



INTERNATIONAL ATOMICENERGY AGENCY UNITED NATIONS EDUCATIONAL ECIENTIFIC AND CULTURAL ORGANIZATION



INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1 CAPLE: CENTRATOM - TELEX 400393 - I

SMR/208 - 40

SPRING COLLEGE IN MATERIALS SCIENCE

ON

"METALLIC MATERIALS"

<u>(11 May - 19 June 1987)</u>

SURFACE TREATMENT AND COATINGS OF MATERIALS (Part IV)

R. BULLOUGH

Materials Development Division B552 Harwell Laboratory Oxfordshire OX11 ORA U.K.

These are preliminary lecture notes, intended only for distribution to participants.

LECTURE 4

	INTERFACES AND STRESSES	Slide 7	Closer examination of a typical ceramic
substrate and the pre	<u>Abstract</u> ne interface between a coating and its parent esence of residual stress in a coating can e performance of the coating in service. For	<u></u>	microstructure reveals the presence of microstructure reveals the presence of microcracks prior to failure. These microcracks are the precursor to catastrophic failure and arise from the combination of deposition and environmental stresses.
example, if significates the substrate, then is hard coating is deposed advantage of having a the overlayer is too ceramic coating is here.	TITLE SLIDE : <u>Interfaces and Stresses</u>	<u>Slide 8</u>	In order to establish the likely magnitudes and sensitivities of the residual stress in the coating, it is important to model the deposition process. Essentially, a major part of the problem reduces to building a heat transfer model of the heat input to the substrate and coating during the growth of the coating by the addition of molten ceramic particles. A range of process parameters can then be explored to determine which will critically affect the stress in the coating.
Slide 2	HR16814		
Slide 3	Plasma sprayed coatings.	<u>Slide 9</u>	A parameter which is influential is the initial substrate temperature. This affects the coating stress through the expansion mismatch between the substrate and the coating. It is
<u>Slide 4</u>	As sprayed, ceramic artefacts may fail unexpectedly without the application of any external stress as a result of the stresses built in during processing. Such stresses can		clear that even modest increases in substrate temperature can induce a factor of 3 increase in the residual stress in the coating.
	lead to the complete failure of the component as shown in this slide.	<u>Slide 10</u>	The thermal conductivity of the coating is also a critical parameter as shown in this slide where a change of only 25% in the thermal
<u>Slide 5</u>	In advanced gas turbine engines, the use of ceramic coatings on turbine blades is a route to increasing the operating temperature of the		conductivity can completely reverse the sign of the stress in the coating.
	engine and, therefore, the thermodynamic efficiency. This slide shows representative examples of zirconia coated turbine blades immediately after coating.	<u>Slide_11</u>	The rate at which the coating is deposited is another influential parameter and may again lead to the stress changing from being compressive to tensile. For a brittle material
<u>Slide 6</u>	Clearly, the performance of the coating and turbine blade has to be established under typical operating conditions. This slide shows		such as a ceramic, tensile stresses are to be avoided since they lead to crack growth and rapid failure.
	coated turbine blades after exposure to 1100°C for extended periods of time. It is important to note that the coating has begun to fail at the interface with the metal substrate and that the metal substrate has oxidised badly.	<u>Slide 12</u>	The coating thickness can also have a dramatic effect on the stress distribution across a zirconia coating deposited by plasma spraying. This theoretical prediction correlates well with experimental experience where it is known that to deposit zirconia by this technique at a thickness of approximately 2.5mm can lead to

- 2 -

the onset of rapid and unexpected failure of the coating after deposition.

<u>51ide 13</u>	Similarly, it is important to recognise that the simple act of producing a thick coating does not necessarily lead to a linear increase in fracture stress as this slide demonstrates. It is also important to note that because the coating contains defects (such as porosity and cracks), these will act as stress concentrators and may lead to a lowering of the fracture	<u>Slide_18</u>	The results can be conveniently plotted as the dimensionless parameter strain v. the square of the sign of the tilt angle. Typical results are shown in this slide where it is clear that the substrate can critically affect the stress which is measured in the titanium nitride coating.
Slide 14	stress of the ceramic coating compared to a bulk material of the same composition. As well as optimising process variables in order to minimise residual stresses in	<u>Slide 19</u>	It is also possible to separate the expansion mismatch stress from the deposition stress as shown in this example. It is clear that the thermal contribution to the internal stress can be significant.
	coatings, it is possible to change the chemistry of the material which affects the interatomic binding forces through the fracture stress. In this example, it can be seen that the concentration of yttria in yttria stabilised zirconia (YSZ) can change the fracture stress by approximately 50%. Equally, it is important to deposit the coating in a continuous fashion rather than trying to build up successive layers since the latter approach	<u>Slide 20</u>	The effect that residual stress can have on the microstructure of a coating is also evident from this slide. Photograph A shows that at the interface with the substrate, the microstructure consists of small densely packed grains, whilst at the outer surface as shown in photograph B, the grains are larger and more separated.
	introduces additional planar interfaces which act as weak boundaries when a stress is applied.	<u>Slide 21</u>	As a result, it is possible to predict that the yield stress of the material will vary as a function of position within the coating as shown by this schematic slide.
<u>Slide 15</u>	LINK SLIDE : "Physical Vapour Deposition : Stresses and Interfaces"	<u>Slides 22/23</u>	The importance of thermal stresses to the
<u>Slide 16</u>	Normally, physical vapour deposition (PVD) is used to deposit thin films (less than 60µm thick) as shown in this typical example of titanium nitride coatings about 2µm on cutting tools. Stresses can also be built up in these thin layers and, given the harsh working environment, a knowledge of the residual stresses is important in determining the quality of the composite material.		densification of PVD coatings is illustrated in these next two slides. For a Molybdenum coating deposited onto Molybdenum, then there is obviously no thermal stress and the right-hand micrograph shows quite open boundaries between the grain crystallites. However, for a similar coating deposited onto stainless steel, a large thermal stress component is generated and the high magnification scanning electron micrograph on
Slide 17	Classically, residual stresses in these thin film media can be measured by X-ray techniques		the right shows a very dense microstructure has developed as a result.
	as shown schematically in this slide. An X-ray beam is diffracted from a set of crystallographic planes and the change in interplanar spacing is measured as a function of the angle of tilt of the film to the X-ray beam.	<u>51ide 24</u>	The importance of internal stress in the densification of PVD coatings cannot be over-emphasised and for ceramic coatings this effect is also particularly important. On the left is a carbide coating which shows a very dense microstructure; by removal of the substrate constraint on the right, the open boundaries typical of the structured diagrams illustrated in a previous talk can be seen.

- 3 -

•

- 4 -

- 5 -

- 6 -

<u>Slide 25</u>	Due to the large compressive stress in the plane of the foil of titanium nitride coatings, a Poisson's ratio expansion of lattice planes parallel to the coating substrate interface is obtained. Therefore, the increase in unit cell dimension for titanium nitride coatings correlates well with this large internal	<u>Slide 31</u>	Thin film coatings can also be used in advanced heat engines. For example, this slide of a diesel engine exhaust valve shows the beneficial effect of adding a coating to the head to reduce oxidation of the valve steel.
<u>Slide 26</u>	Again, removal of the substrate constraint causes complete relaxation of internal stress and the lattice parameter of the titanium nitride coatings, irrespective of substrate, fall to their unstressed values.	<u>Slide 32</u>	Detailed examination of the coated steel after thermal exposure shows that the elements of the coating (in this case, iron, chromium, aluminium and yttrium) can redistribute into the substrate and up to the free surface as noted previously in the lecture on "Microstructures".
<u>\$1ide 27</u>	LINK SLIDE : "Interface Phenomena"	<u>Slide 33</u>	Detailed microanalysis reveals the extent to which this distribution can take place.
<u>Slide 28</u>	We have already seen in the lecture on "Thin Film Properties" that the adhesion of a thin film can be measured in comparative terms using a scratch tester. As has also been pointed out in the presentation on "Microstructures", the initial interface which is presented for coating should be clean and free from	<u>Slide 34</u>	Further interfacial studies reveal that the interdiffusion region can change crystal structure as a result of the ingress of elements which, for example, stabilise a face-centred cubic as against a body-centred cubic crystal structure.
	second-phase species. In PVD processing, it is possible to clean this interface by ion bombardment and, as the results show, the adhesive force between the coating and the substrate is strongly dependent on the ion cleaning step.	<u>Slide 35</u>	The extent of diffusion into the substrate can be limited by the use of diffusion barriers. For example, the titanium nitride interlayer in this case has reduced the diffusion of the coating into the substrate. Additionally, however, porosity has developed as elements
<u>Slide 29</u>	These photographs show that ion cleaning a substrate and then depositing a coating (photograph B) produces a uniform fracture,		from the substrate can still diffuse into the coating leaving behind vacancies which then form voids.
	whereas (photograph A) a non-cleaned surface fractures in a discontinuous manner as a result of stress concentration effects at the interface with the substrate.	<u>51ide 36</u>	The retardation of interdiffusion effects by titanium nitride interlayers is clearly shown in this slide. The open square shows the reduced interdiffusion of aluminium into
<u>Slide 30</u>	In certain cases it is possible to introduce an additional coating between the titanium nitride and the substrate to increase the adhesive		stainless steel substrate, whilst the full squares show the extent of interdiffusion in the absence of a diffusion barrier.
	force. In this particular case, titanium shows a beneficial effect when deposited underneath titanium nitride onto an M2 tool steel. Again, however, the thickness of the layer is important as this can affect the stress in the layer.	<u>Slide 37</u>	This work is of great importance to the gas turbine industry as failure at interfaces can mean the loss of performance in, for example, a Harrier vertical take-off and landing engine. The turbine blades in the centre of this slide are intended for such an engine.

.



Slide 38	On exposure to high temperatures, a number of changes occur within the coating and the substrate and these are illustrated in this	<u>Slide 45</u>	Optical metallography shows these thermal cracks extend deep into the coating.
	slide. For example, reactive elements such as aluminium and chromium migrate to the free surface to form protective oxidation resistant oxide scales. Similarly, some elements will	<u>Slide 46</u>	However, if the microstructure is peened and then heat-treated, no cracking occurs after 500 cycles.
	migrate to the substrate to form intermetallic precipitates and phase changes.	Slide 47	It is only after 1,200 cycles that evidence of thermal fatigue cracks is seen.
<u>Slides 39/40</u>	All these processes are diffusion rate limited and at high temperatures these effects can be quite significant as shown by these two slides. At lower temperatures, these effects become less of a problem to engine designers as the thermodynamic driving force is reduced.	<u>Slide 48</u>	Optical metallography shows these thermal fatigue cracks extend deep into the microstructure of the coating and penetrate into the substrate. The improvement in performance by peening and then heat-treating is that good metallurgical bonds are formed
Slide 41	The square of the interdiffusion distance when plotted against time is a linear diffusion		between the interfaces of the columnar grains, thereby eliminating leader defects.
	confirming that the processes are indeed diffusion rate limited.	Slide 49	SUMMARY SLIDE
<u>Slide_42</u>	During the deposition of these oxidation corrosion resistant coatings, surface topography plays an important role in the nucleation and growth phase of the deposit. Surface irregularities can lead to the formation of so-called leader defects which must be eliminated from the microstructure to guarantee performance.		The main points arising out of this lecture are that the stress induced in a coating as a result of deposition can be significant and can lead to failure of the coating. Advanced techniques are required to assess the quality of these coatings. The interfaces between the coating and the operating environment and the coating and the substrate are critical. Growth defects are also very important and may lead to
<u>Slide 43</u>	This slide illustrates a leader defect in an advanced alloy coating. The interfaces in the coating which can give rise to problems can also be between the columnar grains as shown in this slide where, during high temperature oxidation, a defect between the columnar grains has led to the preferential ingress of oxygen, and therefore oxidation of the coating deep inside the microstructure.		premature failure along interfacial boundaries.
<u>Slide 44</u>	It is important to further process these oxidation resistant coatings and this is carried out in two ways. This slide shows if the microstructure is heat-treated and then glass bead peened to close off defects, then thermal cracking is initiated after 300 cycles.		

~ 8 - 8 -



1. Into faces and Strenes

PLASMA SPRAYED COATINGS

•

.

,





-13-



Coramic antifact - feulad due to built in stress ming forening. No extend stress



- 14-

Representative ZNOL costard tastine blade granter efficiency (terrelignin)





COATING UNDER DEPOSITION



Mobel Predictions





-20 -



VARIATION OF COATING THICKNESS

Thick costings can dendope taising



FRACTURE STRESS VERSUS ESTIMATED PROBABILITY OF FAILURE FOR TUNGSTEN COATINGS SPRAYED AT 76 g/min SHOWING THE EFFECT OF COATING THICKNESS -23-







PHYSICAL VAPOUR DEPOSITION: INTERFACES AND STRESSES

. .

.



PUD TAPS for Theody holes

LECTURE 4 : SLIDE 17 $N_{P_{1}}N_{5}$ Ns

-26 -

(a) Measurement of do

Coating Substrate

--

 $\nabla / / \Lambda$

(b) Measurement of dy

Ψ

ò.

Xing lestyrs for manig attende

←_______





LECTURE 4 : SLIDE 19







.



LECTURE 4 : SLIDE 21





- NO BONDING in THIS
 - GASE



د Stress , ص (GPa)



i

i



LECTURE 4 : SLIDE 27









- 39 -



Interformer hateren country + 1. hat sale







- 45 -

Human Andas

.





_50.um,

_25µm





-50-

LECTURE 4 : SLIDE 42

- 49-



.

· · ·







. . . **!**

.

-53-

LECTURE 4 : SLIDE 45

- 54 -

LECTURE 4 : SLIDE 46



- 57 -

LECTURE 4 : SLIDE 49

	5	g
--	---	---

Mechanism for the Shallation of Polycrystalline Coatings

R. Bullough , Harwell, U.K.

1. The Model

- 2. Analysis
- 3. Results

4. Conclusions and Required Development of this Model.

Model was originally developed for DIAMOND shallation - so for interest we give results for both DIAMOND and STAINLESS STEEL. Note however SIP DIAMOND COATINGS for 'HARD' device fabrication can now be made.

	SUMMARY
Α.	STRESSES IN COATINGS CAN BE SIGNIFICANT AND LEAD TO FAILURE
Β.	ADVANCED TECHNIQUES ARE REQUIRED TO MEASURE AND MODEL STRESSES
с.	INTERFACES ARE VERY IMPORTANT
D.	GROWTH DEFECTS ARE VERY IMPORTANT

-59-

-60-

1

MODEL



Essential conjectures are that:

- 1. A critical microcrack size in the interface is needed for any cracking.
- 2. If $a > a_{min}$ the crack will open to stable size a_{max} .
- 3. As p increases the stresses in the interface at the core of the disclination will increase: a_{min} will decrease and a_{max} will increase.

We wish to quantify above conjectures.

Spallation will occur if

either

1. single interface crack reaches p in length.

or

 Cracks join up from adjacent 'buckles' or from adjacent terminating grain boundaries (Latter case if a d). 2. Analysis

3

Step 1

Stress field of single edge dislocation of strength b in a half space (x > 0).



$$P_{XX}^{(q)}(x,y) = A \left\{ \frac{(x-q)[(x-q)^2 - y^2]}{[x-q)^2 + y^2]^2} - \frac{(x+q)[(x+q)^2 - y^2]}{[(x+q)^2 + y^2]^2} + 2q \left[\frac{(3x+q)(x+q)^3 - 6x(x+q)y^2 - y^4}{[(x+q)^2 + y^2]^3} \right] \right\}$$

$$P_{XY}^{(q)}(x,y) = A \left\{ \frac{y[(x-q)^2 - y^2]}{[(x-q)^2 + y^2]} - \frac{y[(x+q)^2 - y^2]}{[(x+q)^2 + y^2]^2} \right\}$$

$$\left. + \frac{4\pi x y [3(x+q)^2 - y^2]}{[(x+q)^2 + y^2]^3} \right\}$$

where

٠.

 $A = \mu b/2e(1-v); \mu = shear modulus, v = Poisson's Ratio.$

Note these stresses (tractions) vanish on $x = 0 \rightarrow$ Free Surface.

-62-

Linear superposition of N such dislocation stresses yield stresses associated with terminating tilt boundary:



Finite sum is tedius - replace by continuous distribution:

$$p_{RR}^{T}(x,y) = \sum_{n=1}^{N} p_{RR}^{(nR)}(x,y)$$
$$= \frac{1}{R} \int_{0}^{p} p_{RR}^{(q)} dq = \frac{A\theta}{b} \left\{ \frac{1}{2} sn \left[\frac{(x+p)^{2}+y^{2}}{(x-p)^{2}+y^{2}} \right] - \frac{y^{2}}{[(x-p)^{2}+y^{2}]} + \frac{2\pi^{2}-2\pi(g+p)+y^{2}}{[(x+p)^{2}+y^{2}]} + \frac{4\pi y^{2}p}{[(x+p)^{2}+y^{2}]^{2}} \right\}$$

$$p_{\pi\gamma}^{T}(x, y) = \sum_{n=1}^{N} p_{\pi\gamma}^{(nt)}(x, y)$$

$$\approx \frac{1}{t} \int_{0}^{P} p_{\pi\gamma}^{(q)} dq = \frac{A!}{b} \left\{ \frac{(\pi - p)\gamma}{[(\pi - p)^{2} + y^{2}]} + \frac{(\pi + p)\gamma}{[(\pi + p)^{2} + y^{2}]} - \frac{6\pi\gamma}{[(\pi + p)^{2} + y^{2}]} + \frac{4\pi\gamma[\pi(\pi + p) + \gamma^{2}]}{[(\pi + p)^{2} + y^{2}]^{2}} \right\}$$

Note stresses again vanish on free surface x = 0.

<u>Step 3</u>

5

Imagine slit crack immediately below tilt boundary in x = pplane parallel to z-axis of length 2a

-64-

and the second



Stress intensity factors K_{II} and K_{II} at tip of such a crack:

$$K_{I} = 2 \begin{bmatrix} \frac{a}{\pi} \end{bmatrix}^{\frac{1}{2}} \int_{0}^{a} \frac{p_{\pi\pi}^{T}(p, y) dy}{\left[a^{2} - y^{2}\right]^{\frac{1}{2}}} \qquad \text{Node I}$$

$$K_{II} = \frac{2}{[\pi a]^{\frac{1}{2}}} \int_{0}^{a} \frac{y p_{XY}^{T}(p, y) dy}{[a^{2} - y^{2}]^{\frac{1}{2}}}$$
 Node II

Crack extension force

 $G(a) = \frac{1-\gamma}{2\mu} [K_{I}^{2} + K_{II}^{2}]$

Integrals are analytic:

We find

where r = a/p.

Finally:

f(r) =

$$G(\mathbf{a}) = \frac{\mu \theta^2 p}{\theta \pi (1-\nu)} f(\mathbf{r})$$

$$f(\mathbf{r}) = \mathbf{r} \left\{ \begin{bmatrix} \ln \left(\frac{2 + (4 + \mathbf{r}^2)^{\frac{1}{2}}}{\mathbf{r}}\right) - \frac{2(6 + \mathbf{r}^2)}{(4 + \mathbf{r}^2)^{\frac{3}{2}}} \right]^2 + \frac{4\mathbf{r}^3}{(4 + \mathbf{r}^2)^3} \right\}$$
where $\mathbf{r} = \mathbf{a}/\mathbf{p}$.
$$Fropagation will occur if$$

$$G(\mathbf{a}) \ge G_{c}$$
For brittle material (Diamond) $G_{c} = 2\mathbf{I} \times \frac{\mu b}{10}$.
Finally:
$$G(\mathbf{a}) = \frac{1}{2\mathbf{I}} + \frac{4\mathbf{r}^3}{10} + \frac{1}{2\mathbf{I}} + \frac{1}{2\mathbf{I$$

$$\frac{G(a)}{G_c} = 0.6 \left[\frac{\mu b}{10G_c}\right] \frac{p}{b} \theta^2 f(r) \qquad (v = 1/3)$$

$$G_c = \frac{2}{3\mu} \kappa_c^2$$

Thus in terms of toughness Kgi

$$\frac{d(a)}{G_c} = 0.6 \begin{bmatrix} \frac{3\mu^2 b}{20\kappa_c^2} \end{bmatrix} \stackrel{\mathbf{R}}{\overset{\mathbf{P}}{\overset{\mathbf{P}}} \stackrel{\mathbf{f}}{\overset{\mathbf{f}}{\overset{\mathbf{f}}}} f(r) \xrightarrow{\text{Extreme}} 0.6 \stackrel{\mathbf{P}}{\overset{\mathbf{P}}{\overset{\mathbf{P}}} \stackrel{\mathbf{f}}{\overset{\mathbf{f}}} f(r).$$

.

i

1. Extreme brittle material (Diamond)

$$\mu = 550 \text{ GPa}, \text{ K}_{c} = 4.3 \text{ MPa} \sqrt{m}$$

2. Low alloy steel (24Cr 1Mo)

~

$$\mu$$
 = 83 GPa, K_c = 23 MPa \sqrt{m}

NEXT 4 TRANS:
$$\frac{G(a)}{C_c}$$
 versus $\frac{a}{p}$ for range of p, θ^2

and a obtained.

.





BREES Indiale

8+0+X

•

4. Conclusions and Required Developments of Nodel

$$\frac{G(a)}{C_c} = 0.6 \left[\frac{3\mu^2 b}{20\kappa_c^2} \right] \frac{p}{b} \theta^2 f(r)$$

- (a) Diamond has high μ , low $K_c \rightarrow \frac{G(a)}{G_c}$ easily reaches <u>unity</u>.
- (b) Steel has both lower μ and higher K_c .
- (c) $\frac{G(a)}{G_c} = p$. Anin drops and Anax rises as p increases.





(*) Can see importance of intermediate high toughness layer.

(e) Ideal problem to solve:

4,



•