is demonstrated in [Figure 2](#).

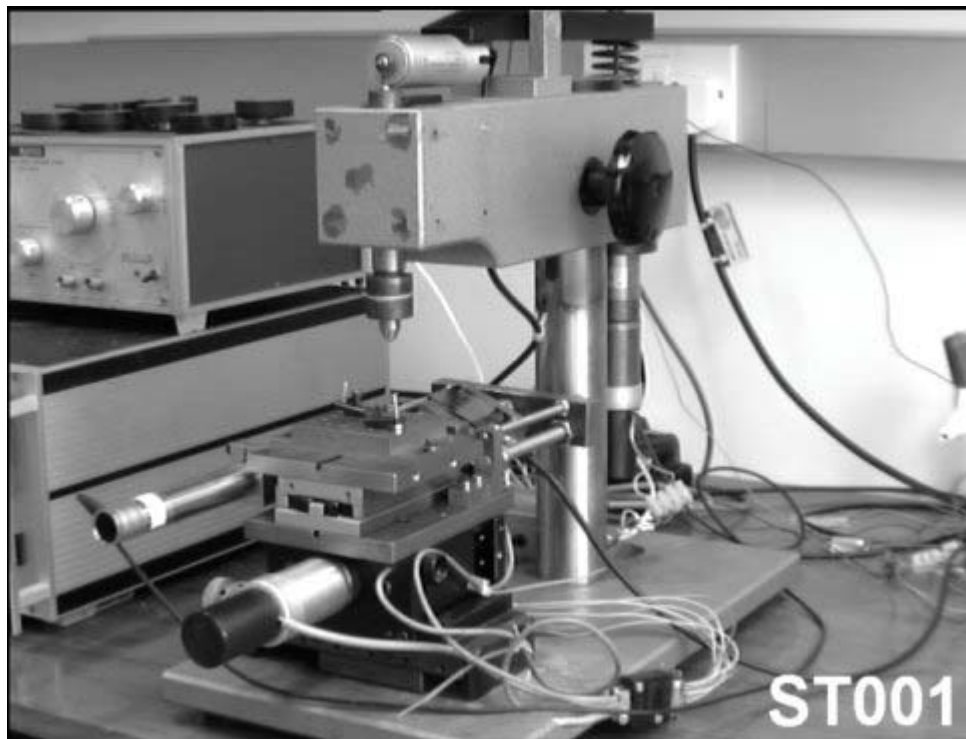


Figure 1 Scratch Test Facility

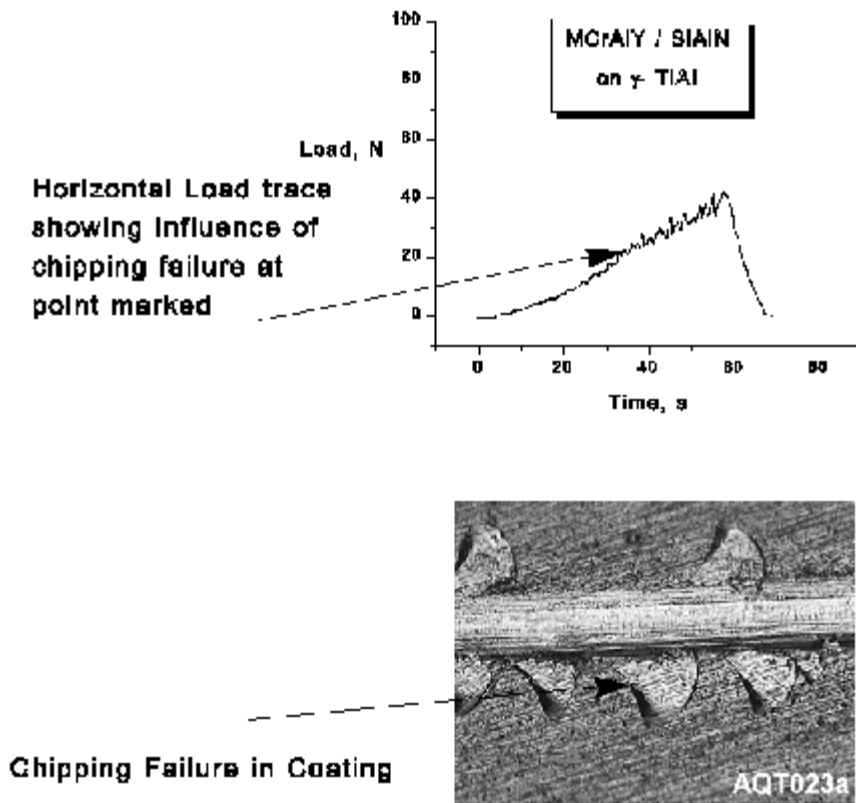


Figure 2 Derivation of critical load during scratch testing for MCrAlY/SiAlN coating on γ TiAl

Failure of the oxide/coating during scratch testing may occur by one of a number of mechanisms [3]. The most important of these in terms of their relevance to spallation are buckling and wedge failures and quantitative interpretation of scratch testing is limited to the latter [4]. The analysis [4], which applies to failure by initial wedge cracking in the surface layer, requires that the critical load for failure is measured as a function of oxide/coating thickness and residual stress.

Ideally a complete matrix of tests should be carried out but when this is not possible, a multiple linear regression analysis may be used to calculate the output parameters, which are values for wedge crack formation stress and interfacial fracture energy. Bull [4] starts with the assumption that the total stress required to detach the surface film, σ_F , is the sum of the residual stress in the film, σ_R , and the stress imposed by the scratch stylus, σ_S . The fracture stress is calculated from a plot of the critical load for spallation as a function of residual stress for a series of surface films of the same thickness. A straight line fit is used and the fracture stress is defined as the intercept i.e failure when the imposed stress is zero; the gradient of the line, a , defines the relationship between the critical load in the scratch test and the imposed stress. This can be represented analytically by the expression:-

$$\sigma_F = \sigma_R + aL_c$$

where

L_c is the critical load measured in the scratch test

aL_c is equivalent to σ_S .

For spallation due to the wedge cracking mechanism, σ_F is the sum of stresses required for wedge cracking, σ_W , and for delamination of the interface, σ_{SP} . Thus

$$\sigma_F = \sigma_W + \sigma_{SP}$$

These terms can be expanded as follows

$$\sigma_W = \left(\frac{4 E_c \gamma}{(1 - \nu_c) \lambda} \right)^{\frac{1}{2}} \sigma_{SP} = \left(\frac{E_c \gamma_F}{(1 - \nu_c) t} \right)^{\frac{1}{2}}$$

where

E_c and ν_c are the Young's modulus and Poisson's ratio respectively of the surface film

γ is the fracture energy of the oxide

λ is the width of the wedge-spalled region

γ_F is the interfacial fracture energy of the interface

t is the oxide thickness

Rearranging and simplifying gives:

$$\sigma_R = A - a L_c + B t^{\frac{1}{2}}$$

where A is given by

$$\left(\frac{4 E_c \gamma}{(1 - \nu_c) \lambda} \right)^{\frac{1}{2}}$$

and B is given by

$$\left(\frac{E_c \gamma_F}{(1 - \nu_c) t} \right)^{\frac{1}{2}}$$

σ_R , L_c and t can all be measured independently, therefore if at least four tests are carried out the constants a , A and B can be derived using curve fitting procedures (A is normally assumed to be a constant for a given film/substrate system) and γ_F can be calculated from B if E_c and ν_c are also known - E_c can be measured by indentation or vibrational techniques and ν_c is usually attributed the value 0.3.

Indentation

Assessment of adhesion from in-plan indentation relies on the measurement of damage around the indent. This type of test is intrinsically simple and can (for room temperature) be carried out on a standard macro hardness machine e.g. Rockwell hardness machine. A typical indent is shown in [Figure 3](#). Quantitative analysis follows that derived by Drory and Hutchinson [5] with some modifications to simplify the derivation of scale adhesion parameters. The critical measurements from the indentation are the radii of the indent, a , and of the delaminated area, r .

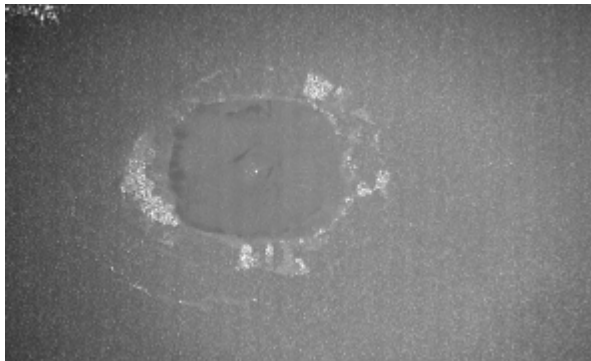


Figure 3 Rockwell Indentation in PM2000 oxidised for 264 h at 1150°C

A wide range of other input parameters need to be measured to fulfil the analysis viz thickness Young's Modulus, Poisson's ratio and residual stress of the oxide and Young's Modulus, yield stress and strain hardening exponent of the substrate. These data may or may not be available for the system under investigation, however, they may all be measured independently.

The original analysis by Drory and Hutchinson [5] depends upon the implicit assumption that, at the limit of delamination the energy needed to cause delamination is in balance with the energy imparted by the indentation process. In order to calculate the latter as a function of radial distance from the indent several properties of the substrate must be known.

It is assumed that the substrate follows a simple deformation law under uniaxial tension of the form:

$$\varepsilon = \frac{\sigma}{E_s} + \frac{3}{7} \frac{\sigma_Y}{E_s} \left(\frac{\sigma}{\sigma_Y} \right)^{\frac{1}{N}}$$

where

ε is true strain

σ is the applied stress

E_s is the Young's modulus of the substrate

σ_Y is the yield stress of the substrate

N is the strain hardening exponent

The radial surface displacement, u^1 , is a function of the normalised distance from the centre of the indent (r/a), σ_Y/E_s , N and Poisson's ratio. In the original analysis [5] this function required a numerical solution, but approximate analytical solutions of the form:-

$$\ln \left(\frac{u^1}{a} \right) = b_0 + b_1 \left(\frac{r}{a} \right) + b_2 \left(\frac{r}{a} \right)^2 + b_3 \left(\frac{r}{a} \right)^3$$

were derived for each combination of σ_Y/E_s and N considered. It is obviously desirable to develop an analytical expression that can describe u^1/a as a function of r/a , σ_Y/E_s , and n for the entire range of conditions considered: the following equation provides a reasonable fit:

$$\log \left(\frac{u^1}{a} \right) = 1.917 + 5.706N - 12.97N^2 + 63.99 \left(\frac{\sigma_Y}{E_s} \right) - 3203 \left(\frac{\sigma_Y}{E_s} \right)^2 - 2.517 \log \left(\frac{r}{a} \right)$$

A comparison between this global expression and the original Drory and Nicholson analytical equations is shown in Figure 4. It can be seen that there is good agreement between the expression at all but the lower limits of r/a considered.

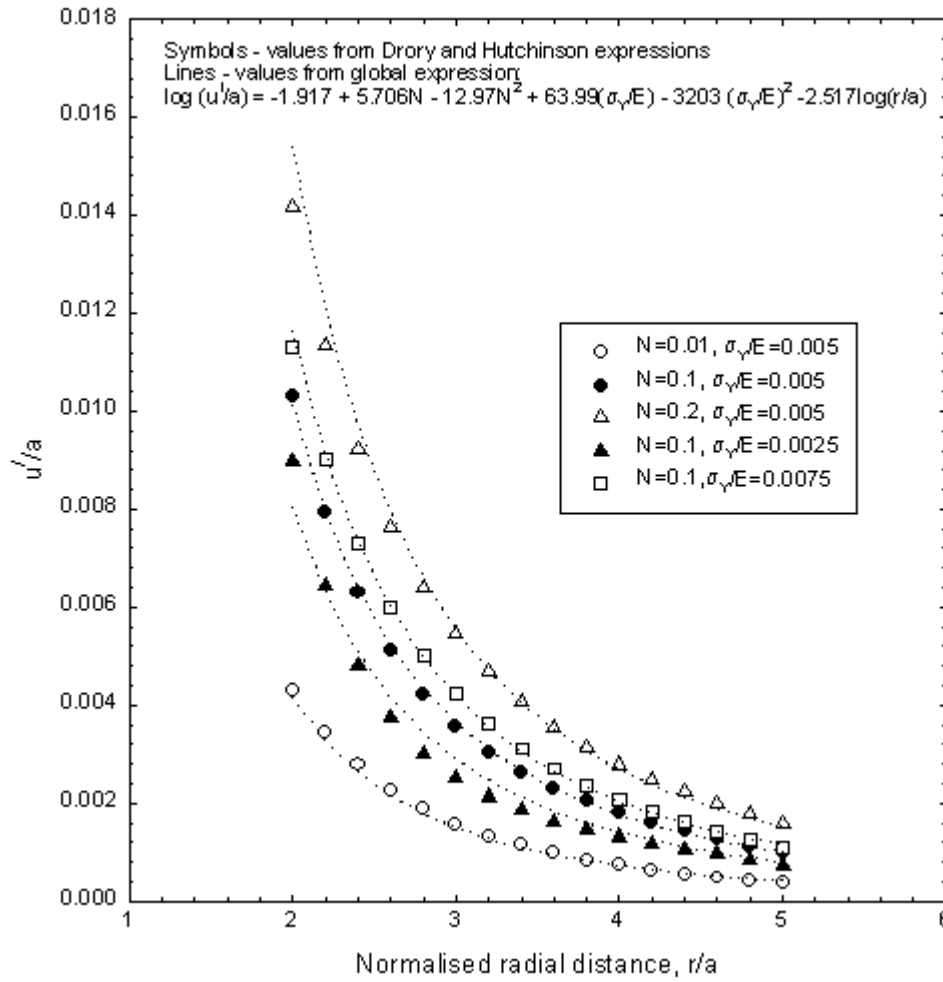


Figure 4 Analytical expression within indentation analysis

The induced radial (ε_r^I) and circumferential (ε_θ^I) surface strains are then given by:-

$$\varepsilon_r^I = \frac{du^I}{dr} \quad \varepsilon_\theta^I = \frac{u^I}{r}$$

These surface strains are then used as in the original analysis to calculate the local radial stress and hence the energy release rate for delamination, G , at any given distance from the indent thus:

$$G = \frac{(1-\nu^2)tE}{2} \left(\frac{\varepsilon_\theta}{1-\nu} + \frac{(\varepsilon_r^I + \nu \varepsilon_\theta^I)}{1-\nu^2} \right)^2$$

The interface toughness, Γ_c , is then defined as the value of G as which delamination stops i.e. at radius r .

The interface toughness is related to the fracture toughness, K_{Ic} , of the interface by the expression:

$$\Gamma_c = \frac{K_{Ic}^2}{E_{ox}}$$

With the large number of input parameters involved in the analysis it is important to discover which are the most influence on the final value for interface toughness. To this end a sensitivity analysis has been carried out and the results are shown in [Figure 5](#). It can be seen that variations in all of the input parameters, with the possible exception of the Young's modulus and yield stress of the substrate, affect the derived value of interface toughness significantly. Figure 5 thus demonstrates that it is important to give care to the measurement of all the input

parameters and in particular to the radii of the indent and the delaminated area.

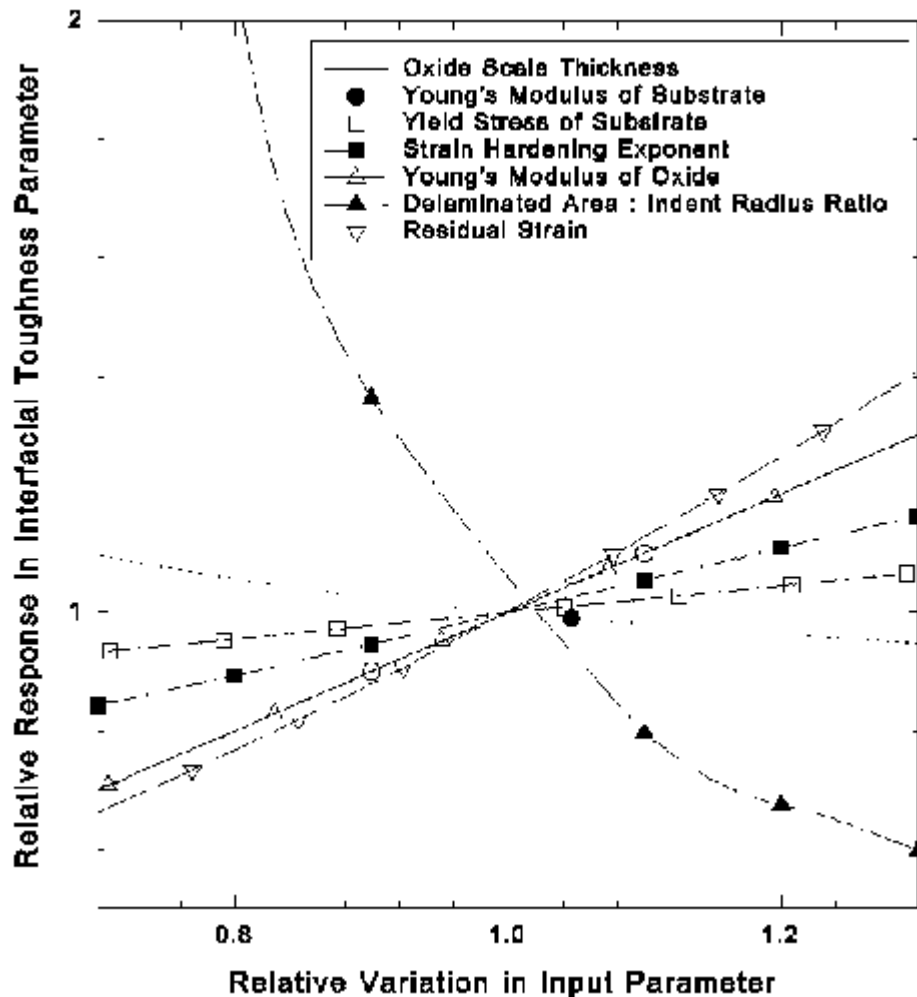


Figure 5 Sensitivity Analysis for Indentation

Typical value for interface toughness obtained by this method are:

30 - 90 J m⁻² for M₃O₄ on a 12-Cr steel

200 - 500 J m⁻² for Al₂O₃ on PM2000

1500 - 3000 J m⁻² for SiAlON coatings on Mar M002

Tensile Straining

The most convenient method to introduce a uniform tensile strain into a specimen is through flexure in a 4-pt bending rig. A schematic representation of the test set-up is shown in [Figure 6](#). Straining is carried out at a constant crosshead speed, usually ~0.1 mm s⁻¹, although at room temperature the exact speed is not important.

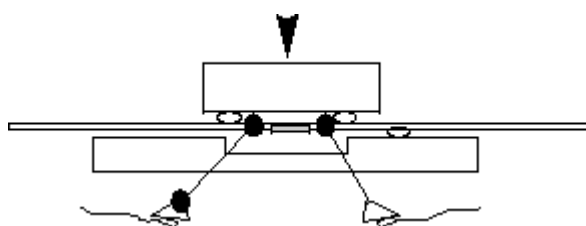


Figure 6 Schematic Representation of the flexural test

Various analyses of the results [6-11] from this type of test are available and have recently been reviewed [12]. The conclusion of this review indicate that the most appropriate model is that of McCartney [10], which is based upon the shear-lag concept of stress distribution. The input parameters required by the McCartney model are minimum crack spacing ($2L$), thickness of scale (b) and substrate ($2a$), Young's and shear moduli of scale and substrate (E^s , μ^s , E^c , μ^c) and the tensile and residual strains in the coating (ε_c and ε_0 respectively). The maximum interfacial shear stress is given by the expression:-

$$\tau(y) = - \frac{kb \sigma^c \sinh ky}{\cosh kL}$$

$$\text{where } k^2 = \frac{3\mu^c \mu^s (aE^s + bE^c)}{abE^c E^s (a\mu^c + b\mu^s)}$$

$$\text{and } \sigma_c = \frac{E_c}{\varepsilon_c + \varepsilon_0}$$

The maximum interfacial shear stress is shown as a function of scale and/or coating thickness for several systems in Figure 7. It can be seen that the systems examined show a progression of increasing interfacial strength in the sequence: iron oxides ? nickel oxide ? alumina.

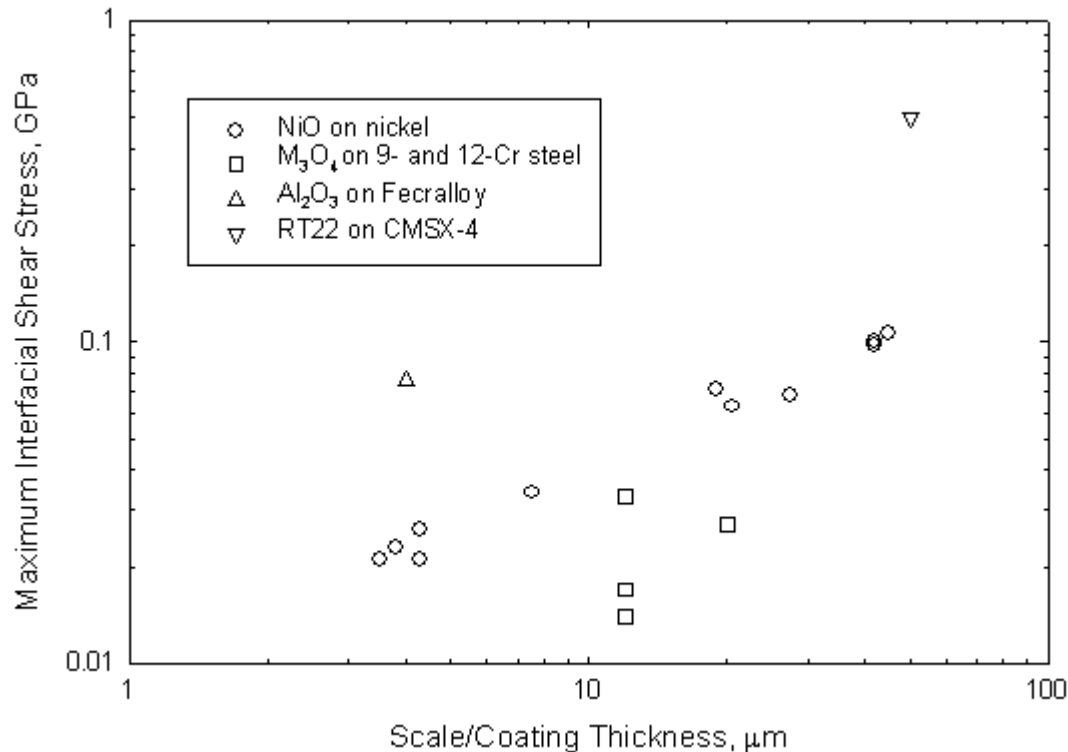


Figure 7 Maximum Interfacial Shear Stress Derived from Flexural Strain Tests for Different Oxide Systems

Validation of Test Methods and Recommendations for Preferred Methods

The three different test methods have been used on a wide range of oxide scales and coatings on alloy substrates and results are summarised in Table I. It is immediately apparent that no single measurement procedure is applicable to the entire range of systems that have been investigated.

It can be seen from the previous sections that there are numerous tests that generate a quantitative measure of scale/coating adhesion. It is unfortunate that each test generates its own unique parameter for adhesion and that it is difficult, if not impossible to correlate the different parameters. In addition any particular test cannot be applied to the entire range of scales/coatings. The choice of test method is therefore determined by the material/system to be

examined.

Critical load data from the scratch test cannot always be related to an adhesion parameter if the value obtained cannot be related to failure initiated by wedge cracking. The indentation test fails if delamination of the scale or coating cannot be induced. Tensile straining of the scale/coating also cannot be quantified if spallation of the surface film cannot be induced or if premature failure of the substrate occurs.

Table I. Comparison of interface adhesion parameters derived from the three measurement methods

Material System		Scratch Test	Indentation	Tensile Straining
Scale/Coating	Substrate	Interfacial Fracture Energy J m^{-2}	Interface Toughness J m^{-2}	Maximum Interfacial Shear Stress GPa
Fe_3O_4	Mild Steel	*	*	*
M_3O_4	E911 (9 Cr steel)	*	*	*
M_3O_4	X19 (12 Cr steel)	*	*	*
Cr_2O_3	Incoloy 800 HT	x	x	?
Al_2O_3	PM2000	*	*	x
Al_2O_3	Fecralloy		?	*
NiO	Nickel		x	*
MCrAlY coating	Mar M002	?	x	
Pd Al coating	Mar M002	x		
Al_2O_3	MCrAlY coating	*	?	

Conclusions

Use of the appropriate measurement technique will generate a quantitative value for adhesion, however not all materials can be investigated by the same technique and, at present, it is not possible to correlate the parameters generated by the different techniques. Measurement and interpretation of scale/coating adhesion thus remains dependent upon the experience of the investigator

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