WEAR RESISTANT COATINGS
ON
CARBON FIBRE COMPOSITES

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ASTRaL

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ASTRaL

The Advanced Surface Technology Research Laboratory (ASTRaL) is a research unit of Lappeenranta University of Technology (LUT) situated in Mikkeli. It is part of the department of Mechanical Engineering.

ASTRaL is a partner in Mikkeli Coatings and Composites Research Centre. This is a partnership between LUT and Mikkeli Polytechnic.

Thin Film Deposition

- Magnetron sputtering
- Atomic Layer Deposition (ALD)
- RF plasma jet internal coating of tubes
- Plasma CVD

Surface Analysis

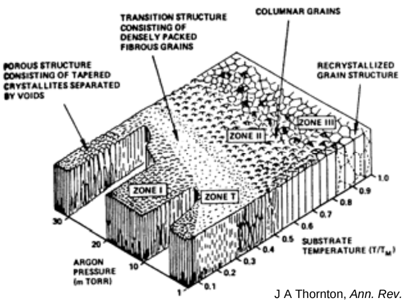
includes

- SIMS
- MicroRaman
- FESEM + EDS
- AFM
- Profilometry

Wear-resistant coatings

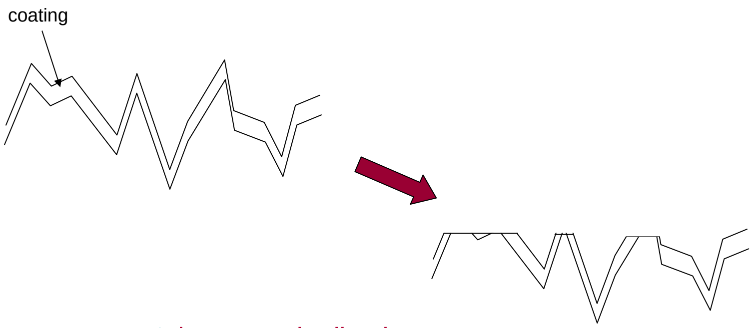
Coating must

- be dense
  normally needs relatively high temperature



J A Thornton, *Ann. Rev. Mater. Sci.*7 (1977) 239

- be smooth (generally)



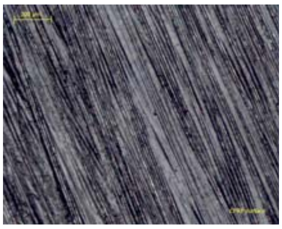
- have good adhesion
- be well supported by substrate

Properties of carbon fibre-reinforced polymer (CFRP)

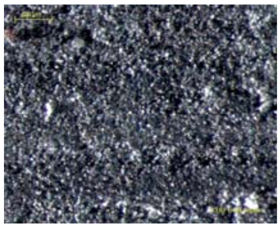
- polymer matrix with carbon fibre reinforcement
- substrate soft
  - vinyl ester matrix ~10 GPa Young's modulus,
  - with fibre reinforcement ~70 GPa
  - little support for hard film
- substrate has variable properties
  - interaction between fibres and matrix
- substrate affected by high temperatures
  - thermosetting polymer
  - vinyl ester glass temperature is low

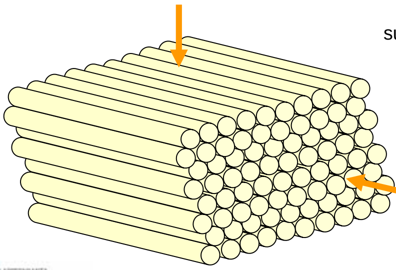
Structure of CFRP

plan view

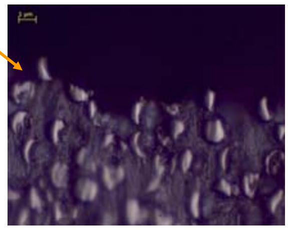


cross-section





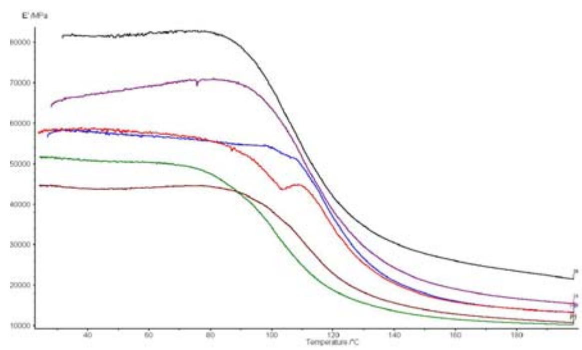
surface



Dynamic mechanical analyser (DMA) measurements on CFRP

measures response of CFRP to oscillating force

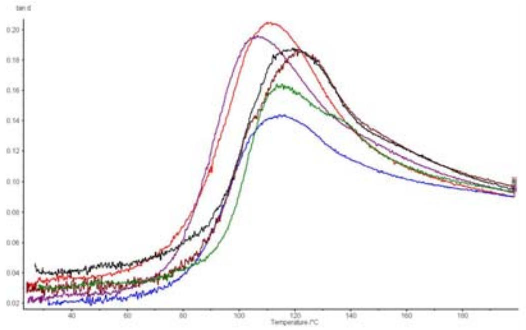
- wide variation in storage modulus from different samples



Dynamic mechanical analyser (DMA) measurements on CFRP

measures response of CFRP to oscillating force

- wide variation in storage modulus from different samples
- low glass transition temperature



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Chromium nitride coatings on CFRP

- Reported hardness of sputtered CrN_x films ~4-30 GPa

Deposition by magnetron sputtering

- Closed field sputtering system
- Pulsed DC reactive sputtering in Ar/N_2 atmosphere
  250 KHz, 1600 ns reverse pulse width
- Pulsed DC bias on substrate
- One target only to keep temperature of substrate low
- Stoichiometry control by feedback from Cr optical emission

Procedure

- Substrate precleaning
- Ar ion bombardment
- Deposition of Cr adhesion layer
- Deposition of CrN_x

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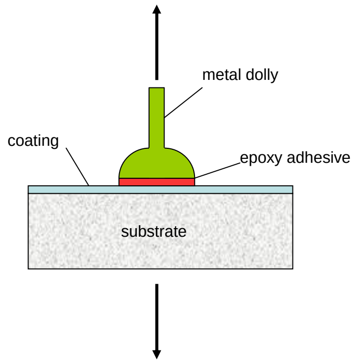
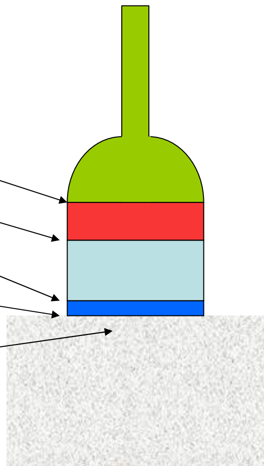
Adhesion

- measured by pull-off adhesion test



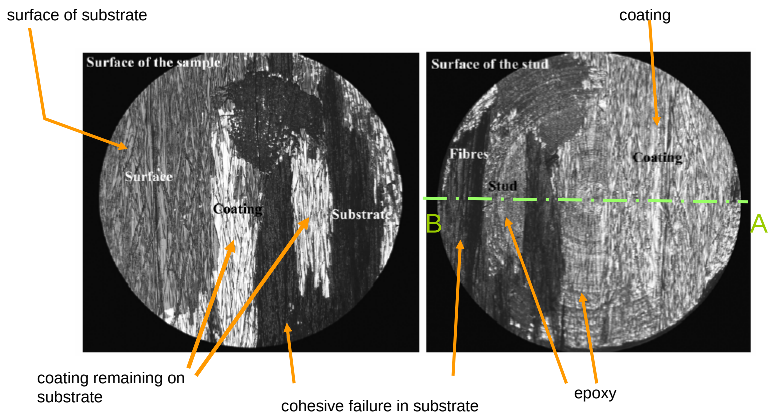
Where is the site of the failure?

- dolly-epoxy
- epoxy-coating
- coating-adhesion layer
- adhesion layer-substrate
- cohesive failure in substrate

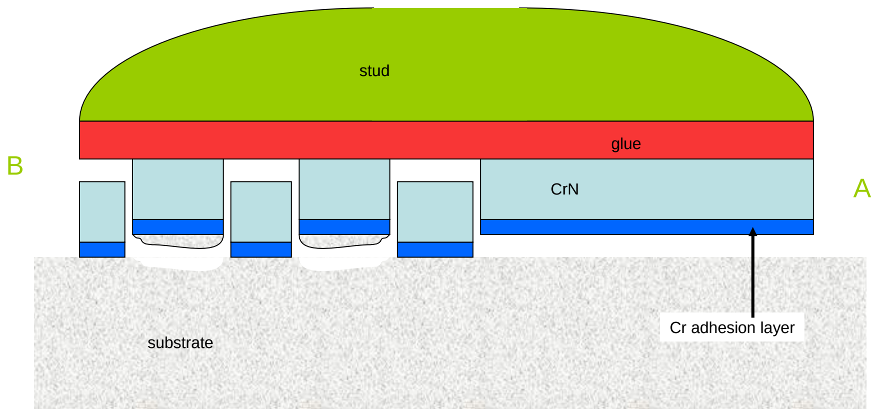


According to ASTM D4541, measurement is valid only if <50% of failure is due to glue.

Microscope pictures of failed specimens showing types of failure



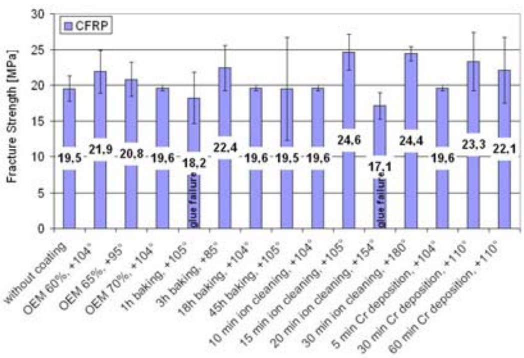
Cross-section of failure A-B



What parameters could affect adhesion?

- prebaking of substrate to remove water
  possible desorption during deposition and oxygen contamination of film
- precleaning of substrate
  ultrasonic solvent cleaning
- ion cleaning *in situ*
  variation in ion energy and time
- nature and existence of adhesion layer
  Cr layer thickness

Adhesion histogram

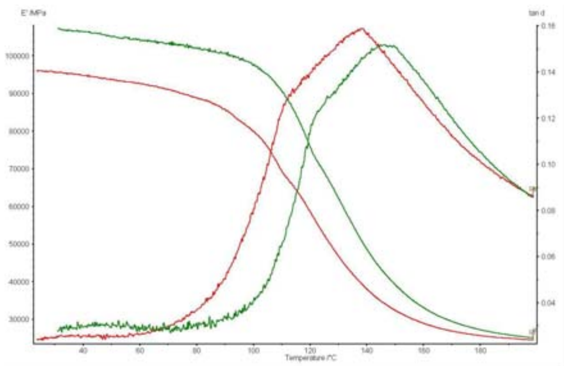


Conclusions: In most cases there is a cohesive failure of the substrate

PARAMETER	CONDITIONS	OBSERVED EFFECT ON ADHESION
baking time	1h, 3h, 18h,45h	no significant difference noticed
ion cleaning	10, 15, 20, 30 min	results suggest that longer ion cleaning time gives better adhesion*, but it also increases the temperature
Cr-layer	5, 30, 60 min	no significant difference noticed
substrate temperature	+85 to +180°C	higher temperature gives better apparent adhesion*, but it could be detrimental to the substrate
OEM-value	70%, 65%, 60%	no significant difference noticed

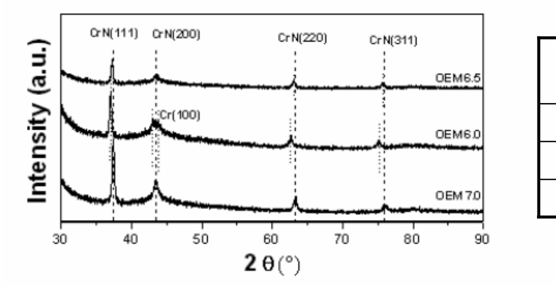
* Since failure is due to cohesion within the substrate, this is due to a change in substrate properties, not a change of adhesion between coating and substrate

DMA after overheating



- Increase in glass temperature
- Increase (?) in storage modulus

The film structure is cubic CrN preferentially (111) oriented



OEM setting	Composition (EDS)
60%	$CrN_{0.85}$
65%	$CrN_{0.83}$
70%	$CrN_{0.78}$

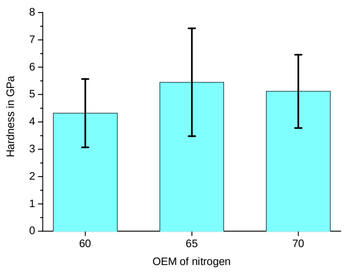
No major change of structure over range of nitridation parameters
(OEM settings with Cr peak at 60, 65 and 70% of initial Cr optical emission peak)

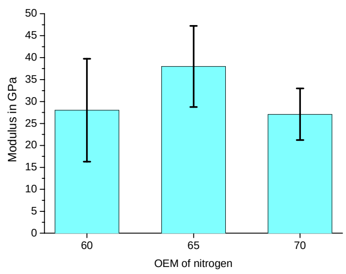
Dilation of lattice for OEM 60% (greater N content?)

Hardness shows no major difference

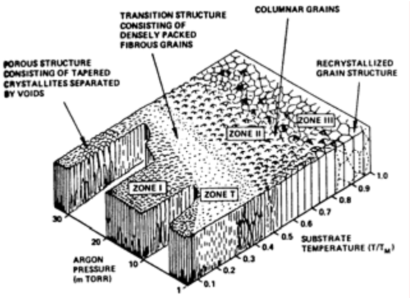
may be dominated by soft substrate even though indentation depth < 10% 0f film thickness

possibly hardest with 65% OEM?



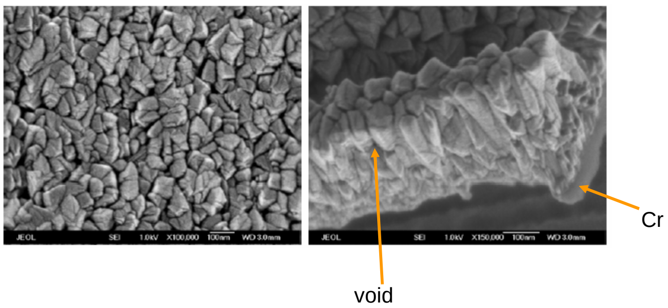


Resistance to wear will also depend on the crystal structure and granularity of the film



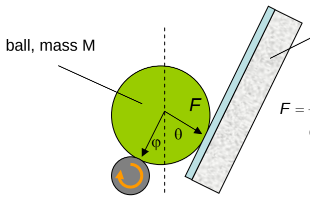
Structure appears not fully dense

- columnar crystals,
- evidence of intergranular voids
- rough, facetted surface



How does it behave under wear conditions?

- How to measure it?
  pin-on-disc too aggressive because of soft substrate
- Used modified ball cratering system with reduced load

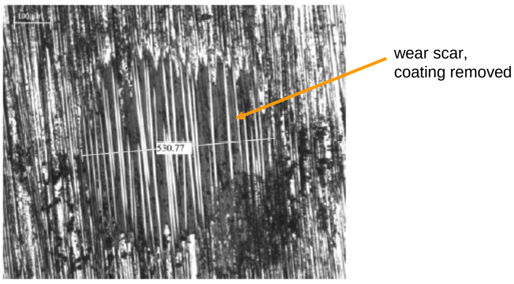


$$F = \frac{Mg}{\cos\theta\left(1+\frac{\tan\theta}{\tan\varphi}\right)}$$

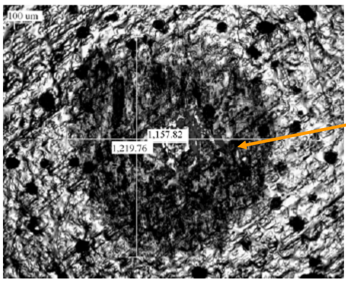
- Measure diameter of wear scar

Presence of fibres near surface means wear is uneven

- Fibres are torn from surface, removing coating



On vinyl ester polymer without fibre reinforcement



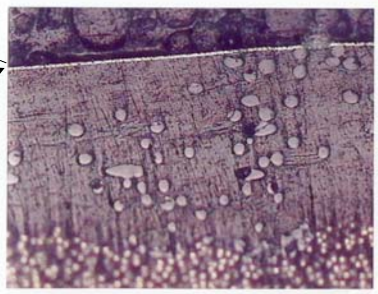
wear scar, coating remains

- Coating is retained in wear scar
- For wear scar diameter = 1200 µm, crater depth = 12 µm (film thickness = 0.8 µm)
- Coating deforms with substrate, but still adheres

Cross-section view of a more suitable substrate structure.

surface

surface coating



resin-only layer (~100 µm)

resin + fibres

Conclusions

- CrN coatings can be successfully deposited on CFRP at low temperatures, ≤ 100°C by reactive magnetron sputtering
- Coating adhesion is higher than cohesive strength of CFRP
- Coating structure still not fully dense
- Wear performance of standard CFRP not good because of carbon fibres at or near the surface
- Improved wear performance on vinyl ester polymer matrix alone
- CFRP should have a surface layer free of fibres for a successful coating