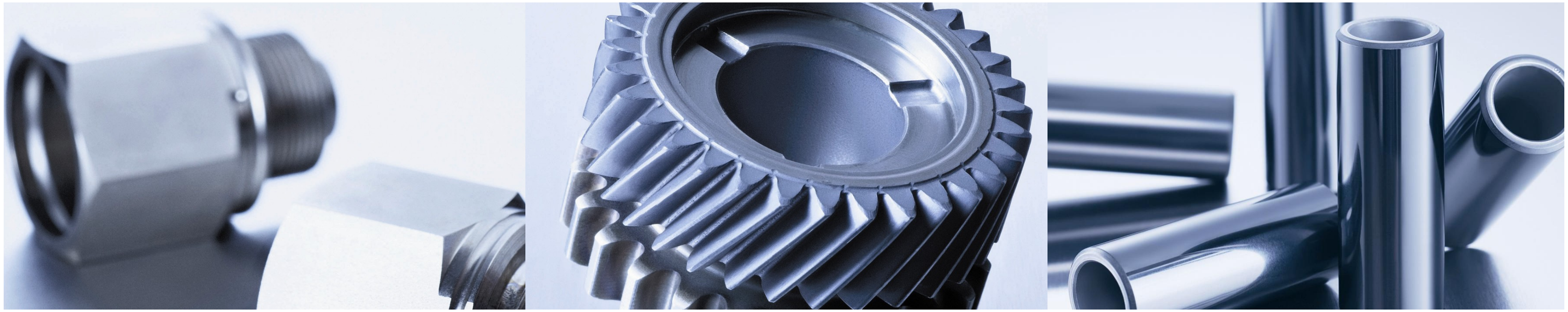


Coatings for fuel cell and super low-friction applications

K.Preinfalk[1], G. Eitzinger[1], Katrin Zorn[1], H. Sun[1], K. Cooke [1], P. Hamilton[2] ,B. Pollet[2], O. Jantschner[3], C. Mitterer[3] - 26.10.2012
1) MIBA Coating Group, 2) University of Birmingham, 3) University of Leoben
htc@miba.com

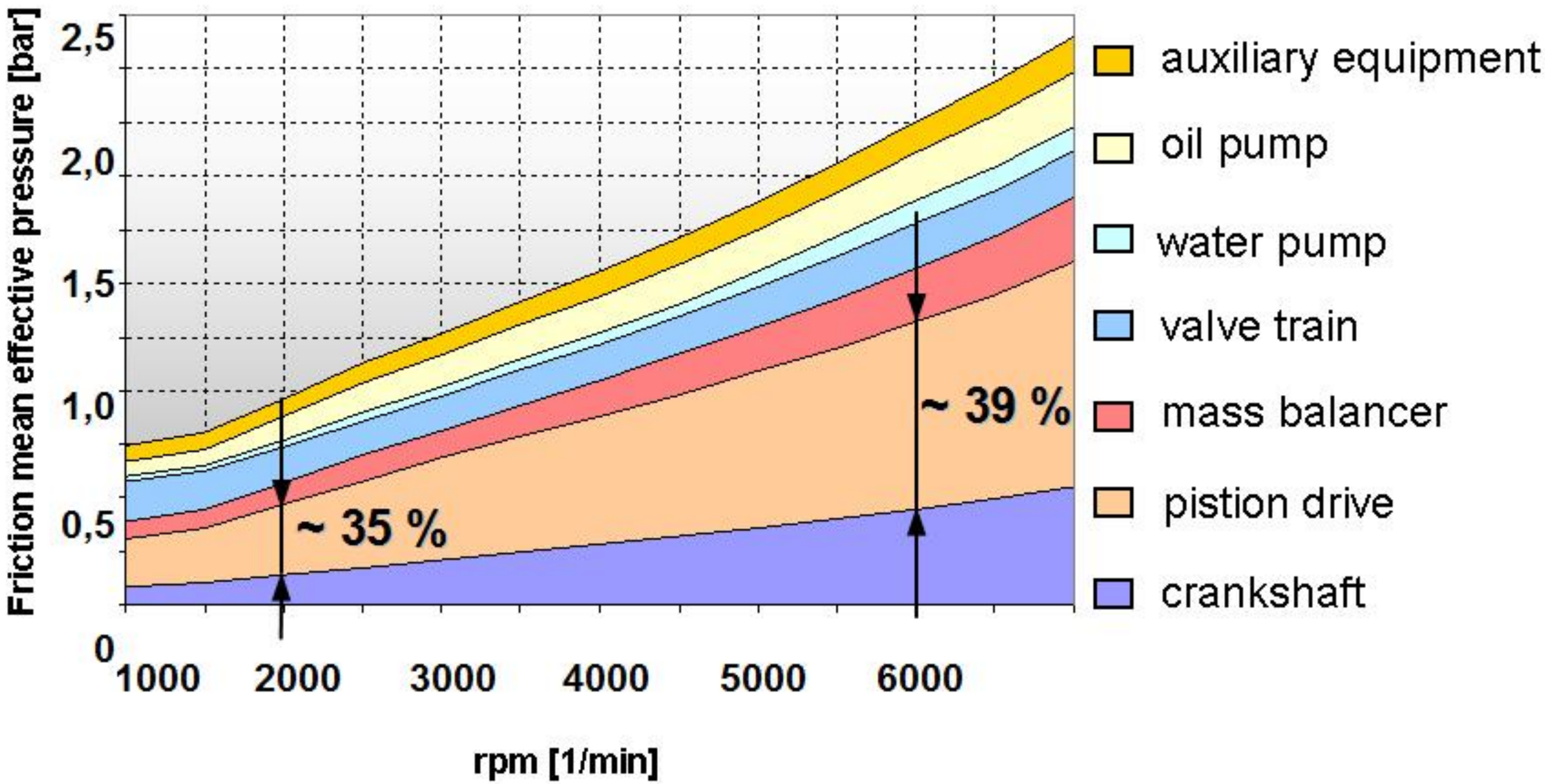
Confidential

Agenda



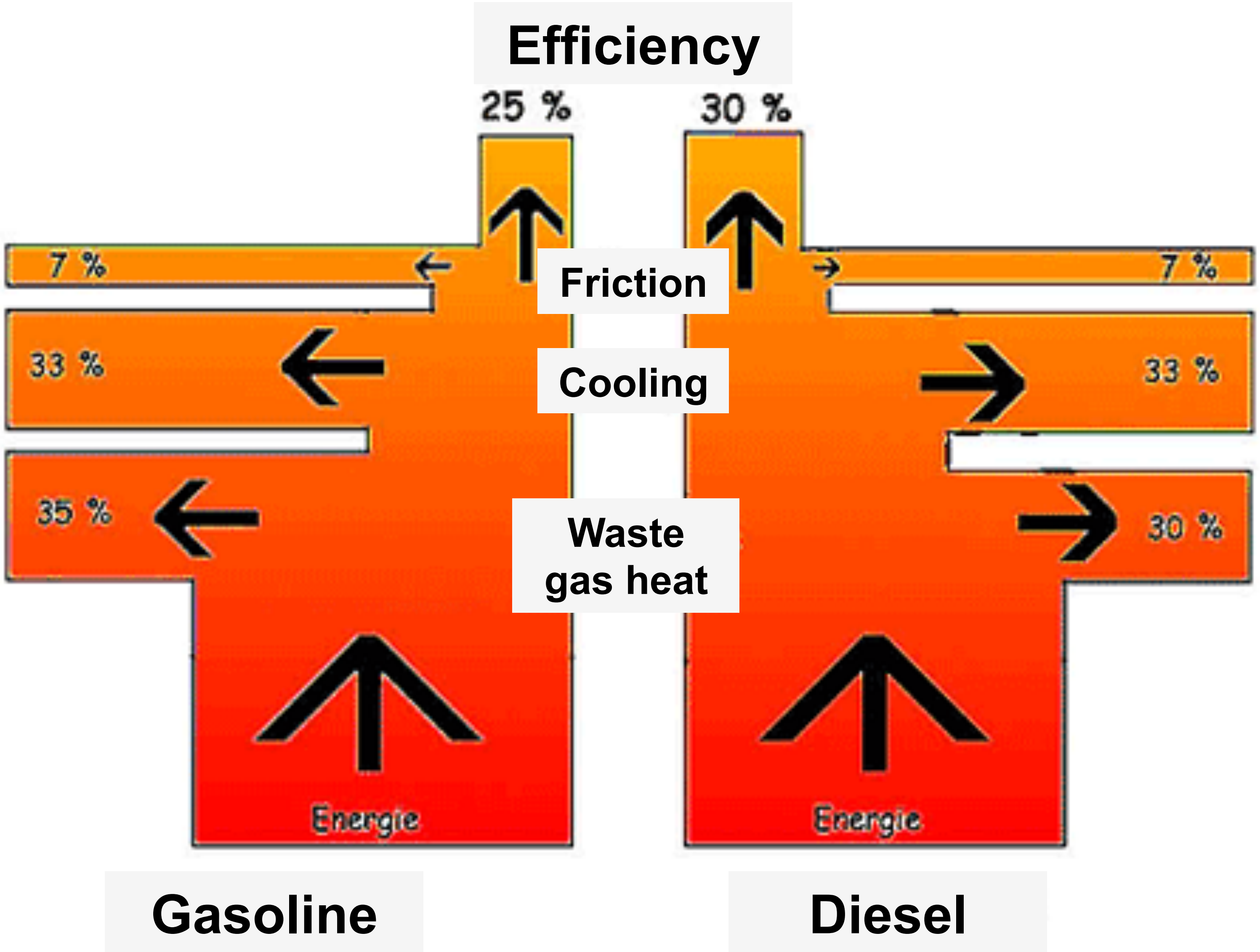
- **Motivation**
- High Temperature DLC
- Coatings for Fuel Cell Applications
- Summary

Motivation

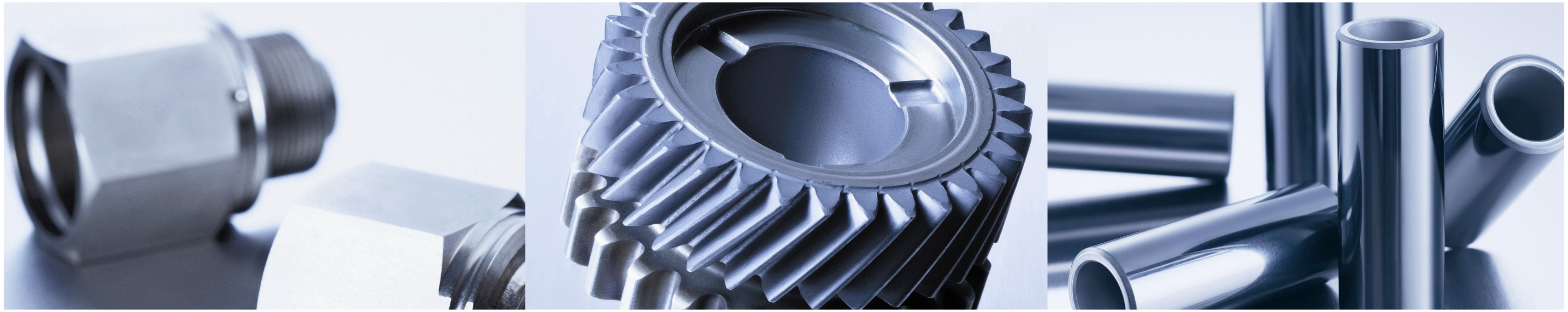


Source: A.Merkle, M.Werner, Technical University of Munich, Institute of Combustion engines ©2008-2009

Efficiency Combustion Engine



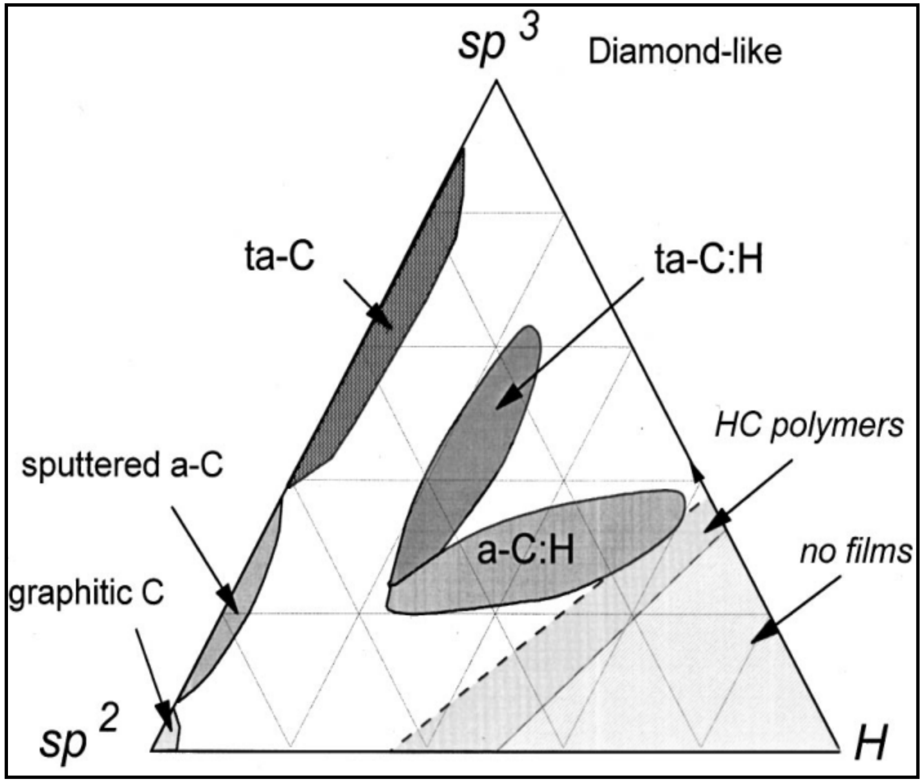
Agenda



- Motivation
- High Temperature DLC
- Coatings for Fuel Cell Applications
- Summary

Diamond like carbon (DLC) How to tune?

- Deposition Temperature:
  - Higher sp3-content, above 300°C up to 80%
  - Higher hardness
  - Higher intrinsic stresses
- Bias Voltage:
  - Higher sp3-content
  - Higher hardness
  - Higher intrinsic stresses
- Addition of metallic species:
  - Effects oxidation resistance
  - Is able to stabilize sp^3
- Addition of H, N, O



Diamond like carbon (DLC) Classification

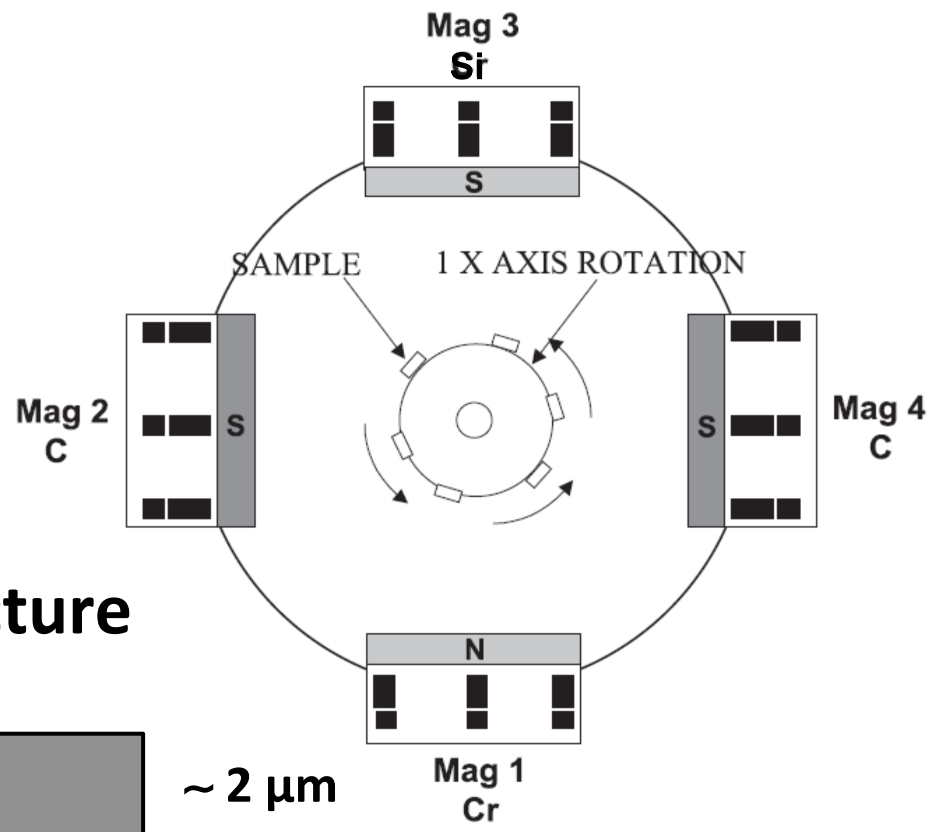
Table 1. Classification of carbon films; see also explanatory material in the text

	Carbon films													
Designation	**1 Plasma polymer films**	**2 Amorphous carbon films (diamond-like carbon films/DLC)**							**3 Crystalline carbon films**					
									Diamond films					**Graphite films**
Thin film/ thick film	Thin film	Thin film							Thin film			Thick film (freestanding)		Thin film
Doping, Additional elements		hydrogen-free			hydrogenated				undoped		doped	undoped	doped	undoped
				modified with metal			modified							
							with metal	with non-metal						
Crystal size on the growth side		(amorphous)							1 nm to 500 nm, nanocrystalline	0,5 µm to 10 µm, microcrystalline	0,1 µm to 5 µm	(5 µm to) 80 µm to 500 µm	80 µm to 500 µm	
Predominating C-C bond type	sp^2 or sp^3, linear bond	sp^2	sp^3	sp^2	sp^2 or sp^3	sp^3	sp^2	sp^2	sp^3	sp^3	sp^3	sp^3	sp^3	sp^2
Film no.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3.1	3.2	3.3	3.4	3.5	3.6
Designation	Plasma polymer film	Hydrogen-free amorphous carbon film	Tetrahedral hydrogen-free amorphous carbon film	Metal-containing hydrogen-free amorphous carbon film	Hydrogenated amorphous carbon film	Tetrahedral hydrogenated amorphous carbon film	Metal-containing hydrogenated amorphous carbon film	Modified hydrogenated amorphous carbon film	Nanocrystalline CVD diamond film	Microcrystalline CVD diamond film	Doped CVD diamond film	CVD diamond	Doped CVD diamond	Graphite film
Recommended abbreviation	–	a-C	ta-C	a-C:Me (Me = W, Ti ...)	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti ...)	a-C:H:X (X = Si, O, N, F, B ...)	–	–	–	–	–	–
Other designations commonly encountered but which should no longer be used		DLC, graphite-like carbon	DLC, i-C, diamond, amorphous diamond	Me-DLC, DLC	DLC, a-DLC, hard carbon	DLC	DLC, Me-DLC, Me-C:H, MeC:H, metal-carbon	DLC	PCD, PD, NCD	PCD, PD	PCD, PD	Diamond ceramic, TFD	Diamond ceramic	
Deposition methods	PA-CVD	PVD	PVD	PVD	PVD, PA-CVD	PVD, PA-CVD	PVD + PA-CVD, PA-CVD	PVD + PA-CVD, PA-CVD	Activated CVD	Activated CVD	Activated CVD	Activated CVD	Activated CVD	CVD, PVD

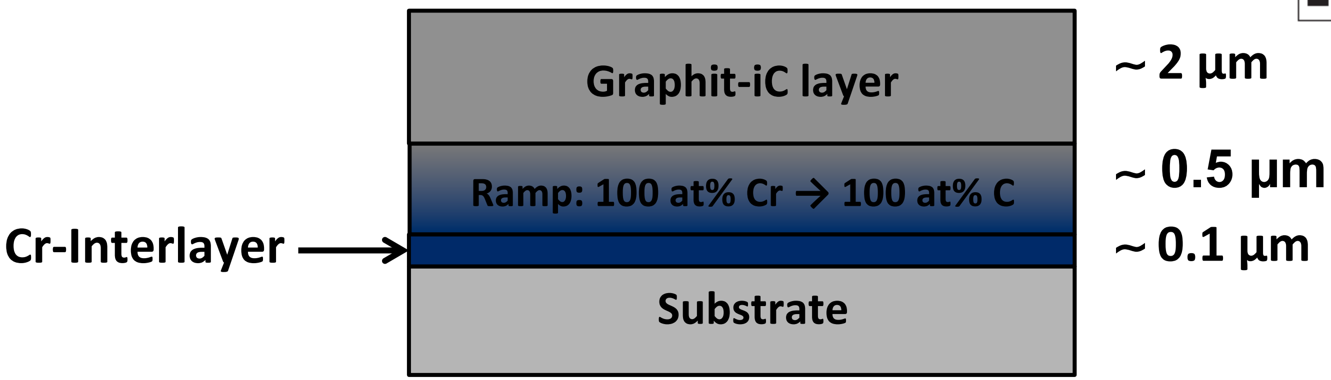
High Temperature DLC Deposition

Deposition parameters:

- Unbalanced magnetron sputtering
- Ar-plasma
- Temperature: < 200°C
- Rotation: 8-10 rpm
- Bias: - 60 V / pulsed 50 kHz
- Deposition Pressure: 0.3-0.4 Pa
- Substrates: M42 tool steel, Si (100)



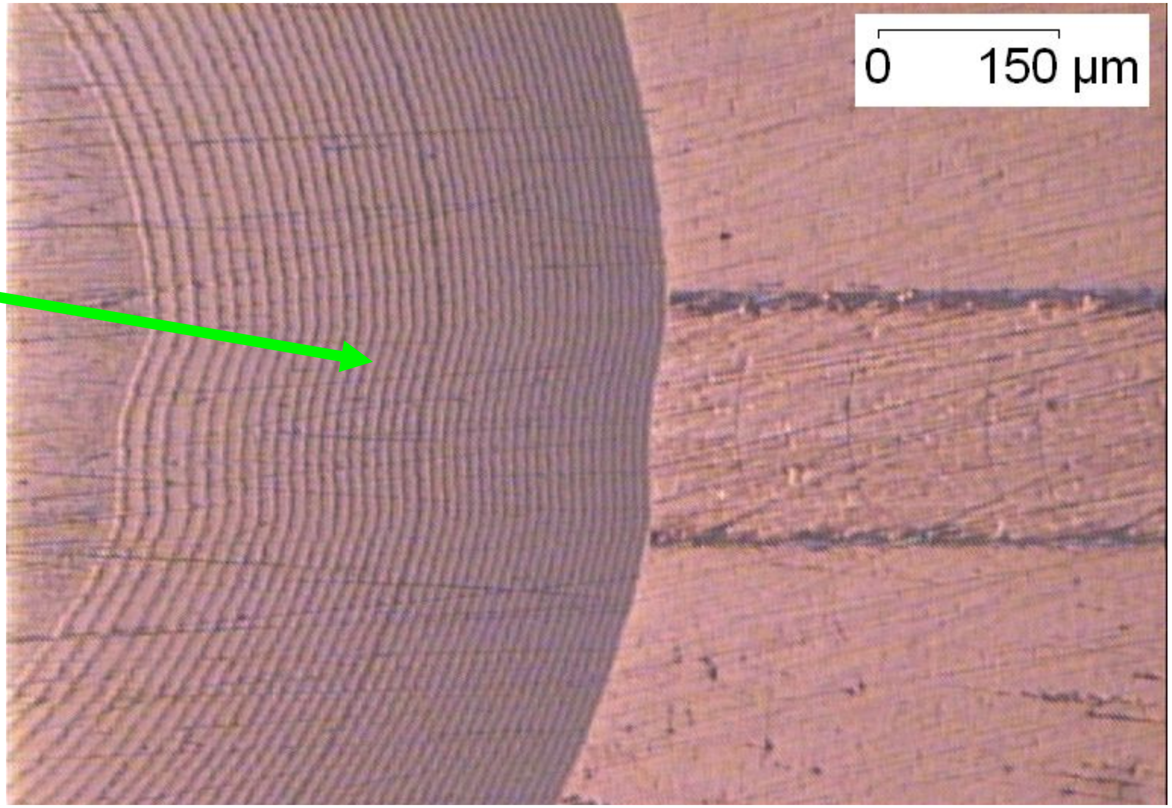
Coating architecture



Increase of loadability with Multilayer

Example of a multilayer structure

- Multilayer structure



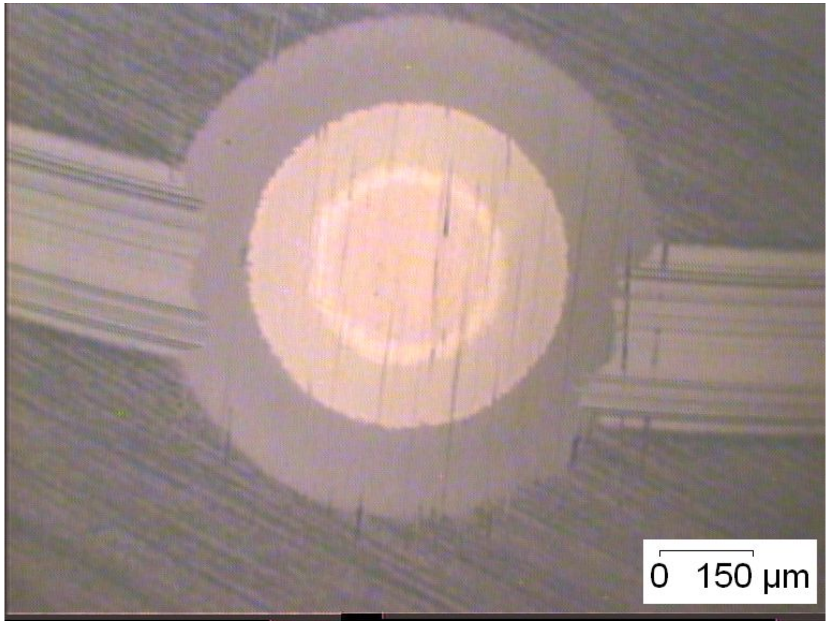
- Crack stops in the ductile multilayer

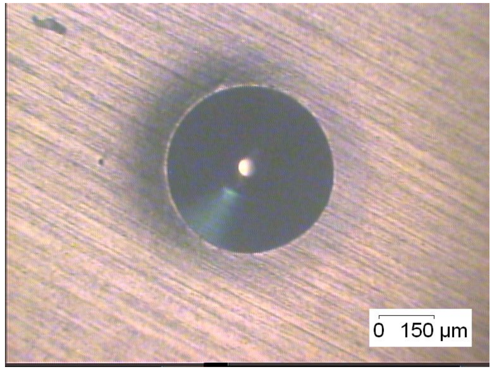
HT DLC Pin on disc - Rockwell

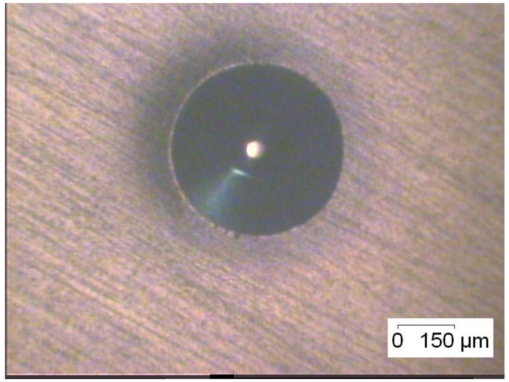
CrN =1.51µm, Gr-iC =3.30µm   Total = 4.81µm

POD at 80N Spec Wear rate = 4.26 x10^{-17} m^3/Nm

Hardness : 2080 HV (Calculated)

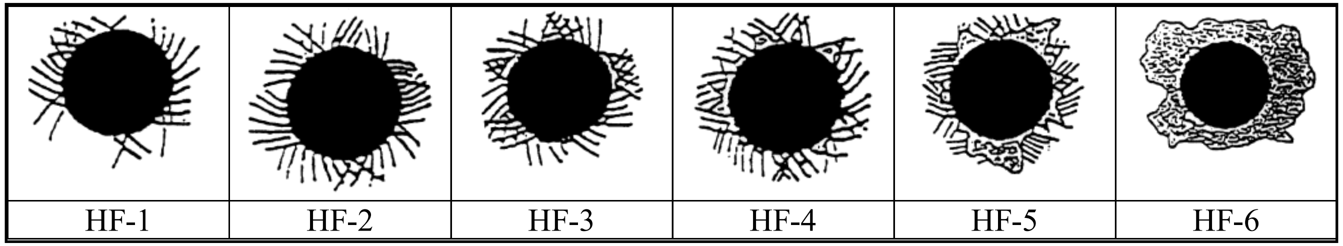


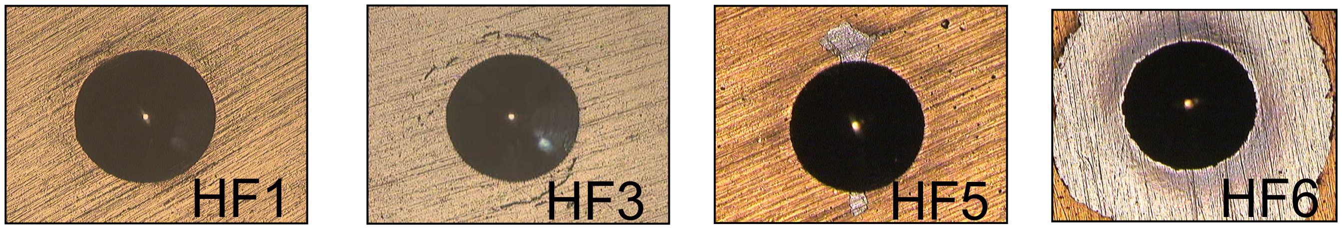




Rockwell C Adhesion Test

- Adhesion criteria developed by the Union of German Engineers (VDI)





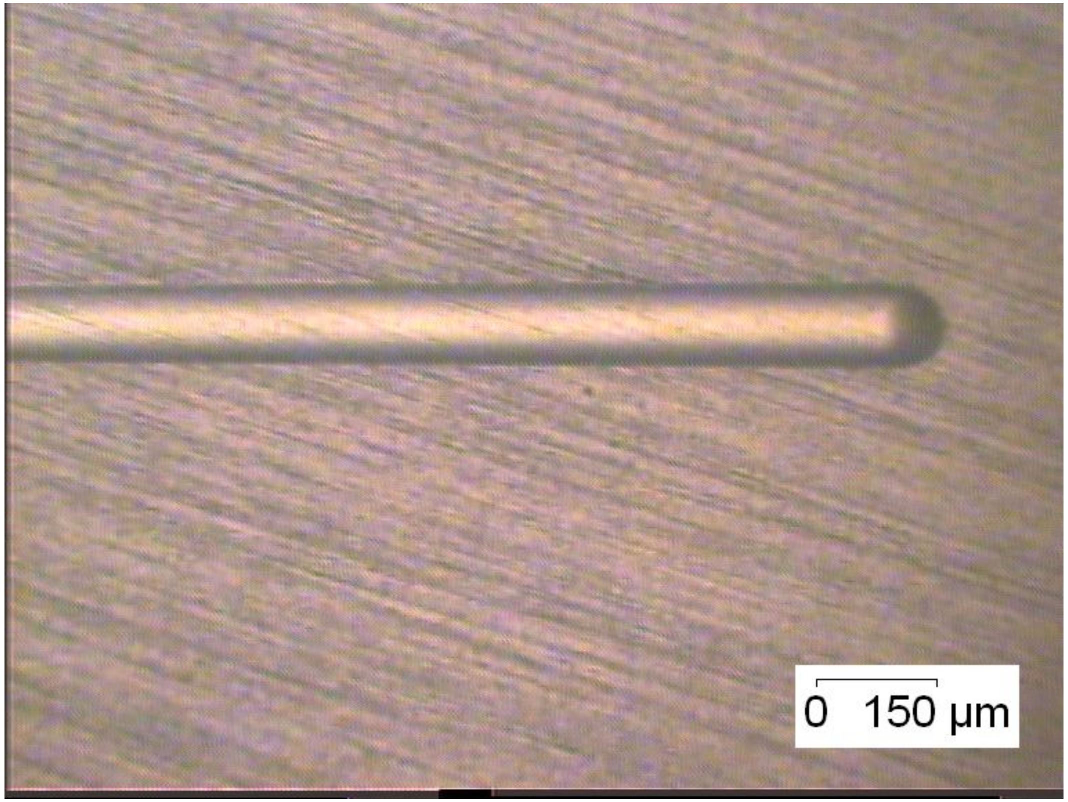
Test parameters:

- Substrate hardness min. 54HRC
- Coating thickness max. 5µm
- Magnification x100

HT DLC – Scratch Test

CrN =1.51µm, Graphitic_iC_HT =3.30µm Total = 4.81µm

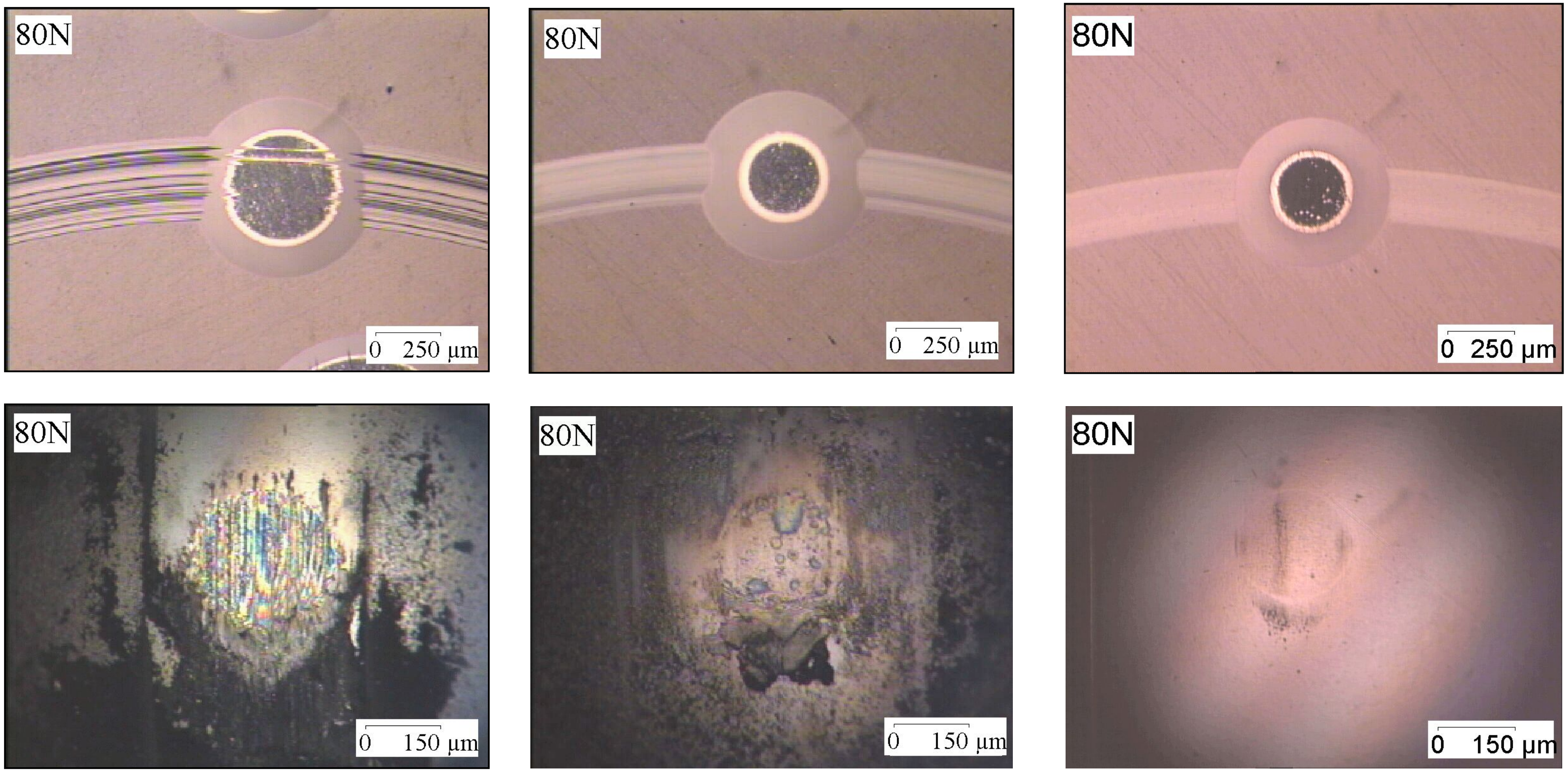
Scratch to 80N



HT DLC – Different Media

Pin on Disk Test Resultate bei 80N gegen WC-Co Pin

Air | **Water** | **Oil**

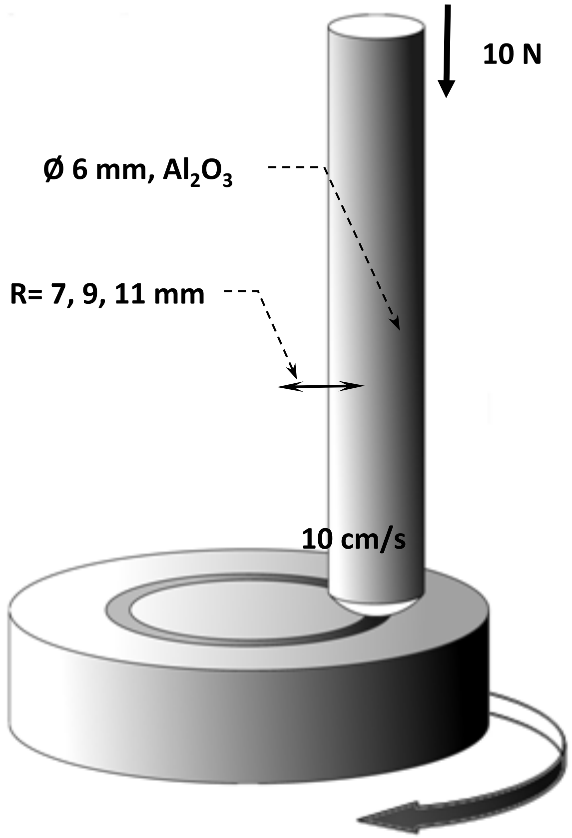


High Temperature DLC – Wear test

CSM Tribometer, Ball-on-disk configuration

Ball: Al2O3, 6 mm Ø
Load: 10 N
Temperature: RT, 250, 325, 400°C
Sliding distance:
  1000 m (RT)
  100 m (250, 325, 400°C)
Linear speed: 10 cm/s
Wear track radius:
  R = 7 mm (RT)
  R = 9 mm (250°C)
  R = 11 mm (325°C)

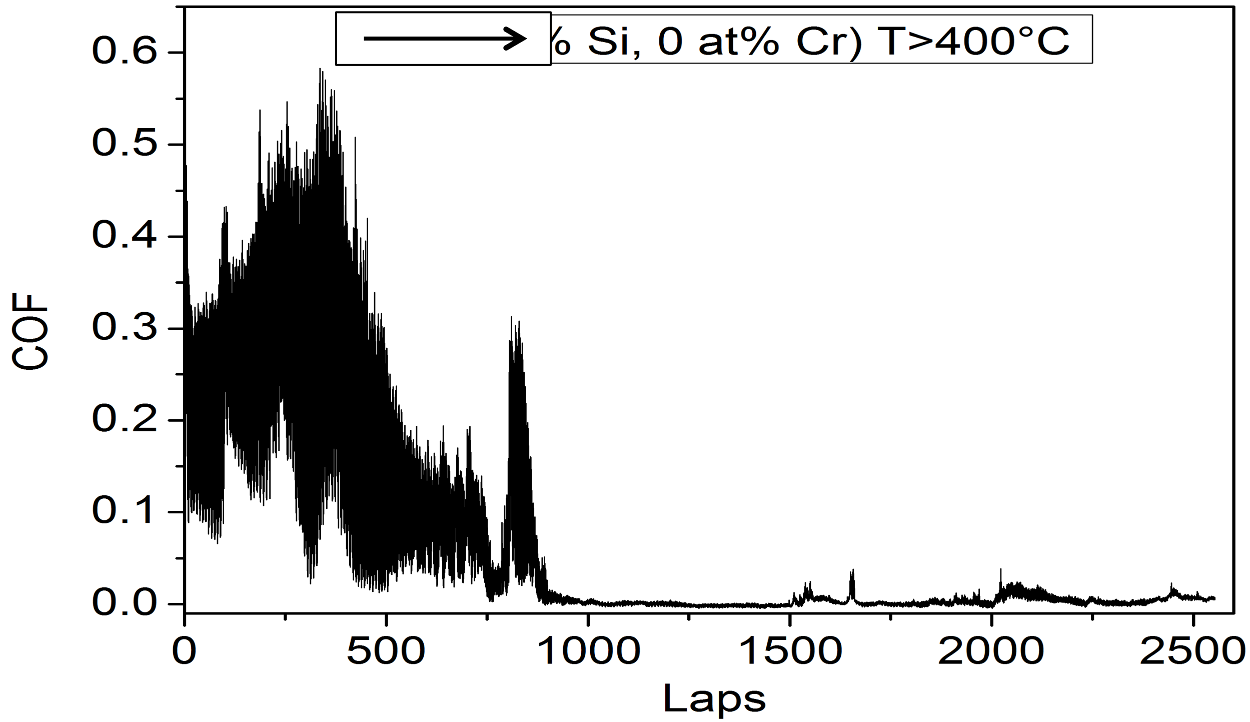
  R = 13 mm (400°C)
Acquisition rate: 10 Hz



Profilometer for wear track analysis

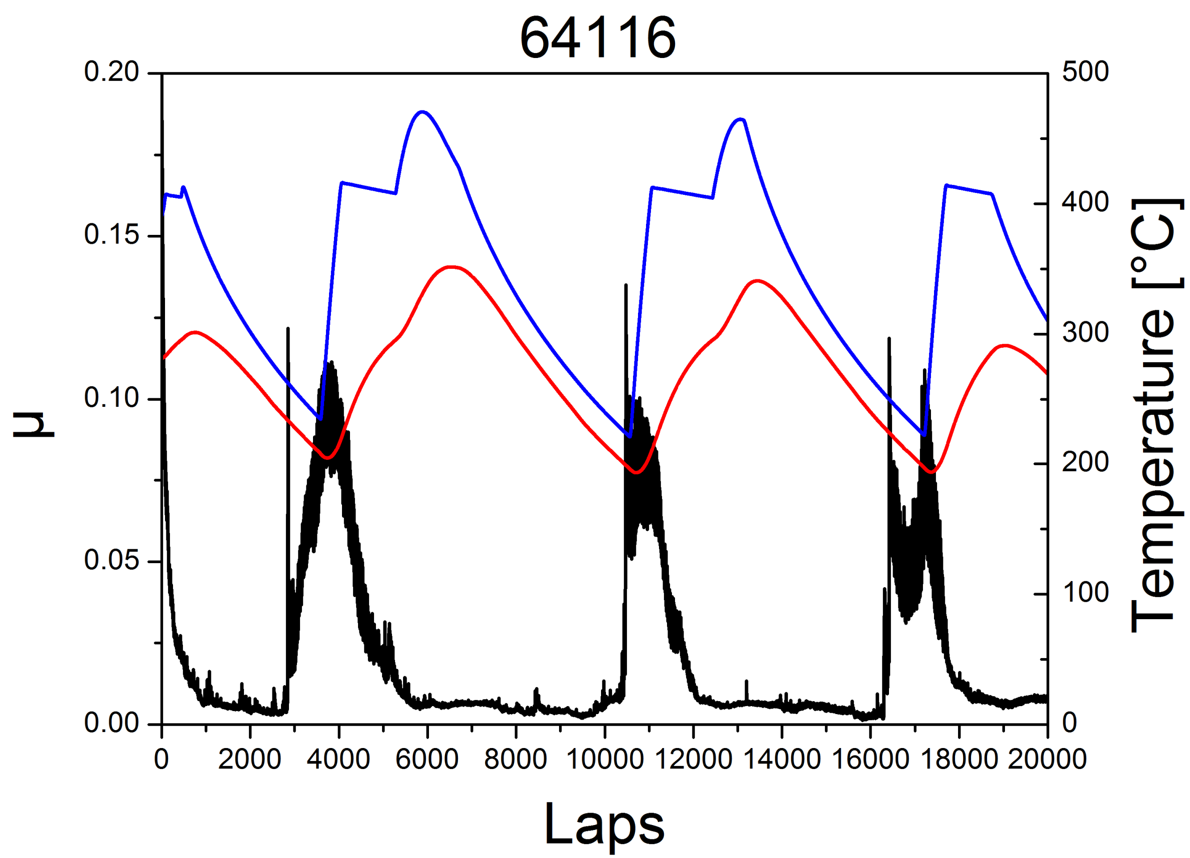
Veeco white light profiler
Calculation of the Wear Rate

HT_DLC Temperature > 400°C



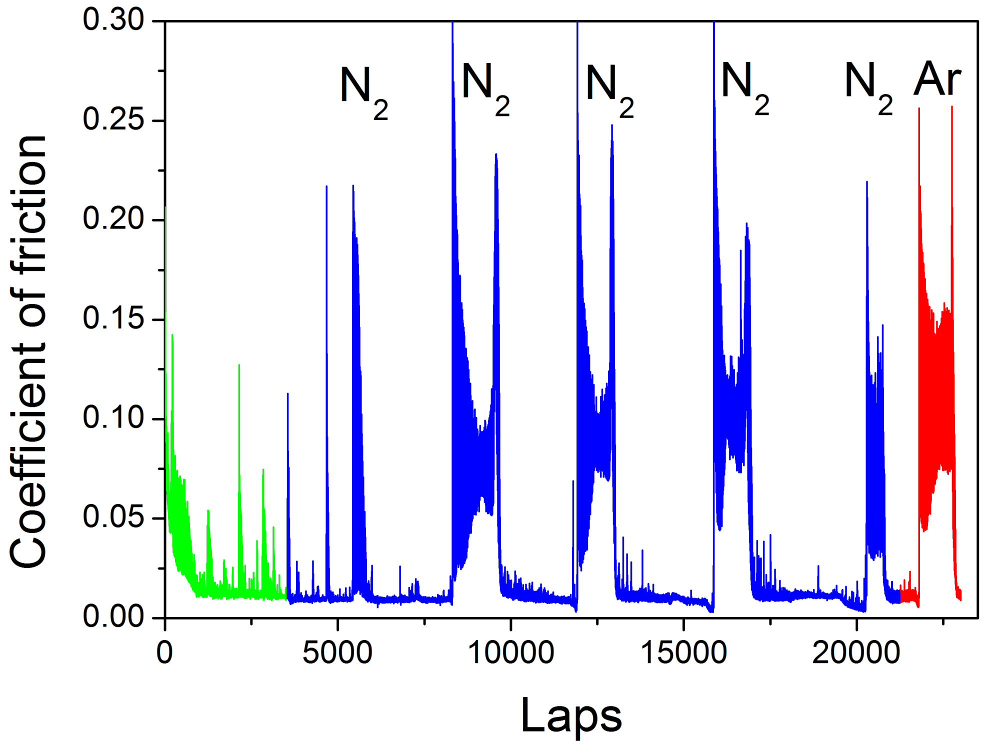
- Si addition leads to very low friction especially at T>250°C
- Si-O-C sliding film formation in oxygen containing environments
- Low friction effect is stable up to 450°C

HT_DLC – Temperature versus COF



- Si-O-C sliding film formation is thermally activated
- Increasing Si-Content → higher Tmin
- Temperature range of sliding film formation between 220 and 240°C

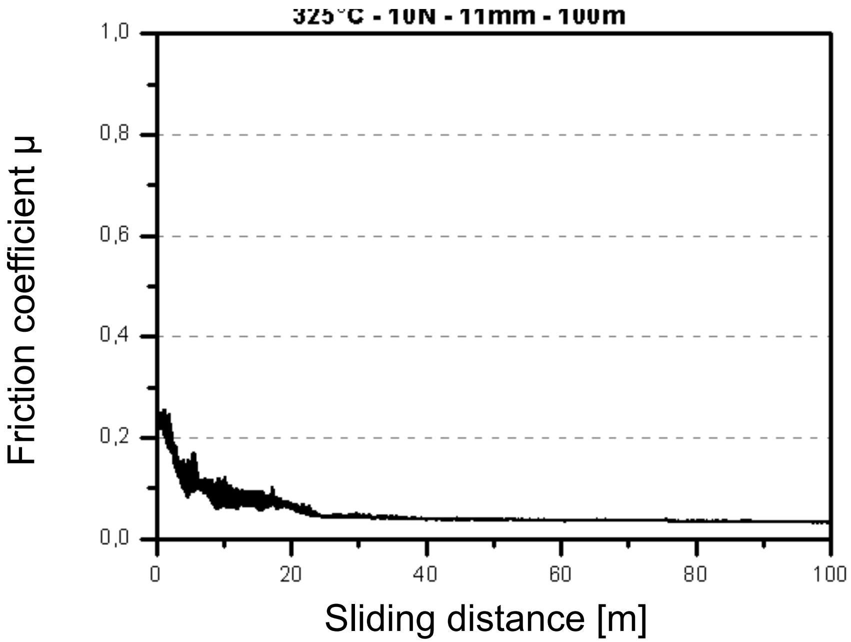
HT_DLC – Different gases versus COF

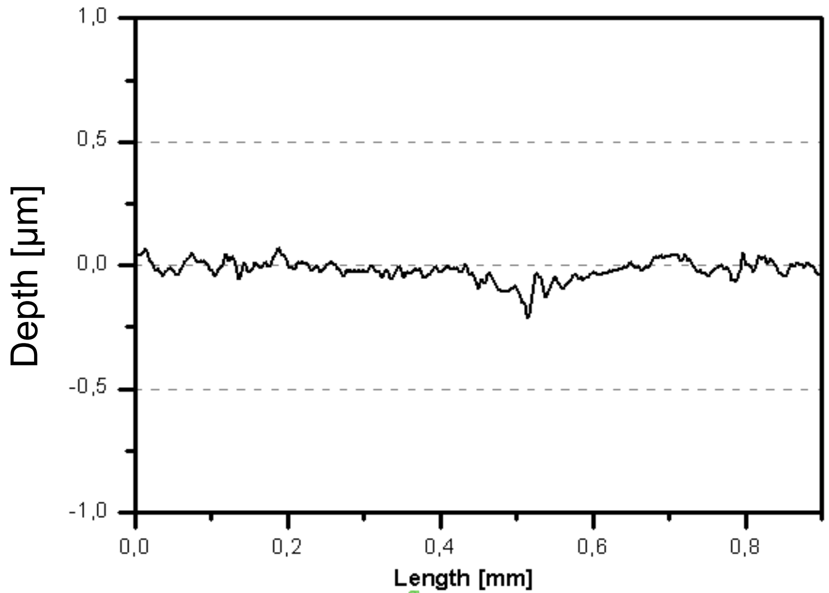


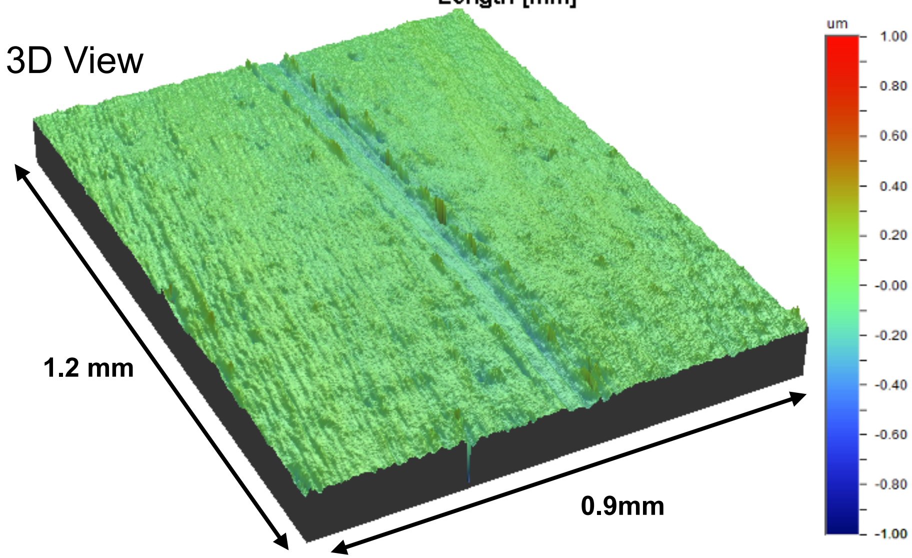
T=250°C

- COF in non-oxygen environments seems to be graphite-shearing dominated

Graphit-iC™HT (Hardness ~1900HV)







Ball-on-Disc Test:

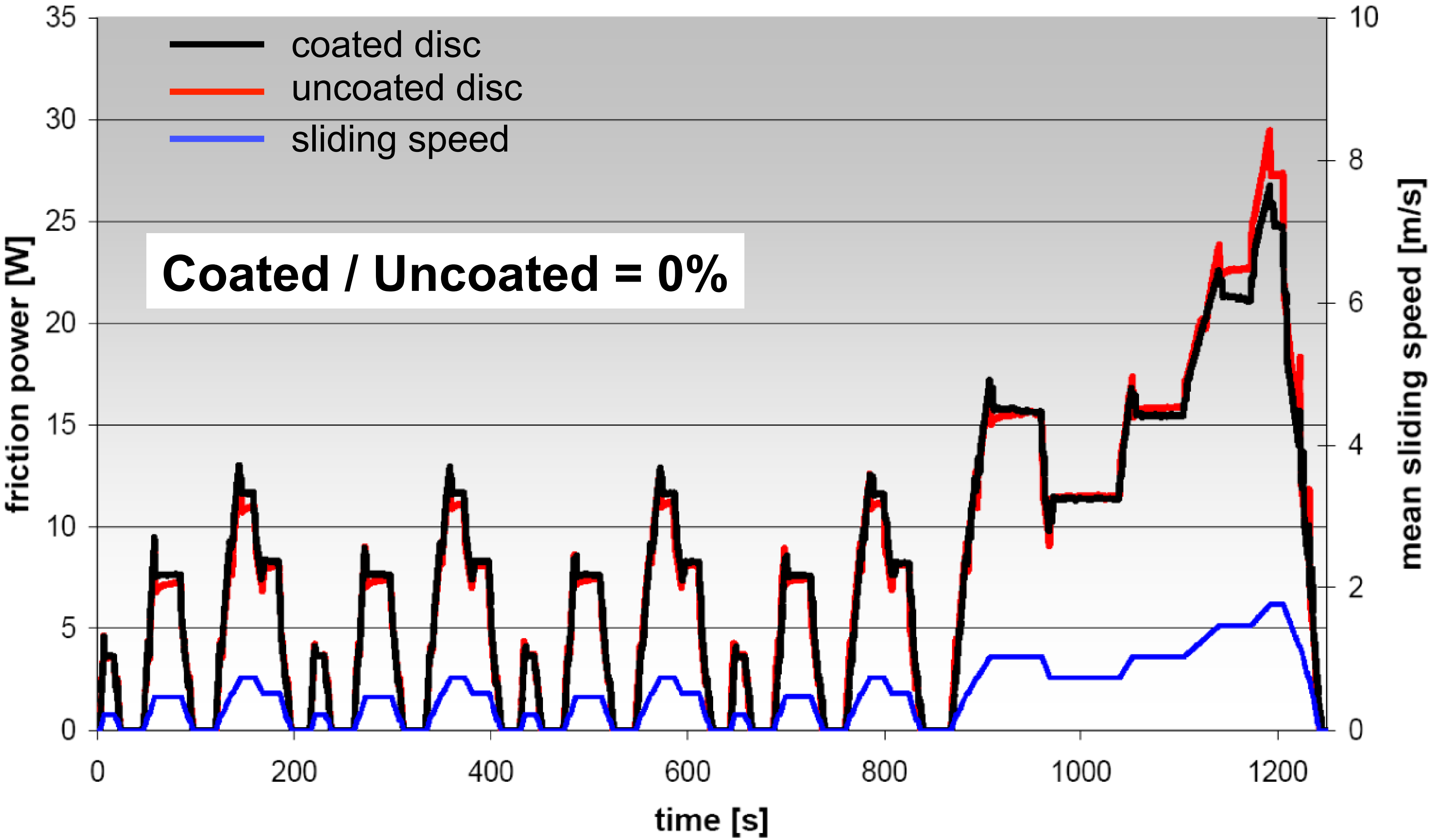
- Applied Load: 10N @ 325°C
- Friction coefficient ~ 0,05
- Very low specific wear

Innovation in Motion

100Cr6 Ring-on-Disc, 2MPa, 25°C

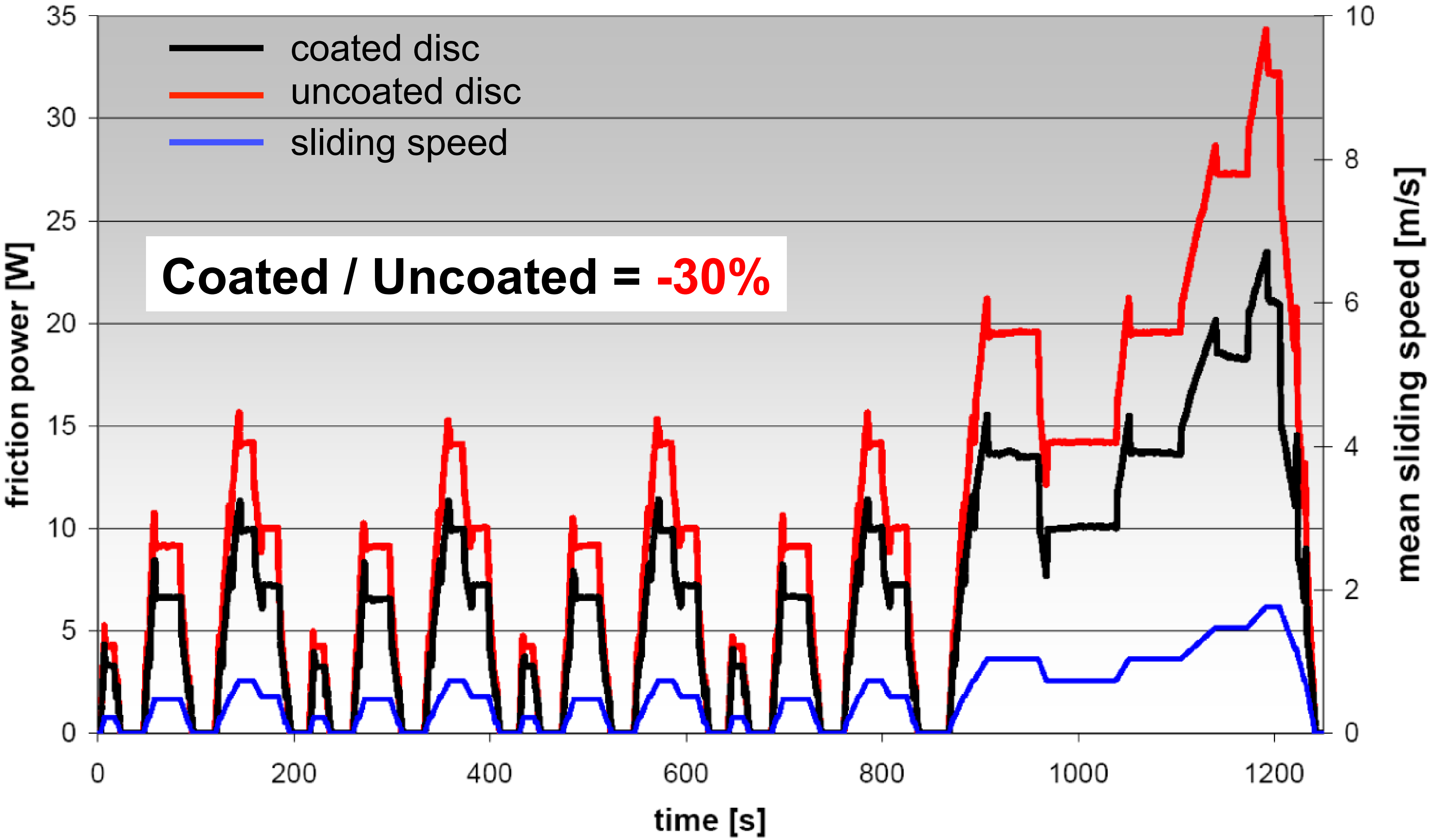
Confidential

Oil: Shell Helix Ultra (5W30)



100Cr6 Ring-on-Disc, 2MPa, 120°C

Oil: Shell Helix Ultra (5W30)



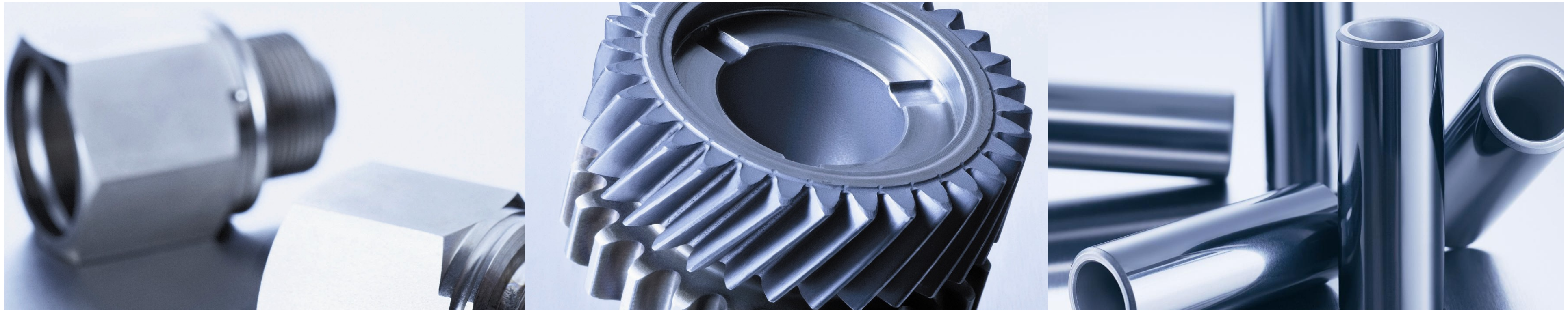
Possible application

- Piston Pins
- Piston skirt
- Liner
- Tappets
- Valves
- Cam
- Conrod
- Camshafts
- Turbocharger cmponents

Agenda

Innovation in Motion

Confidential

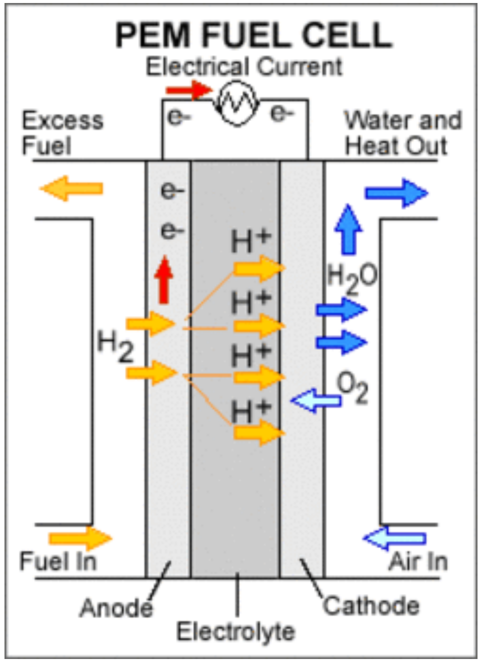


- Motivation
- High Temperature DLC
- **Coatings for Fuel Cell Applications**
- Summary

Hydrogen PEM FuelCells and Bipolar Plates

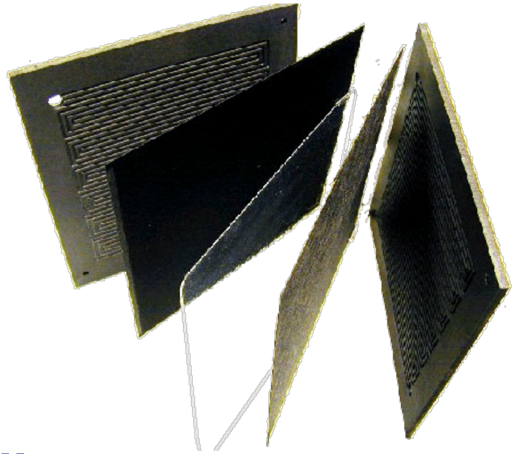
The numerous applications and the environmental movement are triggering the market demand

- **backup power**
- **Automotive market**
- **Portable devices**



Hydrogen PEM FuelCells and Bipolar Plates

- **Numerous functions to perform**
  - **Separation of gases between single cells**
  - **A solid structure for the stack**
  - **Current collection**
  - **Uniform distribution of reaction gases**
  - **Water and heat management out of the cell**



- **Contribute a significant proportion of**
  - **Cost; Weight; Volume**

- **Can have dramatic effect on fuel cell performance**

Metallic Bipolar Plates

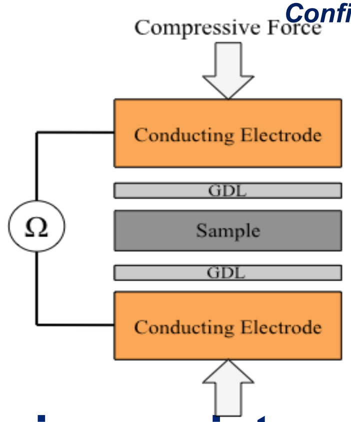
- **Good mechanical strength; electrical conductivity; thermal conductivity**
- **Can be easily and consistently manufactured to accommodate flow patterns**
- **Can be recycled**
- **Need high corrosion resistance**

1. **Acidic environment, pH3-5; Oxidising gases, O2 from air; Also at 0-1000mV**
2. **Sulphate and fluorine ions from Nafion membrane degradation**
3. **Operating at 60-120°C**

Metallic Bipolar Plates

- **Metal ions from corrosion process migrate to membrane**
- **This reduces lowers the ionic conductivity of the membrane and poisons the catalyst, therefore reducing fuel cell performance**
- **Any corrosion layer may reduce electrical conductivity of plates**
- **Therefore increase voltage loss of fuel cells due to higher electrical resistance**

Experiment and testing



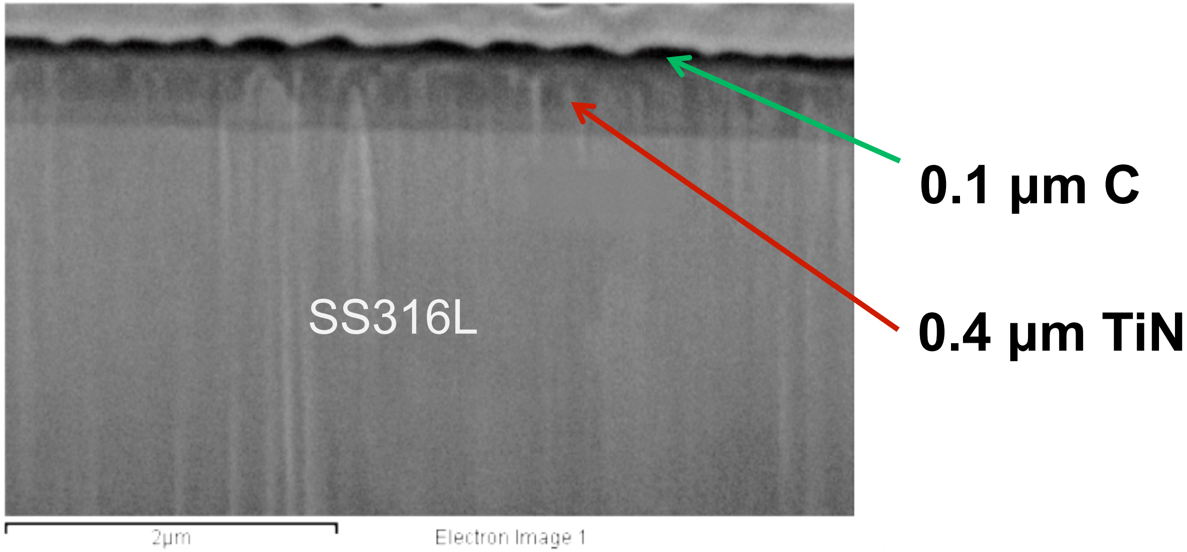
- **Interfacial contact resistances (ICR)**
  measuring area: 4x4 cm2
  GDLs: Toray H120
  compressing pressure: 140 & 20-280N/cm2
  recording time: after 300sec.

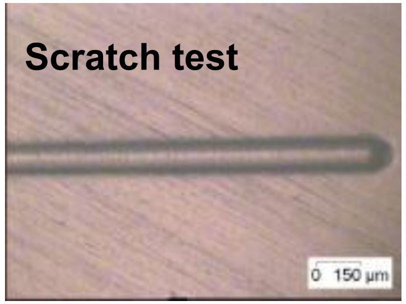
- **Potentiodynamic electrochemical testing (corrosion resistance)**
  measuring area: 1 cm2
  electrolyte: 250 ml of 0.5M H2SO4.
  bath temperature: 70°C
  bubbled air or H2
  reference electrode: Hg/Hg2SO4/K2SO4sat (MSE),(0.68V vs SHE)
  scan rate: 1 mV/s

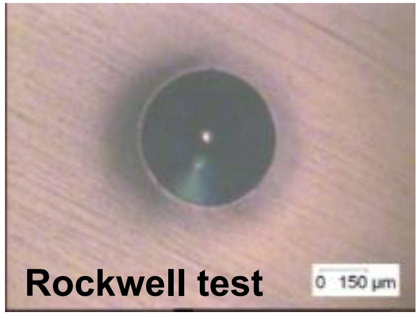
- **AFM and Roughness analysis**
  Atomic force microscopy (AFM)
  FIB-SEM

Coating Structure and Adhesion

Typical TiN+C coating

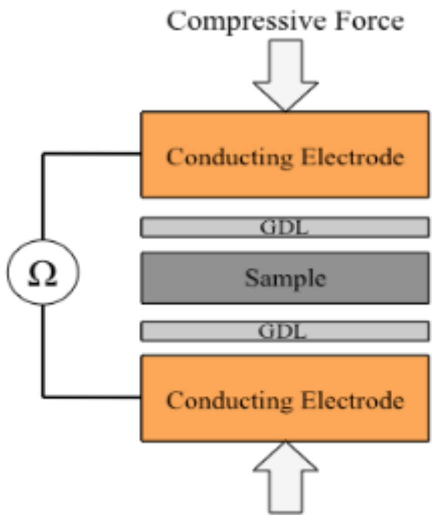




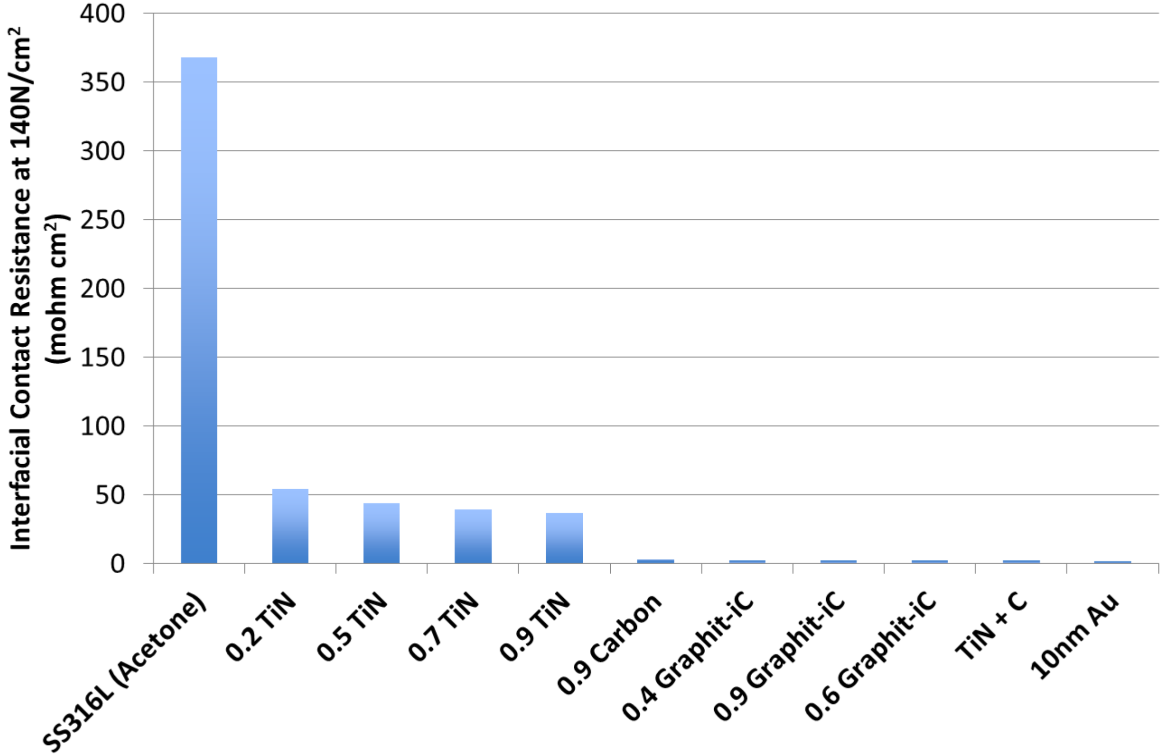


- **Good adhesion and cohesion on M42 witness sample**
- **Typical coating thickness: TiN (0.4 µm) + C (0.1 µm)**
- **Hardness of the coating: Hp=~2,000 Hv**

Interfacial contact resistances (ICR) -1

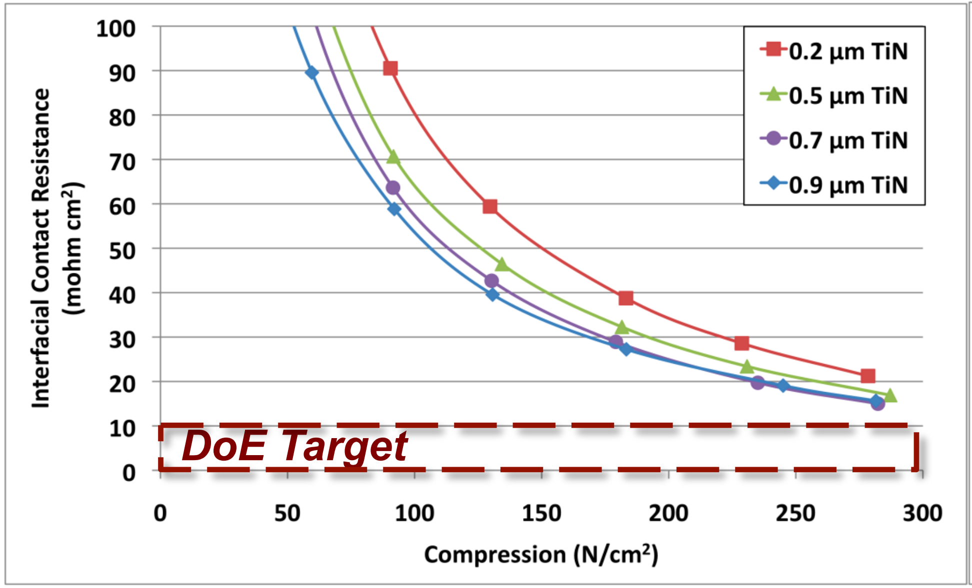


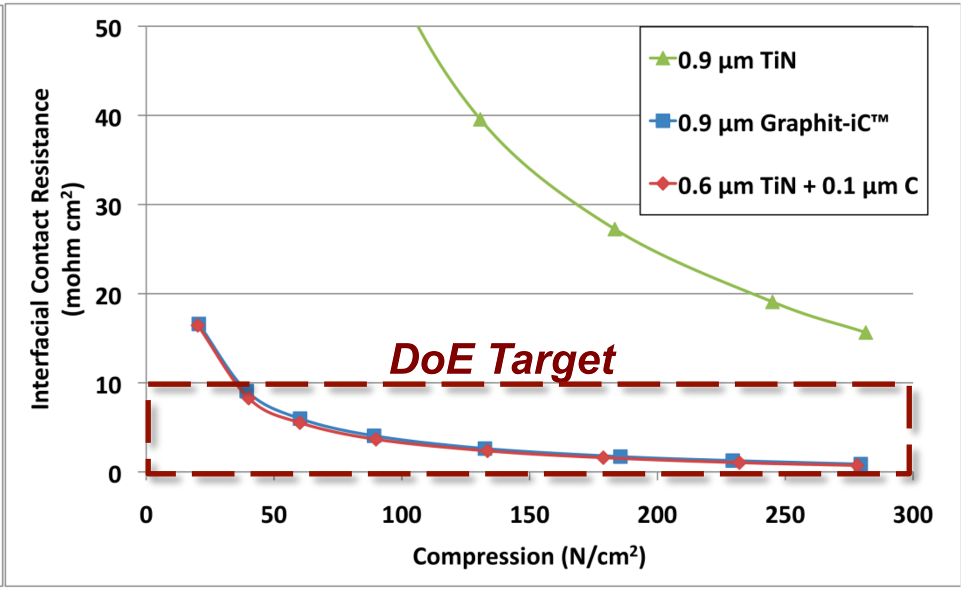
16cm^2 in area, total resistance under a particular pressure; usually 140Ncm^{-2}



- **Uncoated AISI 316L plate: highest ICR value of 368 mΩcm2;**
- **TiN coated plates : lower in value, in the range 30-50 mΩcm2**
- **In particular, the C and Graphit-iC™ coatings : approaching the value of the 10 nm Au thin film, 1-2mΩcm2 meeting the DoE target of <10 mohm cm2**

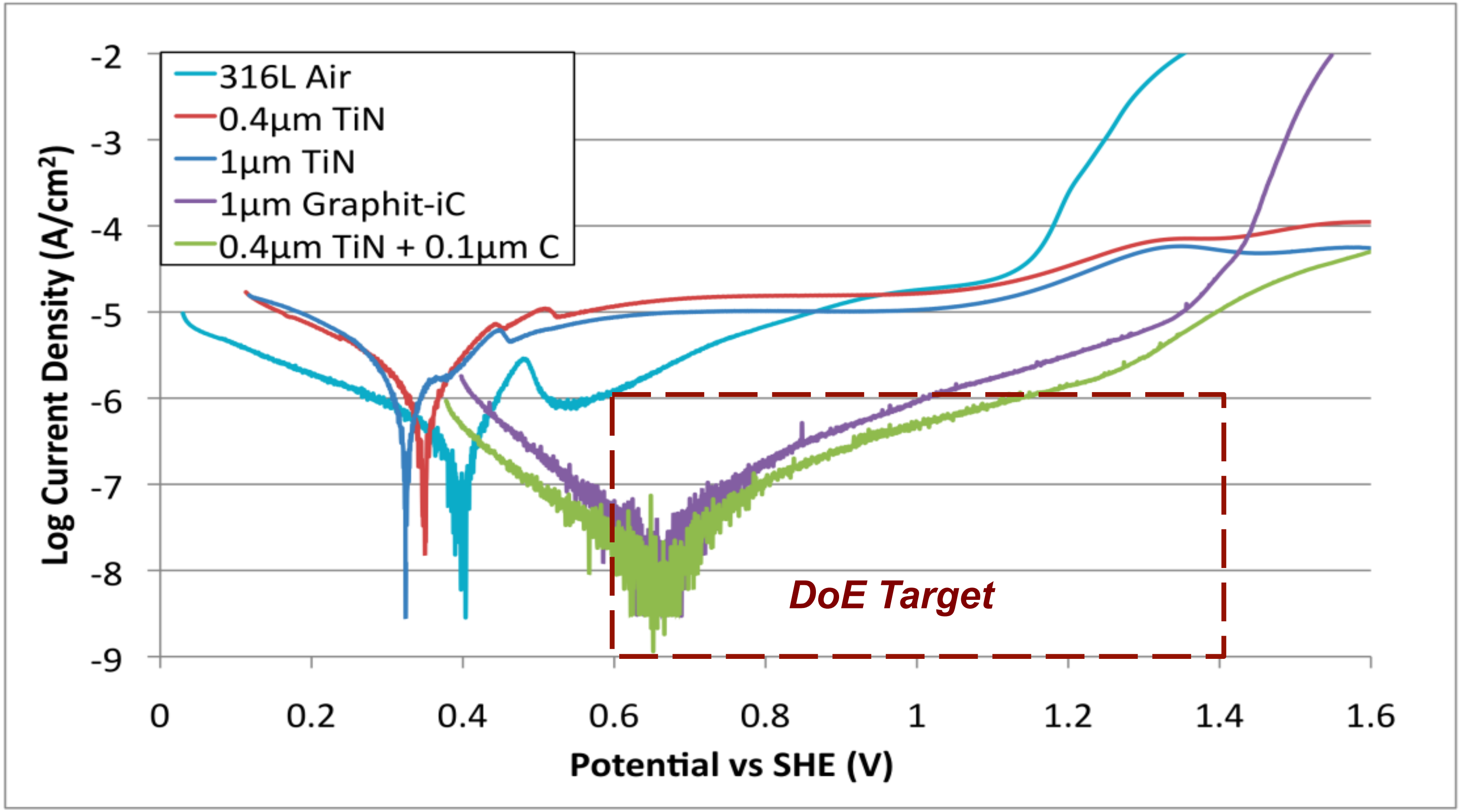
Interfacial contact resistances (ICR) -2





- **Typical behaviour : ICR decreases as the pressure is increased.**
- **Small change in ICR with [the change of the] TiN coating thickness between 0.2 and 0.9 µm, under a pressure range of 30 to 170 Ncm-2.**
- **C coating on top of the TiN coatings reduce the ICR value further to similar values as seen for the single layer Graphit-iC™ coating**

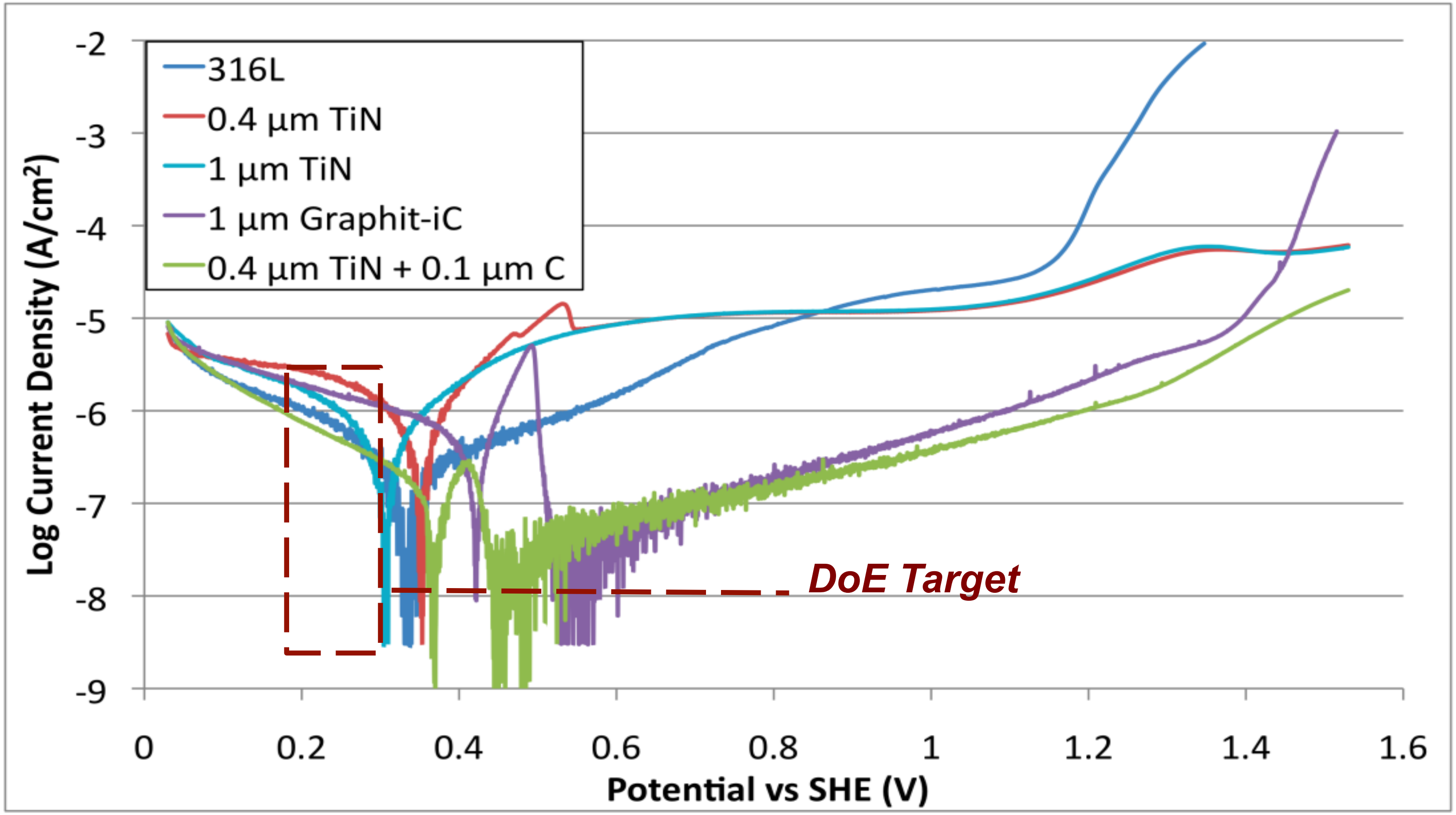
Electrochemical Characteristics



(a) Simulated cathode with bubbled air

Potentiodynamic curves at 1 mV/s obtained from samples in 0.5M H_2SO_4 solution at 70° C

Electrochemical Characteristics



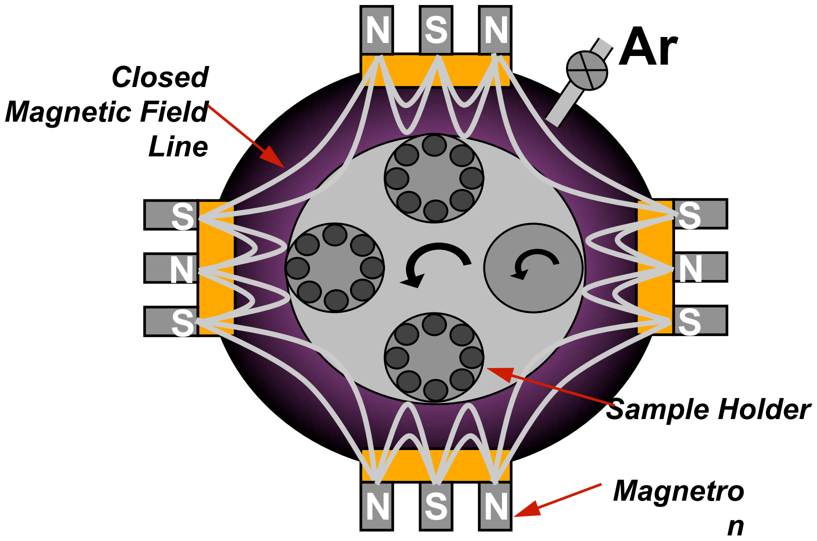
(b) Simulated anode with bubbled hydrogen

Potentiodynamic curves at 1 mV/s obtained from samples in 0.5M H_2SO_4 solution at 70° C

Electrochemical Characteristics

- **Increasing the thickness of TiN coatings only improves the corrosion resistance marginally.**
- **Graphit-iC™ coatings improve the corrosion resistance of BPPs.**
-
- **The TiN+C coated 316L showed greater corrosion resistance than the Graphit-iC™ coating, especially at carbon corrosion potentials of ~1.4V.**
- **Slight corrosion behaviour differences have been shown between anode and cathode conditions.**
- **At the stable stage, TiN+C > Graphite-iC > TiN >> Stainless Steel**
- **TiN+C meets the DoE target of <1µA/cm2 under simulated cathodic standby (0.9V) and operating (0.6V) potentials, however it is still slightly too high in simulated anodic conditions**

Coating Equipment and Volumes



Coating equipment for different volume scenarios:

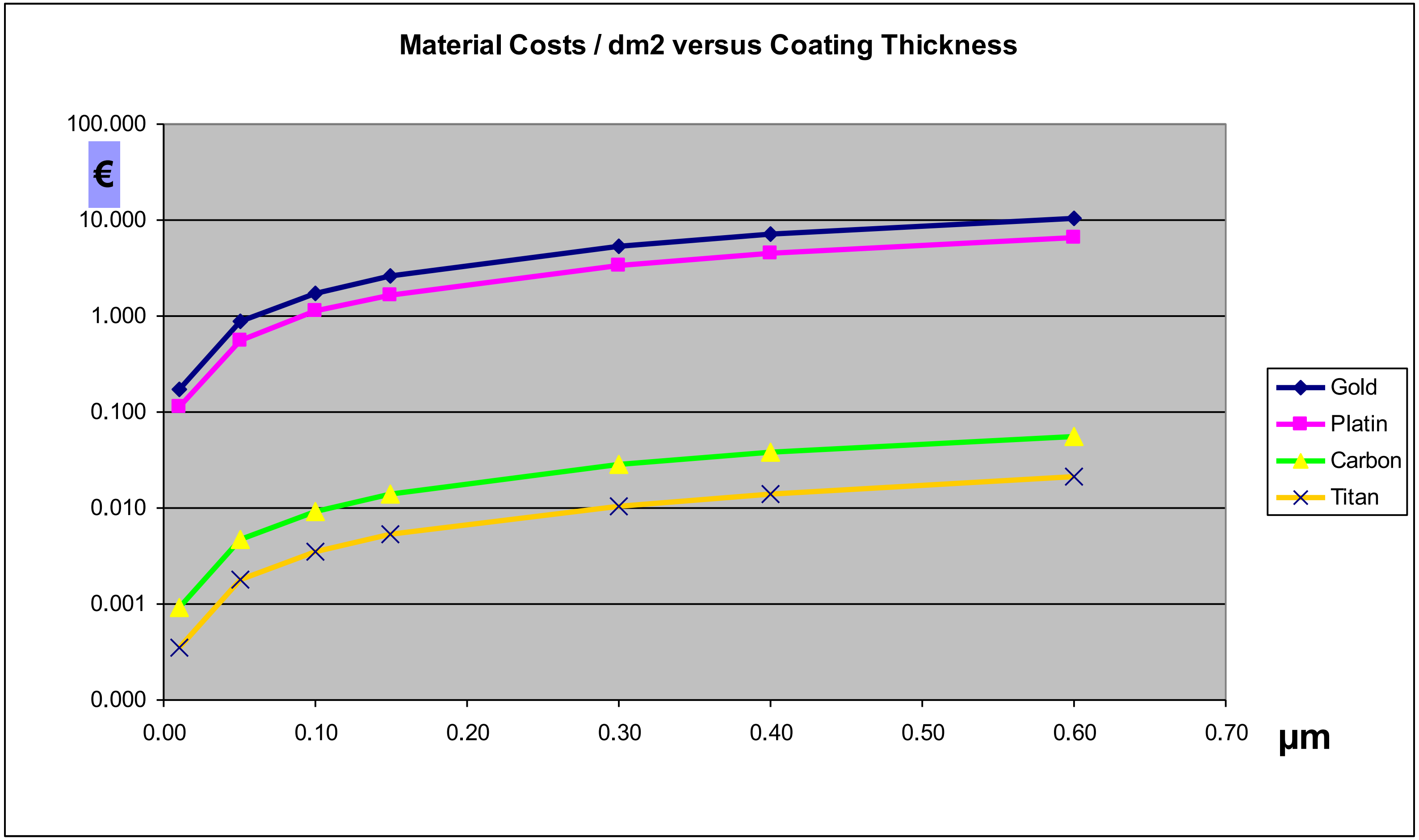
- **Equipment for prototypes and lower volumes**
- **Equipment for volumes up to 300k parts/year:**

In-line [device], air-to-air equipment with higher efficiency compared to conventional batch equipment

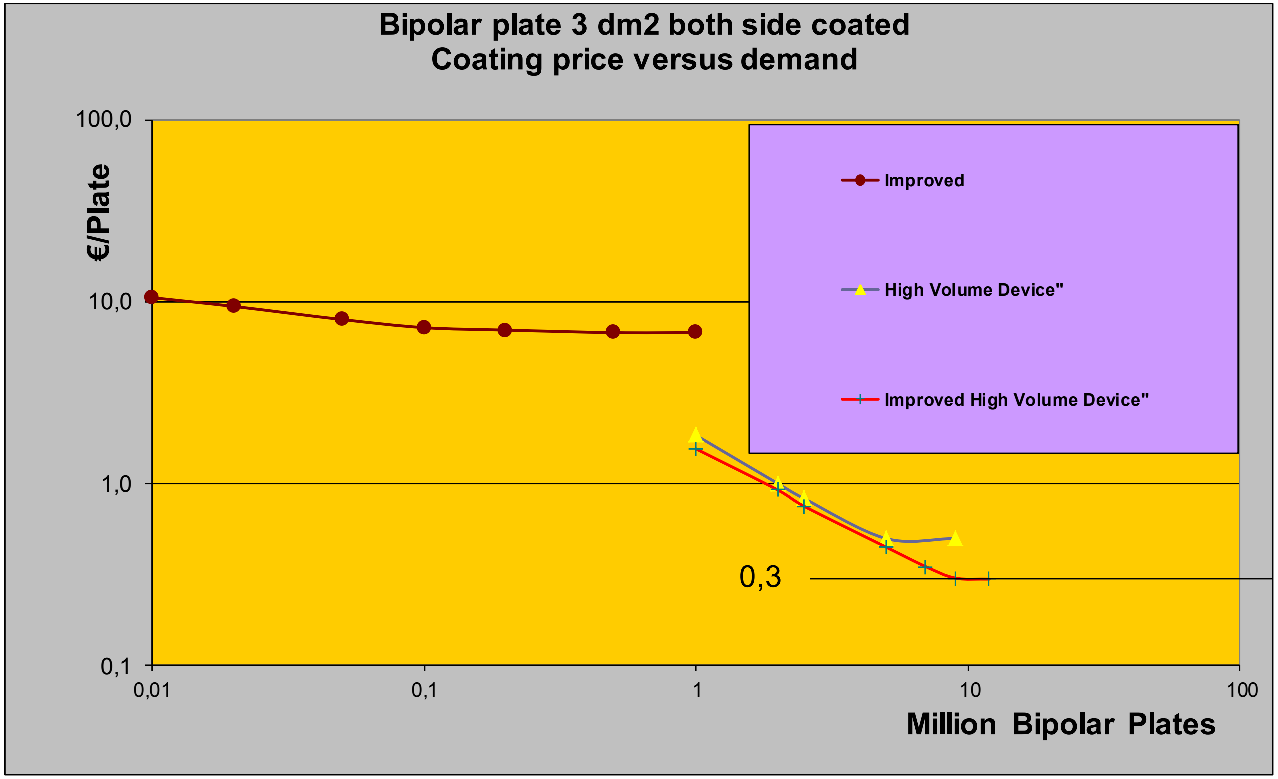
Innovation in Motion

Coating Material Cost Examples

Confidential



Coating Cost Estimation

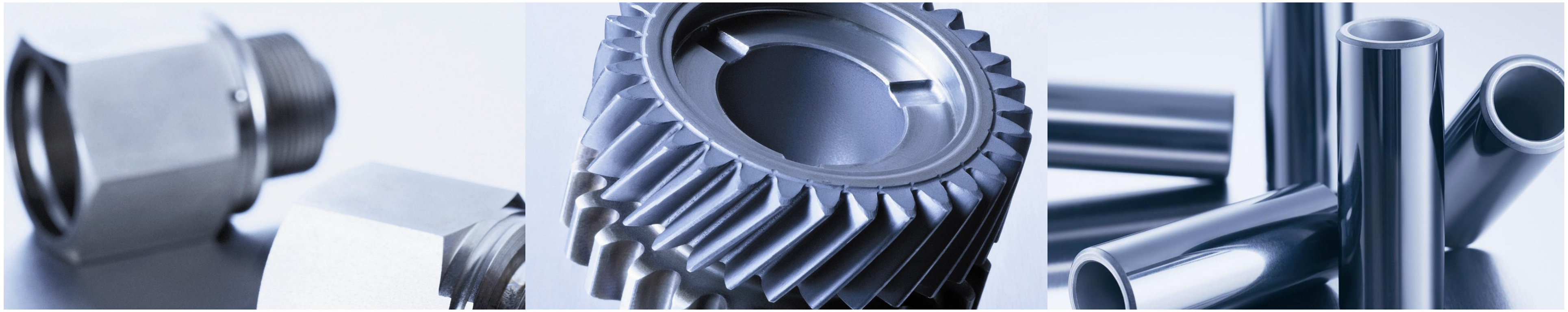


both side coated high volumes

< 10 € for 1 m^2

<0,12 $ for 1 dm^2

Agenda



- Motivation
- High Temperature DLC
- Coatings for Fuel Cell Applications
- Summary

Summary:

- Coatings, including TiN, carbon-based coatings, Graphit-iC™ or double-layer TiN+C coatings, can significantly reduce the interfacial contact resistance (ICR) of AISI316 stainless steel PEMFC bipolar plates.

- In comparison with the bare AISI316L plates, TiN coatings provide corrosion protection to the stainless steel BPPs under simulated PEMFC operating conditions

- Graphit-iC™ coatings offer much better corrosion resistance for both the anode and cathode.

- TiN+C coatings offer the best performance so far from all the potentiodynamic polarization tests carried out under the bubbled air and hydrogen gas in an acidic solution [to] which simulates the PEMFC [the] cathode and anode environments respectively.

Summary

- Reducing CO2 emission is one of the top priorities for the automotive industry and us
- Coatings technology is a key for reduction of friction
- Tailor made coatings are also a key driver for automotive fuel cell applications
- Regarding Performance and Costs

Thank you for your attention. Questions ?