Issue 139 | August 2022

THE Journal

PCMI
Photo Chemical Machining Institute

Technical Journal August 2022

This Journal contains the technical papers and presentations from the PCMI Spring Technical Conference held in Cologne, Germany from May 8 - 12, 2022

INTERNATIONAL
TECHNICAL CONFERENCE
OCTOBER 8 - 12, 2022
PHOENIX, ARIZONA
PCMI

You are invited to attend the PCMI 2022 Fall Conference at the Hilton Phoenix Resort at the Peak, in Phoenix, Arizona, from October 8-12, 2022!

The program will feature technical and management sessions, networking with colleagues from around the world, a facility tour, and the opportunity to explore emerging PCM technologies.

SESSIONS IN DEVELOPMENT

Click on each session title to read the abstract.

- Automation Strategy for Wet Processing Equipment
- Commercial By-Products from Etching Process
- Current Developments and Improvements Using Zapp MicroEtch and Zapp SuperEtch: A Case Study
- Environmental Concerns and Trends Panel Discussion
- Front End Processing - Pre-Cleaning
- Future of Film – Moving Forward
- Group Discussion | Drying Small Parts
- Improving Efficiency & Profitability inside a Clean Room
- Improving Dry Film Adhesion in the Photo Chemical Milling Process
- Manufacturing Demand from a Customer's Perspective
- New Member Product and Service Showcase
- Strengthening the Weakest Links in the PCM Process Chain: #5 Cleaning/Metal Preparation Before Lamination
- Welcome to Phoenix
- What to Expect During the PMA Facility Tour on Tuesday, October 11, 2022

CLICK HERE TO REGISTER

MORE INFORMATION

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The PCMI Journal is the official publication of the Photo Chemical Machining Institute. Its purpose is to serve the needs of the PCMI members: to keep them up-to-date on activities of the PCMI, and to provide technical information about the industry. To make the PCMI Journal as valuable as possible, we ask that members contribute technical articles and newsworthy items, including new material on state-of-the-art photo chemical machining – equipment, techniques, etc.

We also accept articles that have appeared in other publications if they are relevant to our members. All material should be forwarded electronically in PDF format to: cflaherty@pcmi.org

Advertising is accepted for both the PCMI Journals and the annual PCMI Membership Directory.

For information concerning ad deadlines, formats, sizes and rates contact the PCMI Office:

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Letter From the President

Greetings, PCMI Members!

I hope you have managed to stay cool during the high heat that seems to have enveloped the globe this summer.

I also hope you are managing to overcome the challenges posed by the ongoing supply chain issues, labor shortages, and travel interruptions we have all experience during the last few months.

While I know we are in vacation season, please take a few moments to review the agenda for the upcoming PCMI Conference in the United States from October 8th – 12th in Phoenix, Arizona.

The Fall Conference Committee has developed a terrific line-up of technical and management sessions that will enhance your knowledge of photochemical machining, fortify your management acumen and provide opportunities for networking with your friends and colleagues in the PCM industry.

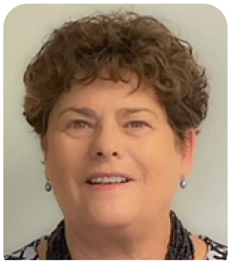
While some concern remains regarding new COVID variants, we are moving full speed ahead with plans for the Fall Conference. PCMI's priority is our members' health and safety, so we will remain vigilant on new developments and ensure that the hotel adheres to local guidelines, if there are any in effect during the conference.

I could not attend the recent PCMI Conference held in Germany, but by all accounts, it was a tremendously successful in-person learning experience after so many Pandemic-related postponements. I am confident the Fall Conference will be equally successful, and I look forward to seeing you in Phoenix.

In closing, I want you to know that your PCMI membership is valued, and I thank you for your continued support of our industry Institute.

Sincerely,

Peter Jefferies
PCMI President
Heatric, a Division of Meggitt



Hello PCMI Members,

I hope you are enjoying the warm weather and summer holidays!

We are pleased to present this PCMI Summer Technical Journal, which contains the technical papers and presentations from the PCMI Spring Technical Conference held in Cologne, Germany, from May 8 - 12, 2022.

The Spring In-Person Conference was a successful technical program and networking event after many COVID-19 postponements. For this success, we wish to acknowledge the work of the Germany Conference Committee, which included:

- David Allen, Cranfield University
- Steffen Herz, Ätztechnik Herz GmbH & Co Kg
- Peter Jefferies, Heatric, Division of Meggitt
- Lawson Lightfoot, Lightfoot Consulting
- Paul Campbell, Zapp Precision Metals GmbH
- Paolo Iellici, Lasertech Srl
- Eric Kemperman, Etchform BV
- Claudia Schemann, Metaq GmbH

We also want to give special recognition to Paul Campbell and his colleague Michaela Heinrich from Zapp Precision Metals GmbH. Together they worked tirelessly on behalf of PCMI to ensure that the social programs, tours, and events were organized and went off without a hitch. We are grateful for their assistance.

Moving forward, we are excited to see our PCMI members again for the Fall International Technical Conference to be held at the Hilton Phoenix Resort at the Peak in Phoenix, Arizona, from October 8-12, 2022.

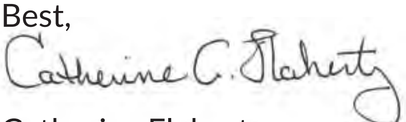
The technical sessions are designed to provide you with new knowledge and benefit PCM company management. The networking will allow you to interact, learn, and engage with your industry peers.

More information can be found in the Journal, on the inside front cover, and by clicking on **this link** which will take you to the PCMI Conference Website Page.

As you begin making your plans for the Fall Conference, do not hesitate to contact me directly if you need help or have questions. You can reach me at **cflaherty@pcmi.org** or in the US at 508-385-0085

I look forward to seeing you in Phoenix!

Best,



Catherine Flaherty
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Please Plan to Attend the

Building, Improving, and Maintaining an Efficient Cleanroom Webinar

December 1, 2022

11:00 am EST - 12:00 pm EST

Webinar Abstract

The content of the presentation focuses on the concepts of designing a cleanroom. Cleanrooms have been used for years in many industries, pharmaceuticals, optics, geospatial, food prep, research, semiconductors and many more. In these challenging times of pandemics, Indoor Air Quality has been brought to the forefront, not only in cleanrooms but all over. This presentation will have a special focus on air flow, filtration, and maintenance that have always been a focus of cleanroom operations, but now these design ideas are being implemented in classrooms, gyms, offices, etc. A focus on cleaning the air to comply with many regulations of the CDC, WHO, IEST, ASHARE and other agencies. This is a confusing time for many, and this presentation is designed to provide education on new and older technologies and coordination with all these guidelines and regulations.

About the Speaker

Roger Zaccour is a Stark Tech's Cleanroom Solutions leader, delivering engineering expertise and solutions for controlled environments.

Mr. Zaccour has more than 20 years of experience and knowledge in sterile and non-sterile cleanroom environments, providing customized solutions to meet ISO classification standards specified for each unique space. Mr. Zaccour is a highly dedicated and goal-oriented professional with extensive knowledge of building products and services and engineering. He possesses a comprehensive understanding of the construction process, including contract preparation, estimating, scheduling, and design, which is used to deliver turnkey cleanroom solutions.

All of the PCMI Webinar Recordings are Available for Purchase!

Click here to view the abstracts for recent webinars and contact Katie Burke if you wish to purchase a recording. Katie can be reached in the United States at 508-385-0085 or katie@pcmi.org.

Emeritus Professor David Allen started his career as a chemist (BSc, 1968) and moved into photochemistry research (PhD, 1972) while studying at Cardiff University. Following post-doctoral research at Warwick University and imaging technology development in industry, David joined Cranfield University in 1976. He was appointed a Technical Liaison Member to the Photo Chemical Machining Institute (PCMI) in 1981 and is currently on the Board of Directors of PCMI responsible for education. David became Professor of Microengineering at Cranfield University in 1998 and was elected as a Fellow of The International Academy for Production Engineering (CIRP) in 2006.

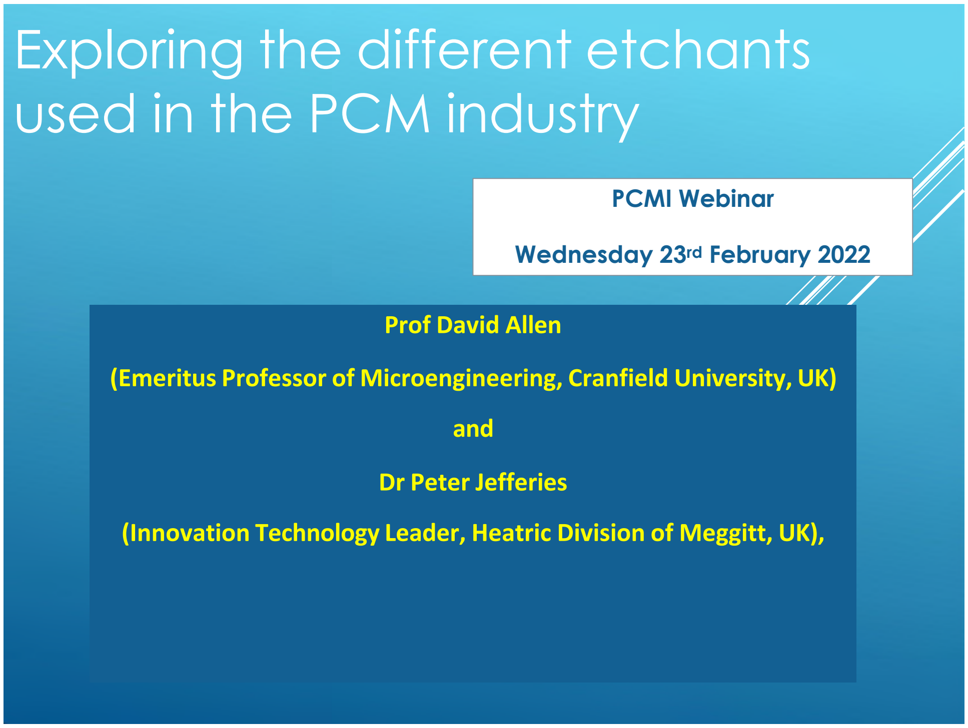
David has published:
- Two PCM books: “The Principles and Practice of Photochemical Machining and Photoetching” (1986) and “Photochemical Machining and Photoelectroforming” (2015, reprinted 2016, 2017 and 2019)
- Five book chapters on non-conventional machining and contributed the chapter on ‘Etching’ to the on-line CIRP Encyclopedia of Production Engineering
- Seven confidential industrial PCM consortium reports
- 202 journal and conference papers and was awarded the higher doctoral degree of DSc from Cranfield University in 2013 for his thesis entitled “Contributions to Photochemical Machining and Photoelectroforming”.

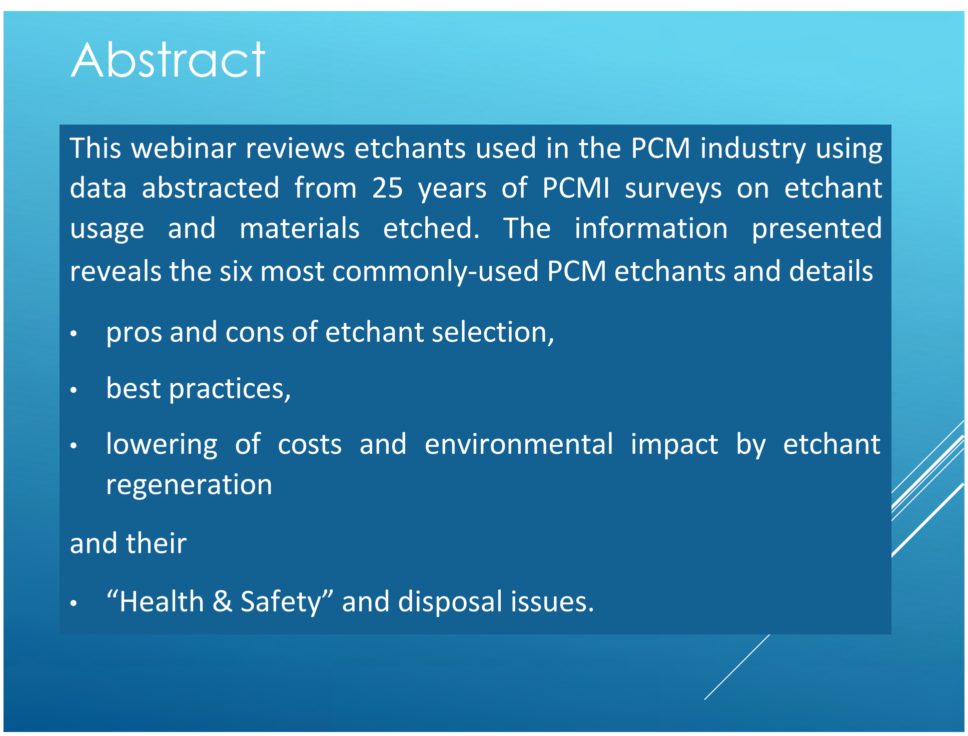
David retired from academia in 2011 and he now carries out consultancy and staff training in PCM companies across the world. He has worked with 26 different companies over the past 10 years.

Dr. Peter Jefferies has over 40 years of experience in precision engineering by novel techniques, including manufacturing parts by chemical etching and electroforming techniques. This knowledge is further supported by sound business acumen, having held senior positions in several businesses and running his own technical consultancy. Academically Peters is one of a handful who has obtained three post-graduate degrees from Cranfield University.

Peter is currently working for the Meggitt Group as a consultant supporting Meggitt’s etching facilities around the globe.

Peter was elected to serve on the PCMI Board of Directors in 2014 and has served as President since 2020. Peter also serves on the Education Committee abd Conference, and Committees.


Exploring the different etchants used in the PCM industry
PCMI Webinar
Wednesday 23rd February 2022
Prof David Allen
(Emeritus Professor of Microengineering, Cranfield University, UK)
and
Dr Peter Jefferies
(Innovation Technology Leader, Heatric Division of Meggitt, UK),


Abstract
This webinar reviews etchants used in the PCM industry using data abstracted from 25 years of PCMI surveys on etchant usage and materials etched. The information presented reveals the six most commonly-used PCM etchants and details
• pros and cons of etchant selection,
• best practices,
• lowering of costs and environmental impact by etchant regeneration
and their
• "Health & Safety" and disposal issues.

Let’s deal with the data review first

Benjamin Disraeli (1804 -1881), the 19th century British Prime Minister, is attributed with the quotation:

“There are three kinds of lies:

lies, damned lies and statistics.”

We shall concentrate in this presentation on statistics generated by PCMI member companies over a period of some 25 years.

So please remember that these are your statistics that I am quoting back to you! This is not a subjective opinion.

PCM - making parts from metals

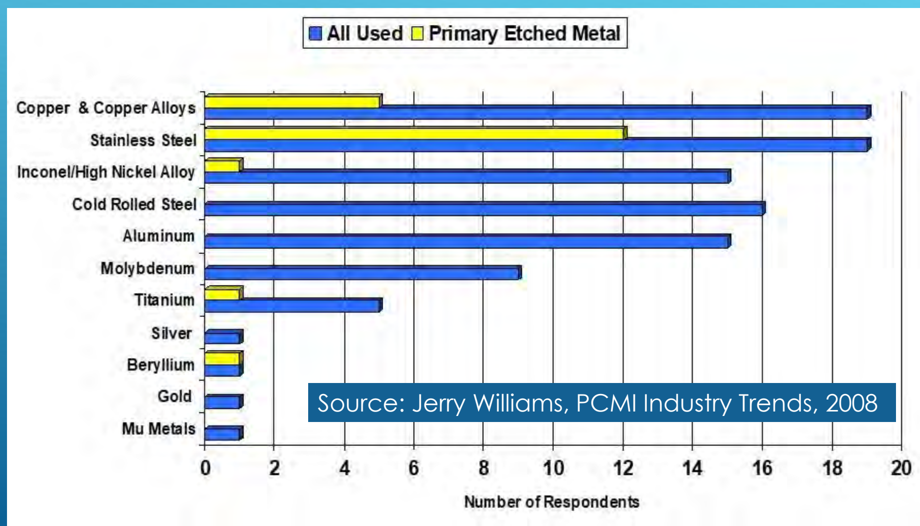
In general, the metals etched in the PCM process are durable materials that need profiling, shaping and forming.

Parts may be

- Technical, requiring specific dimensions within defined tolerances or
- Decorative, requiring a pleasing aesthetic appearance with an unblemished surface finish.

We shall now examine the range of metals that are etched in the PCM industry (using examples from published PCMI Industry Trends)

Typical photoetched metals



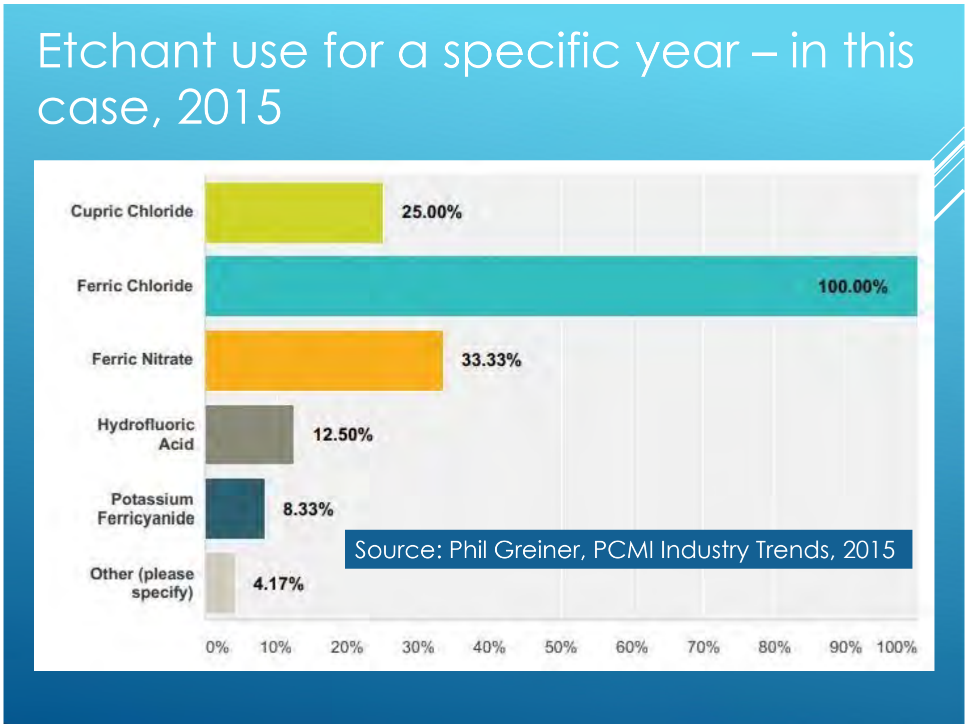
PCM - making parts from metals

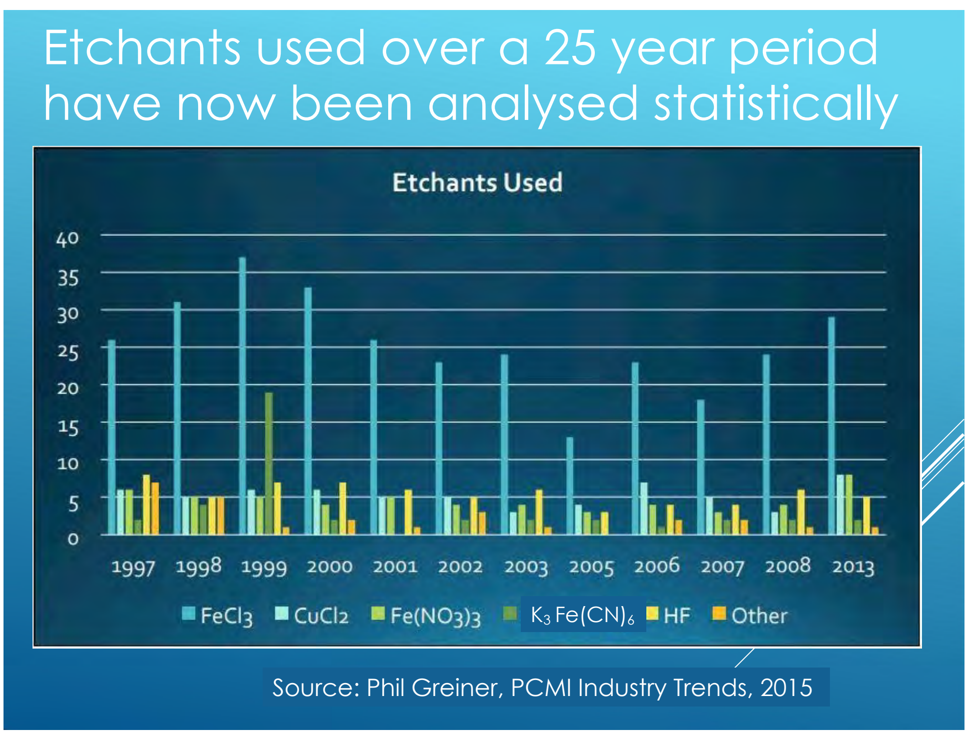
It would be ideal if there was a universal, cheap, environment-friendly etchant that would etch all the metals previously referred to.

Unfortunately that is not possible. The more corrosion-resistant metals require more powerful etchants with high oxidation potentials and not all oxidation by-products are soluble.

Best practice therefore includes the science of matching etchant with metal.

We shall now examine the range of etchants that are used in the PCM industry (again, using examples from published PCMI Industry Trends)


Etchant use for a specific year – in this case, 2015
Cupric Chloride
25.00%
Ferric Chloride
100.00%
Ferric Nitrate
33.33%
Hydrofluoric Acid
12.50%
Potassium Ferricyanide
8.33%
Other (please specify)
4.17%
Source: Phil Greiner, PCMI Industry Trends, 2015
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%


Etchants used over a 25 year period have now been analysed statistically
Etchants Used
40
35
30
25
20
15
10
5
0
1997
1998
1999
2000
2001
2002
2003
2005
2006
2007
2008
2013
FeCl3
CuCl2
Fe(NO3)3
K3 Fe(CN)6
HF
Other
Source: Phil Greiner, PCMI Industry Trends, 2015

My analysis suggests the following order of popular usage

#1 Ferric chloride, $FeCl_3$

#2 Hydrofluoric acid, HF

#3 Cupric chloride, $CuCl_2$

#4 Ferric nitrate, $Fe(NO_3)_3$

#5 Potassium ferricyanide, $K_3Fe(CN)_6$

#6 Iodine/Potassium iodide, I_2/KI

NB. #6 is the only identifiable formulation from "other", "special" and "proprietary" etchants listed.

Ferric chloride etchants

Stainless steel finger spring,
Courtesy of Elcon Precision LLC.,
San Jose, CA, USA

Metals and ferric chloride etchant

Metal / Etchant	Ferric chloride	Pros and Cons
Stainless steels	Y	Cheap and versatile. Build-up of Ni^{2+} and Cr^{3+} ions in solution. Build-up of Ni^{2+} ions can lead to an undesirable rough surface finish.
Carbon steels	Y	Cheap and versatile. Build-up of carbon and tarry residues in solution when etching high carbon steels.
Nickel & nickel-iron alloys	Y	Cheap and versatile. Build-up of Ni^{2+} ions in solution can lead to an undesirable rough surface finish.
Brass, copper & copper alloys (e.g. Be-Cu, Cu-Ni-Zn)	Y	Cheap and versatile. Complex etch chemistry develops as Cu^{2+} ions build up in solution - the chemistry of etching with cupric chloride is simpler in comparison. Build-up of other alloy metal ions, such as Be^{2+}, needs special attention for disposal.

Metals and ferric chloride etchant

Metal / Etchant	Ferric chloride	Pros and Cons
Aluminium & its alloys	Y	Exothermic reaction means that process needs modification (usually dilution). Can use diluted “spent” ferric chloride for economy. Can also be etched in alkaline solutions as Al is amphoteric but modern aqueous-processable DFRs can be attacked by this type of etchant.
Molybdenum	Y	Very slow etch rate and poor for high volume production (discussed later).

Metal / Etchant	Ferric chloride	Explanation
Tungsten	N	Tungsten is passive and inert.
Silver & its alloys	N	Silver chloride by-product is insoluble so reaction stops after surface attack.
Gold, Palladium, Platinum and Rhodium	N	High oxidation potential of precious metals.
Titanium, Ti-6Al-4V, Ni-Ti shape memory alloys	N	Corrosion-resistant oxide film resists attack.

Use of ferric chloride in high volume production

I would now like to share the screen with Peter Jefferies. Heatric uses vast quantities of ferric chloride in the PCM production of heat exchanger plates, and Peter knows the pros and cons of ferric chloride in great detail.

Courtesy of Heatric Ltd., Birmingham, UK

Meggitt's heat exchanger plates etching facility in Birmingham

Bulk etching of stainless steel and other high-Ni alloys

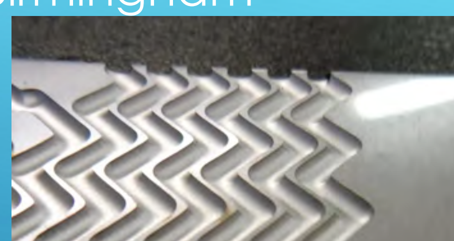
Material size: 600 mm wide, ranging in length up to 1,800 mm long

Nominal etch depth: 1.1 mm

Metal removed per plate: 4 kg

5-7 tonnes of metal etched per week

Using up to 20 tonnes of chlorine liquid per week



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Ferric chloride – advantages and disadvantages of use

Advantages

- Relatively easy to use and control
    - Well understood chemistry (ORP, sg etc.)
- Commercially available from multiple sources
- "Heath and Safety" risks are straightforward to manage
- Etches multiple metals
- Multiple methods of regeneration/rejuvenation
- Equipment easy to source unlike more exotic etchants

Disadvantages

- Need regeneration to keep production rate up in large production
- Increasing costs of regeneration chemistry
- Chlorine costs (15%)
- Increasing difficulty to remove waste streams
    - Filter cake (20%)
    - But more significantly waste ferric (35%)

Meggitt proprietary and confidential. No unauthorised copying or disclosure.

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By-product disposal

Increasing difficulty in sourcing routes for both ferric chloride and effluent treatment filter cake coupled with increasing costs has resulted in Meggitt looking for other options

- Possibility of recycling effluent filter cake and sludge by refining into a product for the additive manufacturing industry
- Trials on de-wetting agents to reduce 'water' volume of waste ferric
- Removal of Ni and Cr from ferric to allow for reuse
    - More next month !!!!

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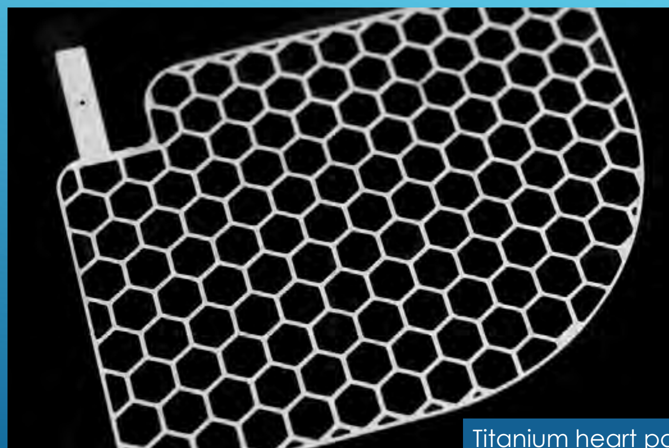
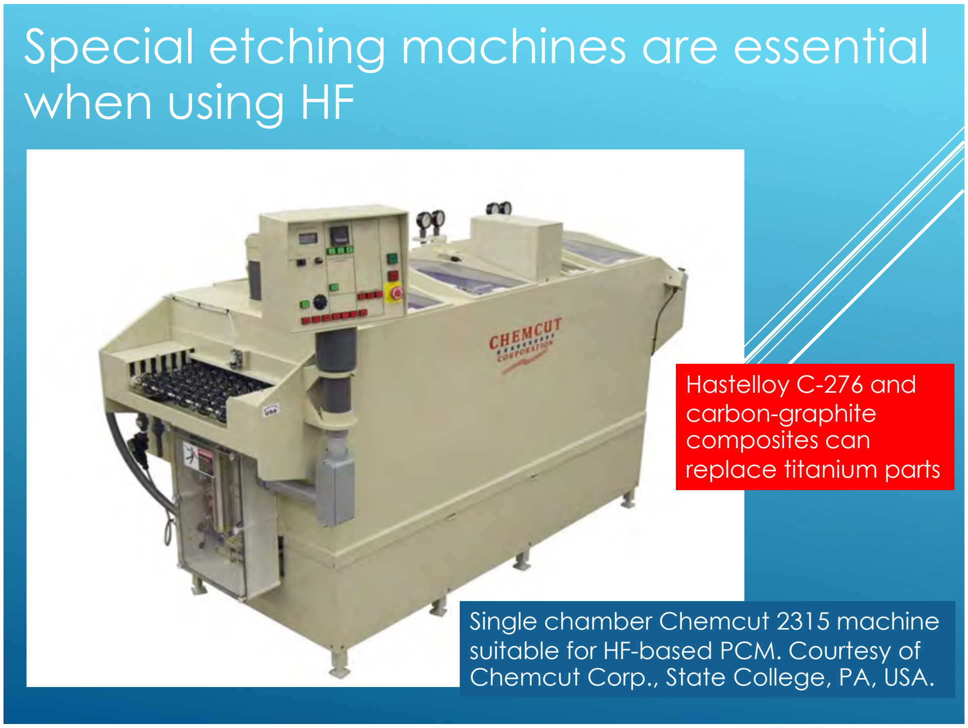
Hydrofluoric acid (HF) etchants



Titanium heart pacemaker battery grid. Courtesy of Precision Micro Ltd., Birmingham, UK

Metals and HF etchants

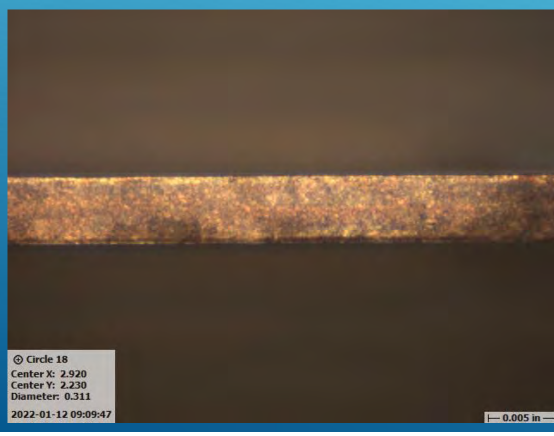
Metal / Etchant	Hydrofluoric acid	Pros and Cons
Titanium, Ti-6Al-4V, Ni-Ti shape memory alloys Molybdenum Tungsten	Y Y* Y* * Immersion etching with a very specific	One of the few etchants that is able to etch titanium-based materials. The most toxic etchant used in PCM. Destroys human tissue and can be fatal so PPE essential to cover whole body. Considerable "Health and Safety" rules associated with its location, handling, pumping and use. HF areas are restricted to authorised staff. Special care needs to be taken with "empty" containers that
	nitric acid	previously stored HF and when cleaning out
	content is	machines that have contained HF.
	used in	Need special etch line as a standard etch machine
	chemical	
	milling	
	applications	Etchant attacks metal/photoresist interface.
	but not PCM	In practice, HF is mainly used in conjunction with nitric acid to prevent hydrogen embrittlement. Difficult to dispose of waste.


Special etching machines are essential when using HF
CHEMCUT
Hastelloy C-276 and carbon-graphite composites can replace titanium parts
Single chamber Chemcut 2315 machine suitable for HF-based PCM. Courtesy of Chemcut Corp., State College, PA, USA.


Cupric chloride etchants
Etched and formed beryllium-copper parts. Courtesy of Orbel Corp., Easton, PA, USA

Metals and cupric chloride etchants

Metal / Etchant	Cupric chloride	Pros and Cons
Brass, copper & copper alloys (e.g. Be-Cu, Cu-Ni-Zn)	Y	No cusp: excellent smooth edge profiles can be obtained. Additions of HCl increase etch rate.



Edge of annealed 0.005" beryllium-copper part etched in cupric chloride. Courtesy of Orbel Corp., Easton, PA, USA

Metals and cupric chloride etchants

Metal / Etchant	Cupric chloride	Pros and Cons
Brass, copper & copper alloys (e.g. Be-Cu, Cu-Ni-Zn)	Y	Easier regeneration with no Fe^{3+} or Fe^{2+} ions in solution to complicate the chemistry but build-up of other alloy metal ions, such as Be^{2+}, needs special attention for disposal.

$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$ but both Fe^{3+} and Cu^{2+} will etch Cu

$Cu^{2+} + Cu \rightarrow 2Cu^{+}$ is a simpler system that eliminates Fe^{n+}

Note: Regeneration is essential for economic viability as cupric chloride is more expensive than ferric chloride.

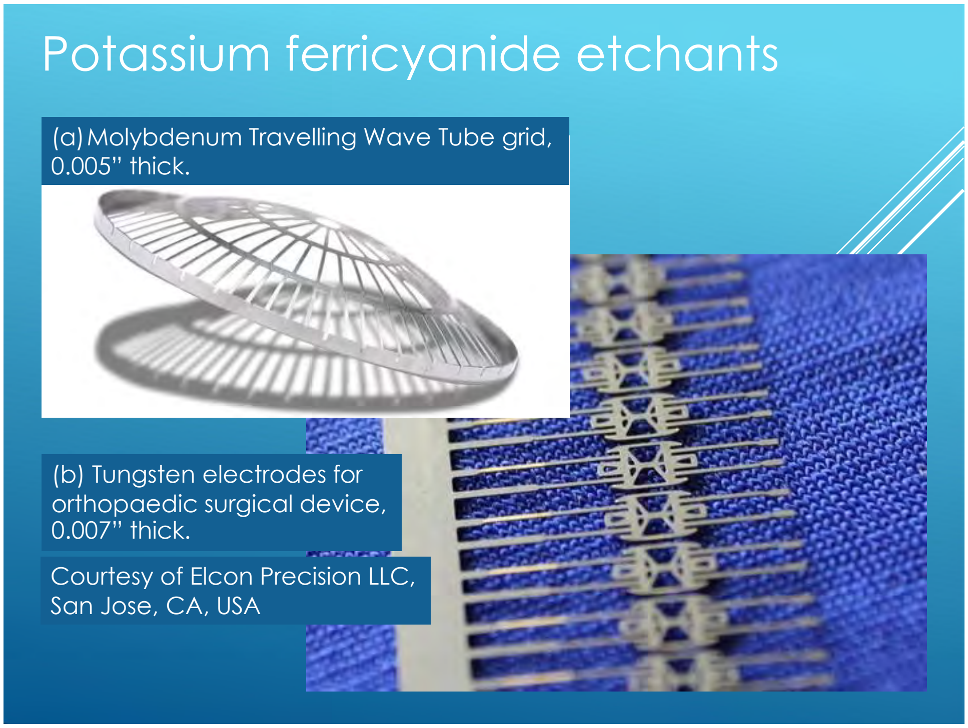
Regeneration chemistry is simple: $Cu^{+} \rightarrow Cu^{2+} + e^{-}$

Ferric nitrate etchants

Etched silver pendants.
Courtesy of Lindsay Duff, UK

Metals and ferric nitrate etchants

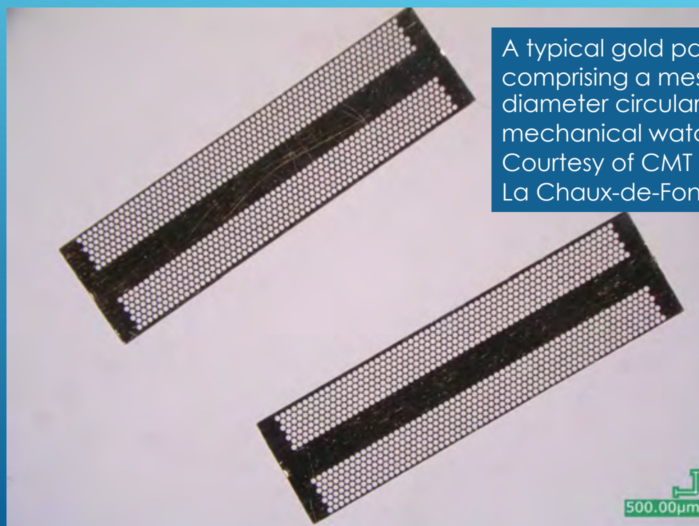
Metal / Etchant	Ferric nitrate	Pros and Cons
Molybdenum	Y	A viable, faster alternative to ferric chloride with the added ability of the etchant to etch silver. Anisotropic etching can occur with some molybdenum crystal structures.
Silver and its alloys	Y	A very popular etchant as silver nitrate is soluble in this etchant. It is safer than the often-used, alternative etchant of dilute nitric acid. Silver can be extracted from spent solution by precipitating it with salt (sodium chloride) solution.



Metals and potassium ferricyanide etchants

Metal / Etchant	Potassium ferricyanide	Pros and Cons
Aluminium and its alloys	Y	Can etch with a good, smooth surface finish. Etchant can be regenerated. Photoresist compatibility. Disposal is problematic
Molybdenum	Y	**Isotropic** etchant can be regenerated. Photoresist compatibility. More complex chemistry c.f. ferric nitrate. Disposal is problematic
Tungsten	Y	One of the very few spray etchants for tungsten. Etchant can be regenerated. Photoresist compatibility. Disposal is problematic
Silver and its alloys	Y	Can etch silver alloys such as ACA (silver-copper-gold) better than iodine/potassium iodide. Etchant can be regenerated. Photoresist compatibility. More complex chemistry c.f. ferric nitrate. Disposal is problematic.

Iodine/potassium iodide etchants



A typical gold part (0.1 mm thick) comprising a mesh of 0.14 mm diameter circular holes for a mechanical watch ringtone. Courtesy of CMT Rickenbach SA, La Chaux-de-Fonds, Switzerland

Iodine/potassium iodide etchants

General formulation:

- 10–40 wt. % potassium iodide,
- 1–10 wt. % iodine and
- water (balance)

General Health and Safety:

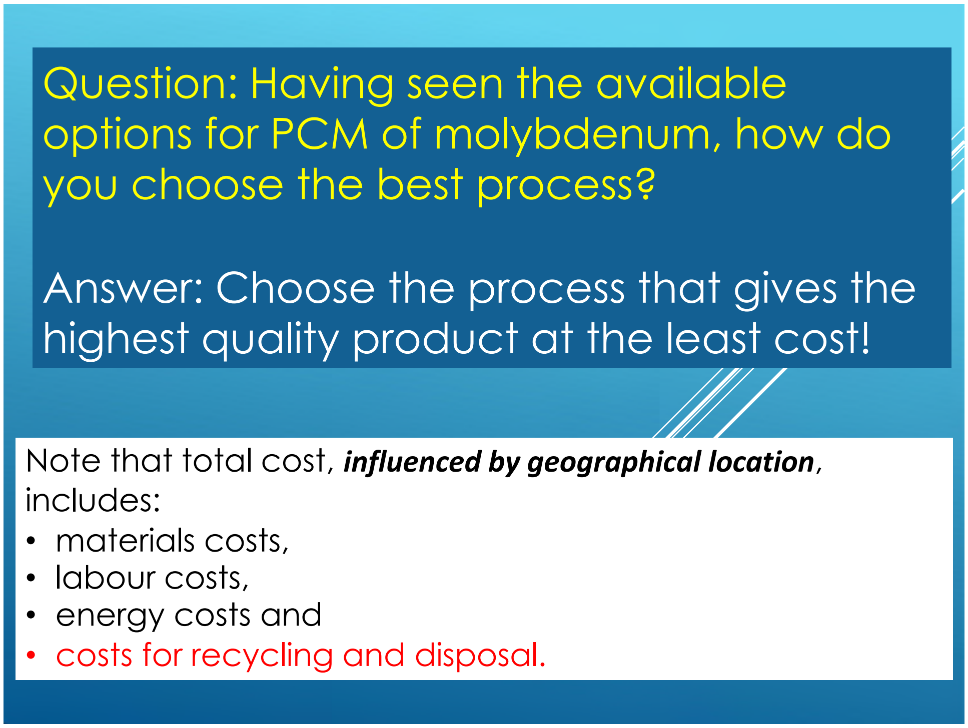
- Iodine is toxic and may be fatal if swallowed or inhaled. It causes damage to the thyroid gland.
- Inhalation of KI dust may irritate respiratory tract.

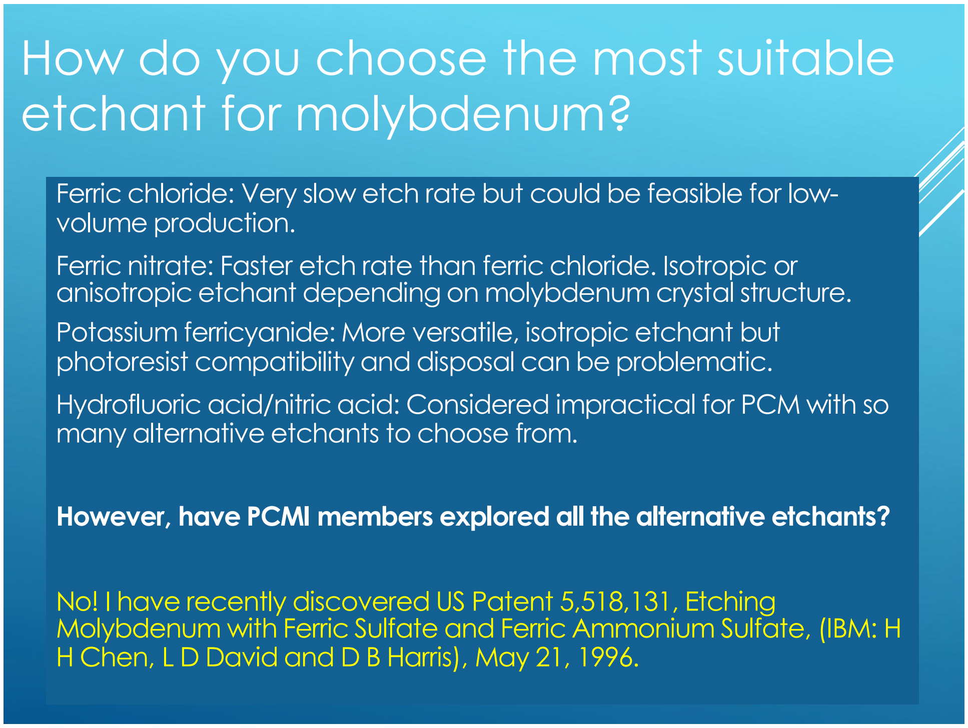
Metals and iodine/potassium iodide etchants

Metal / Etchant	Iodine/ KI	Pros and Cons
Silver and its alloys	Y	Can spray etch a wide range of silver alloys. Silver can be extracted from the etchant after processing by precipitation with sodium chloride. Fumes from the etchant are toxic and require controlled extraction.
Gold, Palladium, Platinum and Rhodium	Y	Can spray etch a wide range of precious metals that can be extracted from the etchant after processing (e.g. US Patents, 5,317,700 and 7,582,136) Less dangerous than gold etchants such as ***aqua regia***. Fumes from the etchant are toxic and require controlled extraction.

Metals and potential etchants

Metal / Etchant	Ferric chloride	Hydrofluoric acid	Cupric chloride	Ferric nitrate	Potassium ferricyanide	Iodine/ KI
Stainless steels	Y					
Carbon steels	Y					
Nickel & nickel-iron alloys	Y					
Brass, copper & copper alloys (e.g. Be-Cu, Cu-Ni-Zn)	Y		Y			
Aluminium & its alloys	Y				Y	
Molybdenum	Y	Y		Y	Y	
Tungsten	N	Y			Y	
Silver and its alloys	N			Y	Y	Y
Gold, Palladium, Platinum and Rhodium	N					Y
Titanium, Ti-6Al-4V, Ni-Ti shape memory alloys	N	Y				


Question: Having seen the available options for PCM of molybdenum, how do you choose the best process?
Answer: Choose the process that gives the highest quality product at the least cost!
Note that total cost, ***influenced by geographical location***, includes:
• materials costs,
• labour costs,
• energy costs and
• costs for recycling and disposal.


How do you choose the most suitable etchant for molybdenum?
Ferric chloride: Very slow etch rate but could be feasible for low-volume production.
Ferric nitrate: Faster etch rate than ferric chloride. Isotropic or anisotropic etchant depending on molybdenum crystal structure.
Potassium ferricyanide: More versatile, isotropic etchant but photoresist compatibility and disposal can be problematic.
Hydrofluoric acid/nitric acid: Considered impractical for PCM with so many alternative etchants to choose from.
However, have PCMI members explored all the alternative etchants?
No! I have recently discovered US Patent 5,518,131, Etching Molybdenum with Ferric Sulfate and Ferric Ammonium Sulfate, (IBM: H H Chen, L D David and D B Harris), May 21, 1996.

Choice of molybdenum etchant

Etchants for Molybdenum	Ferric chloride	Ferric nitrate	Potassium ferricyanide	Ferric sulphate
Etch rate for production requirements	Very slow: etch rate unacceptable	Slower than potassium ferricyanide	Acceptable etch rate	"Comparable to potassium ferricyanide" ŧ
Spray etch rate (µm/minute)	1.5 @ 53°C	5 @ 50°C	8.3 @ 50°C	>2 @ 50°C and is proportional to [Mo] dissolved ŧ
References*	*Arnold *et al*	*Gillbanks	*Bogenschütz *et al*	ŧ David (US Patent 5,518,131)
Etchant pH	< 0 (acid)	Acid	12-13 (alkaline) or 6-8 (neutral)	-0.5 to +0.5 (acid)
Potential technical issues	-	Anisotropic etch in some crystalline microstructures	Alkaline etch can attack DFR / Mo interface	-
Etchant regeneration	Chlorine, sodium chlorate or electrolytic	Air (free), oxygen or ozone	Ozone or electrolytic	Air (free), oxygen or ozone
Etchant disposal	Standard	Standard	Problematic due to CN^- complexes	Easy: by treating with lime
Metal extraction	Not currently practised	Not currently practised	Not currently practised	Possible by solvent extraction
"Health & Safety" issues	Standard	Nitric acid addition increases fumes requiring extraction	Isolate from acids to prevent toxic HCN gas forming	Standard as acidity controlled by addns. of sulphuric acid

***References source: D M Allen *et al*, Photochemical Machining of Molybdenum, Annals of CIRP, 35, 129-132 (1986)**

Six Etchants Summary

Etchant	Ferric chloride	Cupric chloride	Ferric nitrate	Potassium ferricyanide	Hydrofluoric Acid/Nitric Acid	Iodine/KI
Versatility	Excellent	Good	Good	Good	Limited to Ti, Ti alloys but possible to etch Mo and W.	Limited to precious metals
Etchant pH	Acid	Acid	Acid	Alkaline/neutral	Acid	Neutral
Cost of etchant	Cheap	Expensive	Expensive	Expensive	High due to safety requirements	High
Transport & handling	Standard	Standard	Standard	Standard	Additional safety requirement	Standard
"Health & Safety" requirements	Standard practices	Standard practices	Standard practices	Additional safety requirements necessary	Toxic. PPE and substantial additional safety requirements necessary	Additional safety requirements for fume extraction
Etchant regeneration	Yes	Yes – essential for viability	Yes - oxygen	Yes	No	Yes
Extraction of dissolved metals	Not currently practiced	Yes	Yes – add salt (NaCl) to precipitate AgCl	Not currently practiced	Not currently practiced	Yes. Precious metal recovery essential for viability
Waste disposal	Costs increasing	Costs increasing	Costs increasing	Challenging. Costs increasing	Challenging. Costs increasing	Costs increasing

Conclusions

- There is no universal, ideal etchant but, by careful matching of etchant with the metal, all sheet metals can be photochemically machined to fabricate high quality products.
- By reducing "Health & Safety" risks and employing etchant regeneration and waste minimisation techniques, PCM can be carried out at viable cost and with a reduced environmental impact.
- The next development in PCM should focus on metal extraction from used etchants.
- Reclamation of the dissolved metals would lead to lower costs and reduce environmental impact further.

Acknowledgements

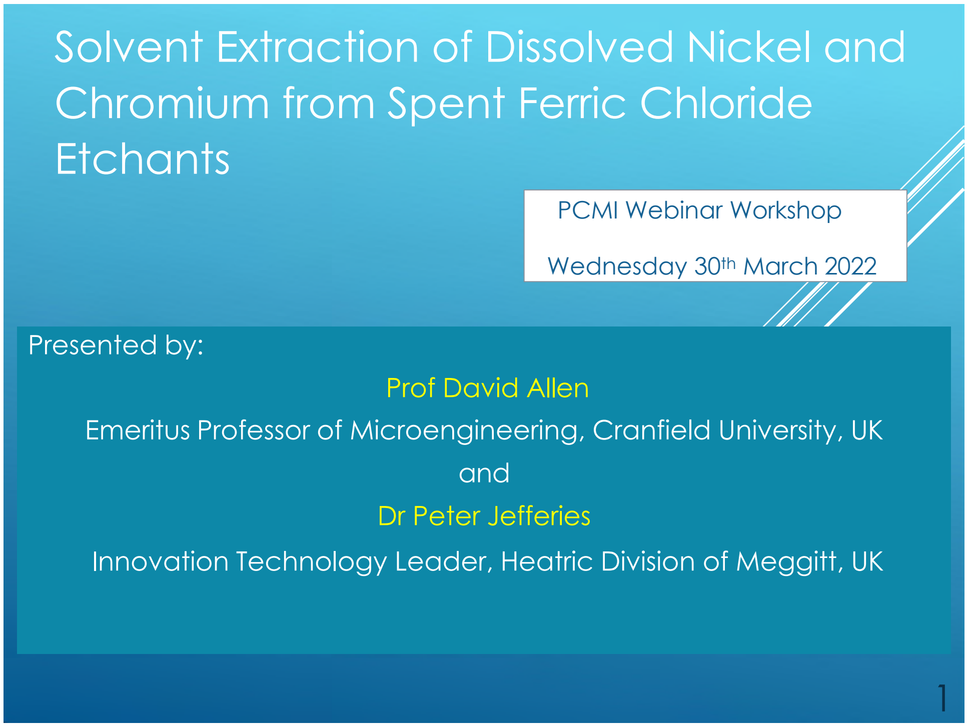
We wish to thank the following for their input and collaboration:

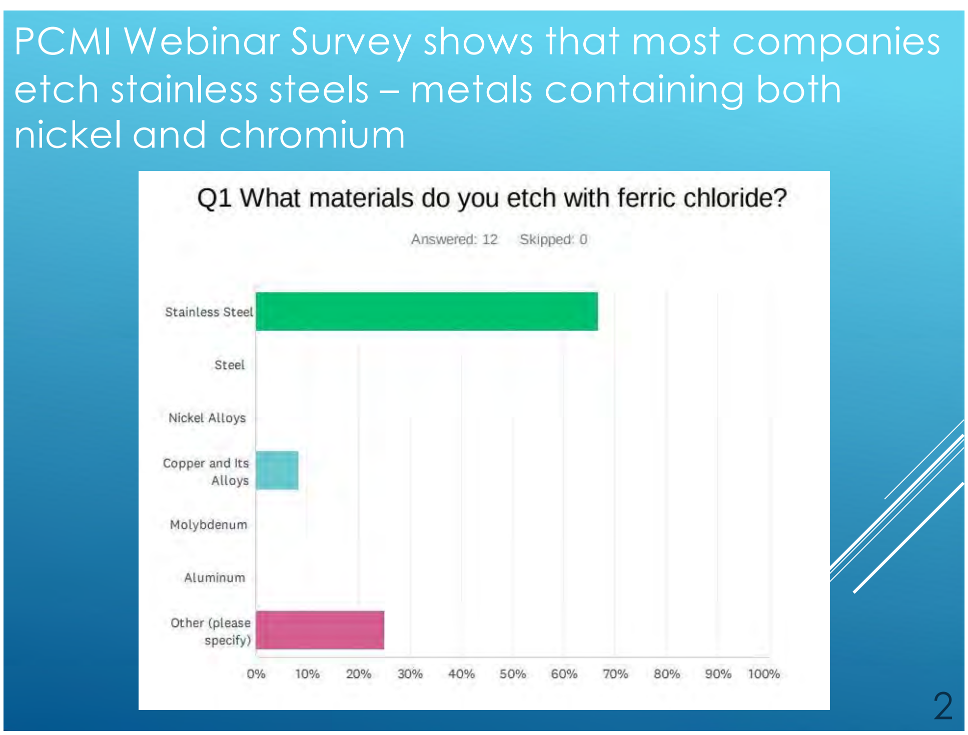
- Kirk Lauver, Chemcut Corporation, State College, PA, USA
- Phil Greiner, Photofabrication Engineering Inc., Milford, MA, USA
- Jerry Williams, United Western Enterprises Inc., Camarillo, CA, USA
- Julien Duvillet, CMT Rickenbach SA, La Chaux-de-Fonds, Switzerland
- Dan Brumlik, Tim Dyer and Nikki Do, Elcon Precision LLC, San Jose, CA, USA
- Ken Marino, Orbel Corporation, Easton, PA, USA
- Lee Weston, Precision Micro Ltd., Birmingham, UK

and

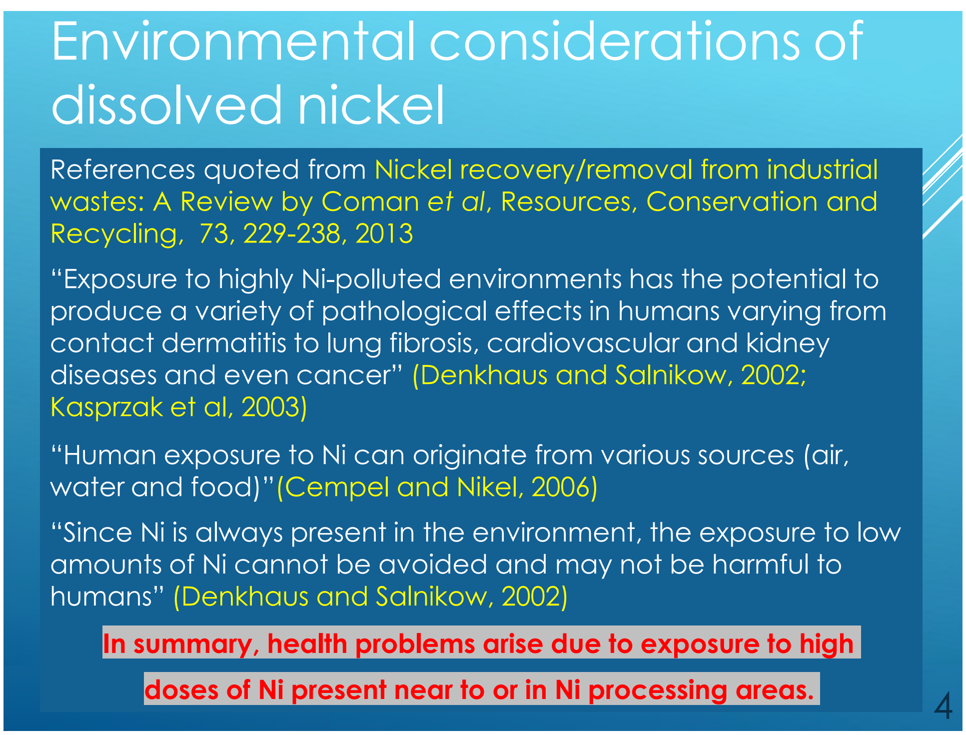
- Dr Larry David for extensive discussions on his US Patent 5,518,131 assigned to IBM Corporation, NY.


Thank you for listening.
Do you have questions for us?
Prof. David Allen
d.allen@cranfield.ac.uk
Dr. Peter Jefferies
peter.jefferies@meggitt.com


Solvent Extraction of Dissolved Nickel and Chromium from Spent Ferric Chloride Etchants
PCMI Webinar Workshop
Wednesday 30th March 2022
Presented by:
Prof David Allen
Emeritus Professor of Microengineering, Cranfield University, UK
and
Dr Peter Jefferies
Innovation Technology Leader, Heatric Division of Meggitt, UK
1


PCMI Webinar Survey shows that most companies etch stainless steels – metals containing both nickel and chromium
Q1 What materials do you etch with ferric chloride?
Answered: 12 Skipped: 0
Stainless Steel
Steel
Nickel Alloys
Copper and Its Alloys
Molybdenum
Aluminum
Other (please specify)
0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%
2


BACKGROUND
D.M. Allen, Extraction and Recycling of Dissolved Nickel from Ferric Chloride Etchant: Economic, Technical and Environmental Considerations" PCMI Journal, 134, 15-29 (2019).
This paper was first presented on Monday 20th May 2019 at the PCMI Spring Conference held at Chantilly, France.
3

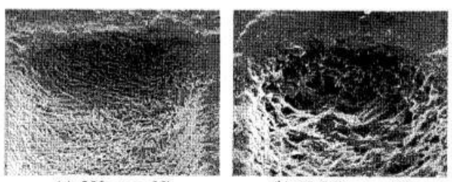

Environmental considerations of dissolved nickel
References quoted from Nickel recovery/removal from industrial wastes: A Review by Coman et al, Resources, Conservation and Recycling, 73, 229-238, 2013
"Exposure to highly Ni-polluted environments has the potential to produce a variety of pathological effects in humans varying from contact dermatitis to lung fibrosis, cardiovascular and kidney diseases and even cancer" (Denkhaus and Salnikow, 2002; Kasprzak et al, 2003)
"Human exposure to Ni can originate from various sources (air, water and food)"(Cempel and Nikel, 2006)
"Since Ni is always present in the environment, the exposure to low amounts of Ni cannot be avoided and may not be harmful to humans" (Denkhaus and Salnikow, 2002)
In summary, health problems arise due to exposure to high doses of Ni present near to or in Ni processing areas.
4

Short review of technical considerations of dissolved nickel

A paper at the PCMI Fall Conference 2018, Long Beach, CA, USA:

D M Allen, PCM of nickel and its alloys and the measurement of nickel ion concentration in ferric chloride etchant, PCMI Journal, 133, 18-32 (2019)

showed that build-up of dissolved nickel ions in ferric chloride etchant produced an undesirable rough etch as illustrated below.



(a) 300 ppm Ni (b) 30,000 ppm Ni

Figure 1. Etch profiles obtained with different concentrations of Ni ion: (a) 300 ppm Ni, (b) 30,000 ppm Ni.

Figure taken from Park *et al*, Clean Technology, 13(4), 2007

5

Control of $[Ni^{2+}]$

My analysis (from RCA patents and published papers by Maynard *et al*) shows the following conditions are required for smooth etching of Invar at temperatures > 70°C

- $[Ni^{2+}]$ < 13.1 g/l for 48.3°Bé $FeCl_3$
- $[Ni^{2+}]$ < 14.8 g/l for 51.5°Bé $FeCl_3$

Similarly, Steffen Herz has stated that for smooth etching of nickel-containing alloys such as stainless steels etched at 54°C

- $[Ni^{2+}]$ < 15 g/l for ~40°Bé $FeCl_3$

whilst Doug Tagami stated that for smooth etching of Ni-Be,

- $[Ni^{2+}]$ < 20 g/l for etching in $FeCl_3$

(but in practice, for minimising downtime in a two-shift operation, $[Ni^{2+}]$ was kept at a maximum of 9.5 g/l); D.M. Allen and H.J.A. White, Nickel etching economics, PCMI Journal, 50, p.5, Fall 1992

6

Review of nickel extraction from spent ferric chloride etchants

1. Electrodialysis
2. Ion exchange
3. Cementation (reductive precipitation)
4. Extractive precipitation
5. Solvent extraction

7

Solvent extraction

Organic solvents have a high environmental impact due to the association of VOCs with photochemical smog, low-level ozone and "Health & Safety" concerns (volatility, low flash point and toxicological effects).

Solvent extraction is therefore a costly process requiring strict control.

However, the process is still being investigated and might be accepted by the PCM industry if the **economics** become favourable with time.

Patents and papers have been written on separating concentrated Fe/Ni mixtures for at least 50 years!

8

Solvent extraction principles:

Liquid–liquid extraction (LLE), also known as solvent extraction and partitioning, is a method to separate compounds or metal complexes, based on their relative solubilities in two different immiscible liquids, usually water (polar) and an organic solvent (non-polar).

There is a net transfer of one or more species from one liquid into another liquid phase, generally from aqueous to organic. The transfer is driven by chemical potential, i.e. once the transfer is complete, the overall system of protons and electrons that make up the solutes and the solvents are in a more stable configuration (lower free energy).

The solvent that is enriched in solute(s) is called extract.

The feed solution that is depleted in solute(s) is called the raffinate.

LLE is a basic technique in chemical laboratories, where it is performed using a variety of apparatus, from separatory funnels to counter-current distribution equipment known as mixer-settlers.

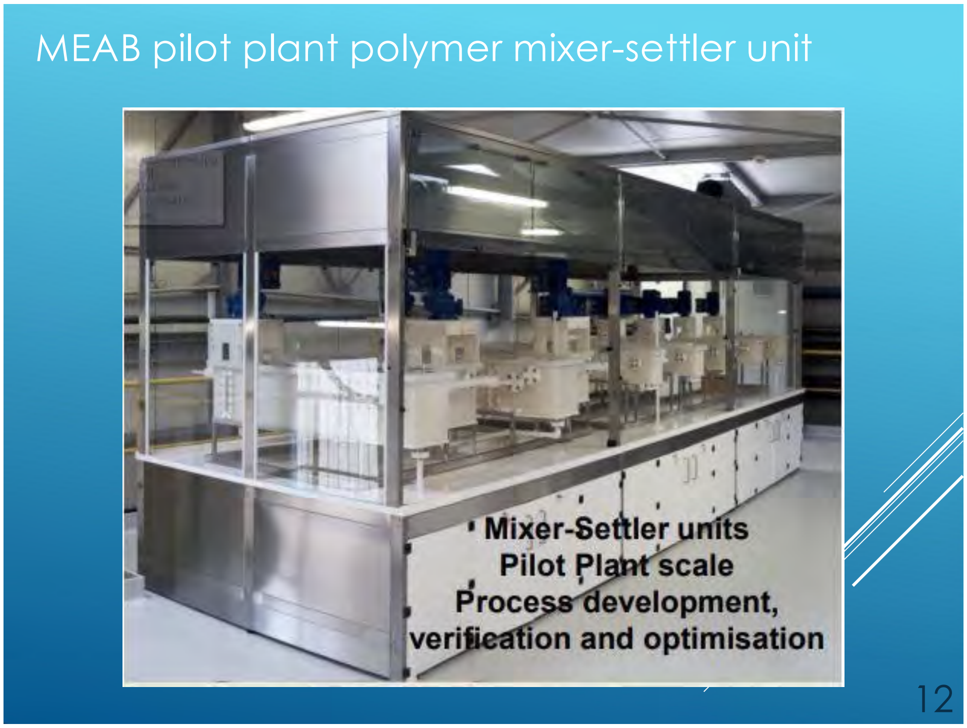
9

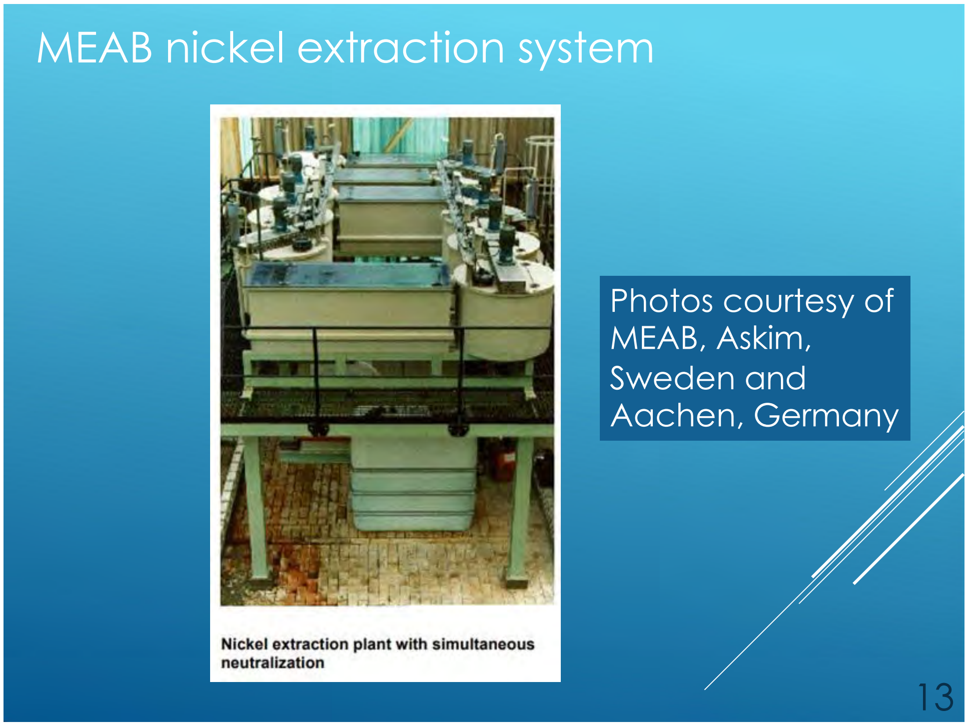
Commercial mixer-settler design in glass

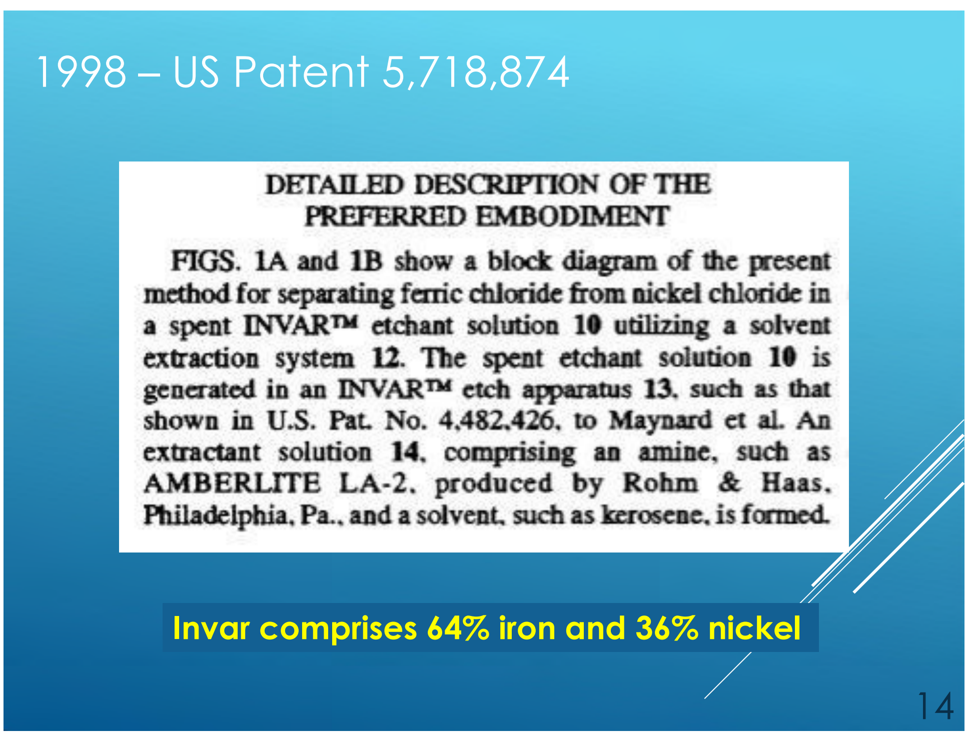
Photograph courtesy of De Dietrich Process Systems

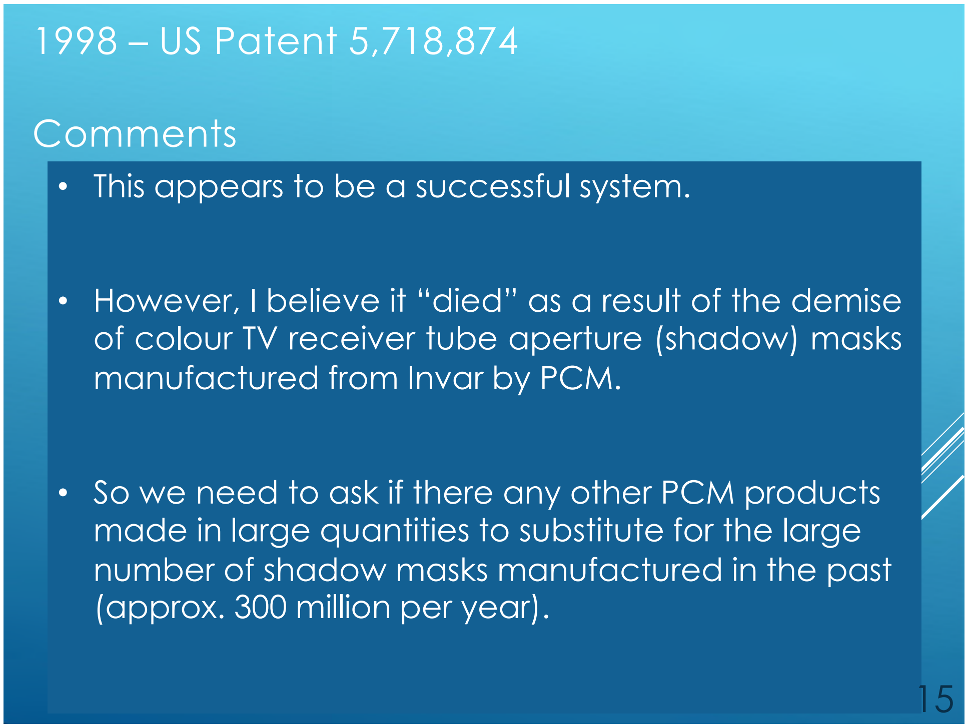
10

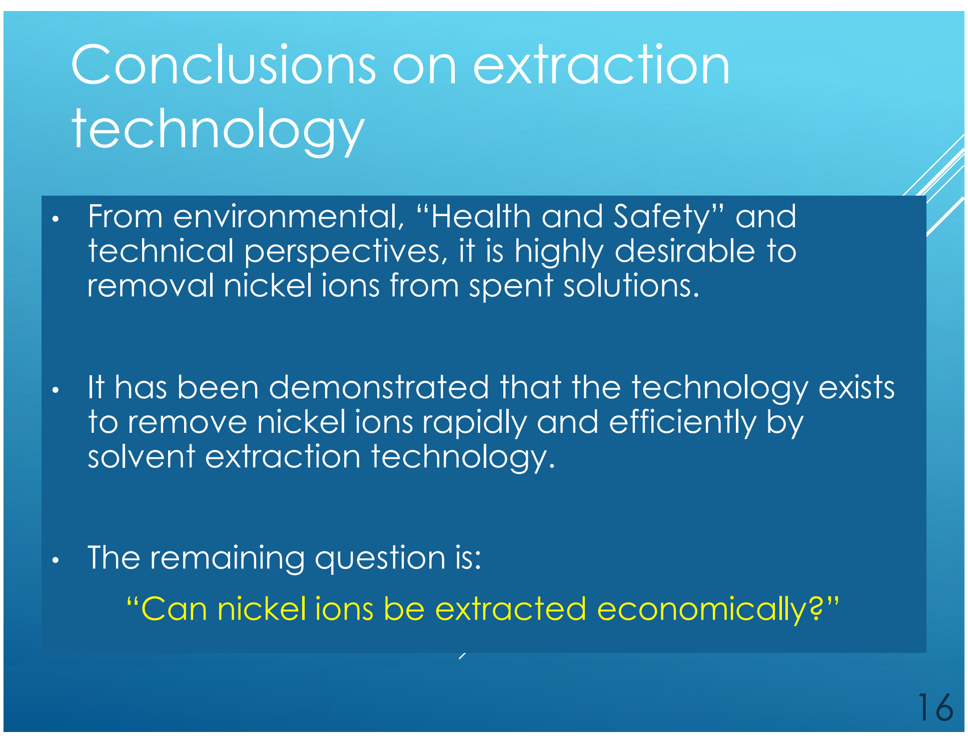

Commercial mixer-settler design in glass
Glass is relatively expensive but transparent
Polymers are cheaper but opaque
11


MEAB pilot plant polymer mixer-settler unit
Mixer-Settler units
Pilot Plant scale
Process development, verification and optimisation
12


MEAB nickel extraction system
Photos courtesy of MEAB, Askim, Sweden and Aachen, Germany
Nickel extraction plant with simultaneous neutralization
13


1998 – US Patent 5,718,874
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT
FIGS. 1A and 1B show a block diagram of the present method for separating ferric chloride from nickel chloride in a spent INVAR™ etchant solution 10 utilizing a solvent extraction system 12. The spent etchant solution 10 is generated in an INVAR™ etch apparatus 13, such as that shown in U.S. Pat. No. 4,482,426, to Maynard et al. An extractant solution 14, comprising an amine, such as AMBERLITE LA-2, produced by Rohm & Haas, Philadelphia, Pa., and a solvent, such as kerosene, is formed.
Invar comprises 64% iron and 36% nickel
14


1998 – US Patent 5,718,874
Comments
• This appears to be a successful system.
• However, I believe it "died" as a result of the demise of colour TV receiver tube aperture (shadow) masks manufactured from Invar by PCM.
• So we need to ask if there any other PCM products made in large quantities to substitute for the large number of shadow masks manufactured in the past (approx. 300 million per year).
15


Conclusions on extraction technology
• From environmental, "Health and Safety" and technical perspectives, it is highly desirable to removal nickel ions from spent solutions.
• It has been demonstrated that the technology exists to remove nickel ions rapidly and efficiently by solvent extraction technology.
• The remaining question is:
"Can nickel ions be extracted economically?"
16

Peter Jefferies | Technical Consultant | Heatric, Division of Meggitt | UK
David Allen | Emeritus Professor | Cranfield University | UK

Financial considerations for extraction of nickel from waste ferric chloride etchant

+ Value of nickel metal extracted

+ In theory, no additional purchases of ferric chloride if etchant regenerated

+ Etchant regeneration cost remains the same

+ No disposal costs for waste etchant, noting that these will always increase with time

- Cost of extraction equipment and electrolysis costs

- Labour and chemical costs

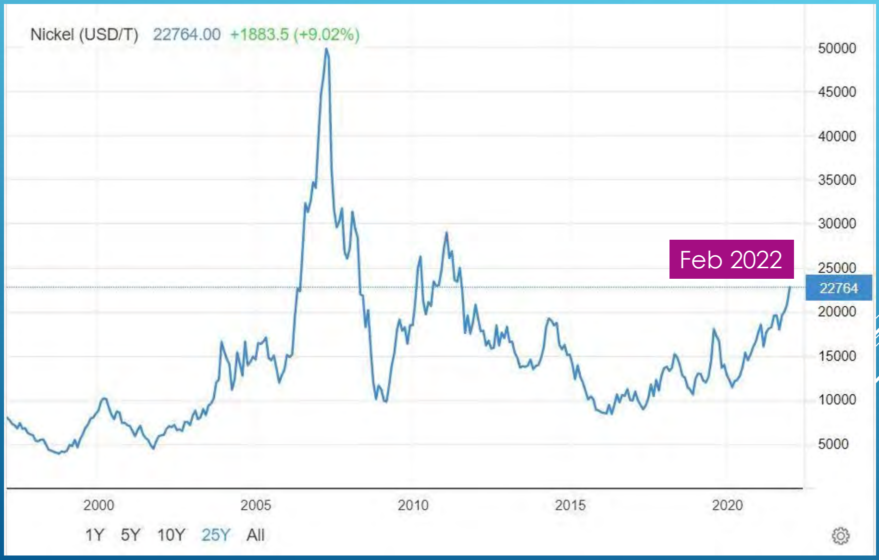
- Solvent "Health and Safety" costs

- Transport costs if extraction carried out off-site

- Note that etchant manufacturers have a vested interest to sell fresh/recycled $FeCl_3$

17

Historical nickel prices over a period of 25 years show considerable variation



18

Nickel futures surged above the $26,400 per tonne level for the first time since May 2011, as western sanctions against Russia over its invasion of Ukraine sparked renewed concerns over the metal supply.

19

Economy of scale

A profitable nickel extraction process must depend on large quantities of spent ferric chloride being generated by etching. This implies large volumes of nickel-containing alloys need to be etched.

Case study

Consider a company such as Heatric that etches PCHEs. This company currently dissolves 400 tonnes of nickel-containing 18/8 stainless steel into ferric chloride etchant per annum. This means 32 tonnes of nickel are dissolved into solution per year.

The price (4th March 2022) of nickel was approx. US$29,600 per tonne.

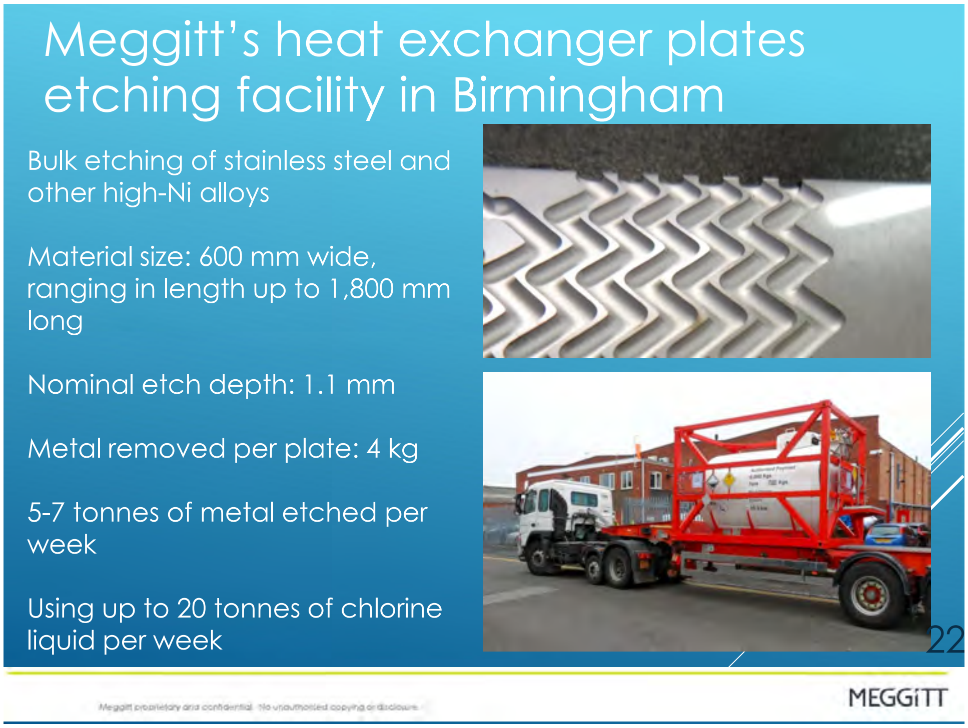
If all 32 tonnes of nickel can be extracted as pure nickel metal, the value of the nickel product would be $947,200 per annum.

If the price of nickel were to revert back to 2007 prices, the value of the nickel product would yield $1,764,000.

The $64 million question is "What is the cost of the extraction process?"

20


Nickel futures jumped more than 65% to $80,025 per tonne, having topped the $100,000 mark for the first time ever as western sanctions against Russia over its invasion of Ukraine sparked concerns over the metal supply. The unprecedented move in the nickel market led the London Metal Exchange to halt trading for the remainder of Tuesday's session. Russia accounts for about 10% of the global nickel supply, mainly for use in stainless steel and electric vehicle batteries.
80025
70000
8th March 2022
50000
40000
30000
20000
10000
2002
2006
2010
2014
2018
2022
1Y 5Y 10Y 25Y All
21


Meggitt's heat exchanger plates etching facility in Birmingham
Bulk etching of stainless steel and other high-Ni alloys
Material size: 600 mm wide, ranging in length up to 1,800 mm long
Nominal etch depth: 1.1 mm
Metal removed per plate: 4 kg
5-7 tonnes of metal etched per week
Using up to 20 tonnes of chlorine liquid per week
22
MEGGITT

Regeneration- the scale of the problem

We have six 8-chamber etch lines running 24hr per day, 7 days per week and generating around 30 tonnes of waste ferric per week.

On average, 2 road tankers per week are used to dispose of this waste.

The issue we face is the high level of Ni and Cr contained in the spent etch solution which results in it being classified as **hazardous waste.**

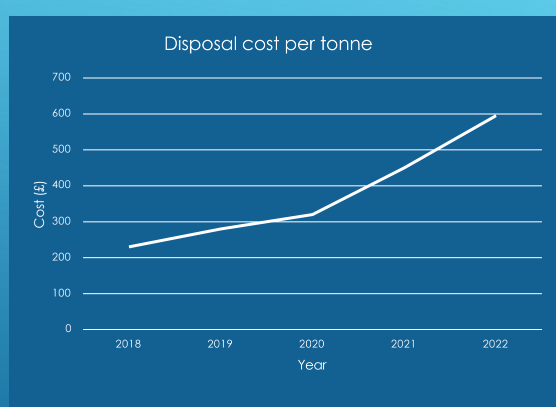
23

Increasing cost: driven by tighter environmental legislation

Over the last few years we have seen consistent increases in disposal costs.

There is also an ever-decreasing number of treatment companies who can take this type of waste. We now have only 3 in the UK who can take these volumes.

Cost to the business in 2021 was over £500k.



24

How much nickel can be extracted from solution?

Wt of metal* dissolved into solution per year (tonnes)	Wt of nickel dissolved into solution per year	Approximate volume of etchant requiring extraction at Ni<15g/litre per year	Approximate volume of etchant requiring extraction at Ni<15g/litre per week
18/8 stainless steel (400)	32,000,000 gm	2,133,000 litres	42,700 litres
18/8 stainless steel (600)	48,000,000 gm	3,200,000 litres	64,000 litres
18/8 stainless steel (1600)	128,000,000 gm	8,532,000 litres	170,600 litres
High 45% nickel alloy (400)	180,000,000 gm	12,000,000 litres	240,000 litres

*Ref: Peter Jefferies, New Product Showcase, PCMI Journal, 123, 178-186, Summer 2014

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Peak production* may comprise:

Wt of metal dissolved into solution per year (tonnes)	Wt of nickel dissolved into solution per year	Approximate volume of etchant requiring extraction at Ni<15g/litre per year	Approximate volume of etchant requiring extraction at Ni<15g/litre per week
18/8 stainless steel (1600)	128,000,000 gm	8,532,000 litres	170,600 litres
High 45% nickel alloy (400)	180,000,000 gm	12,000,000 litres	240,000 litres
*Combination of above metal mix (2000)	308,000,000 gm	20,532,000 litres	410,600 litres

Ref: Peter Jefferies, New Product Showcase, PCMI Journal, 123, 178-186, Summer 2014

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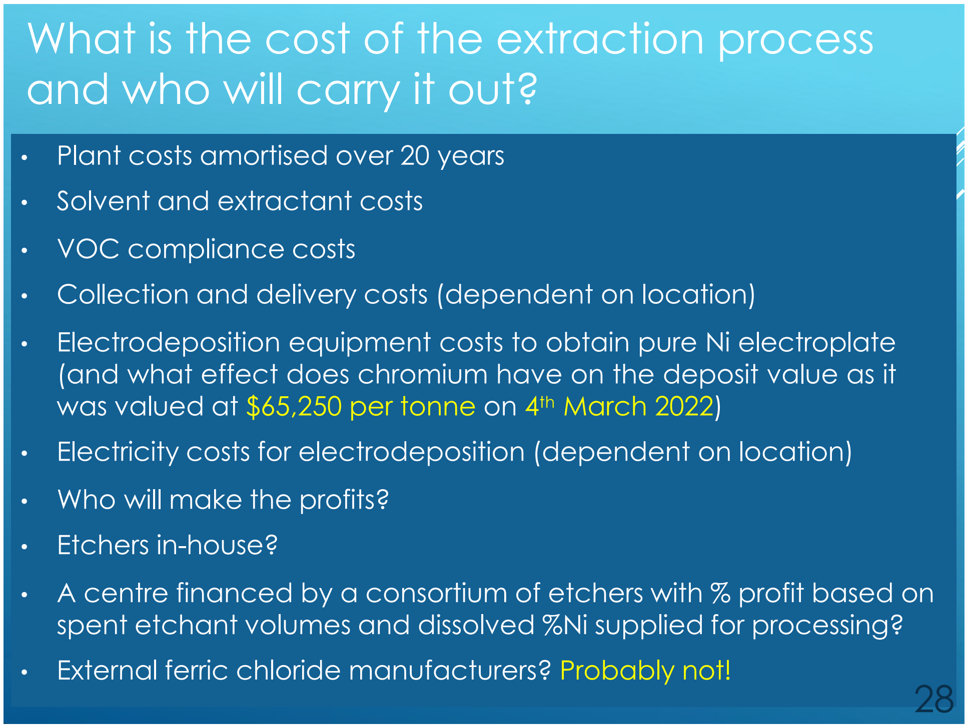
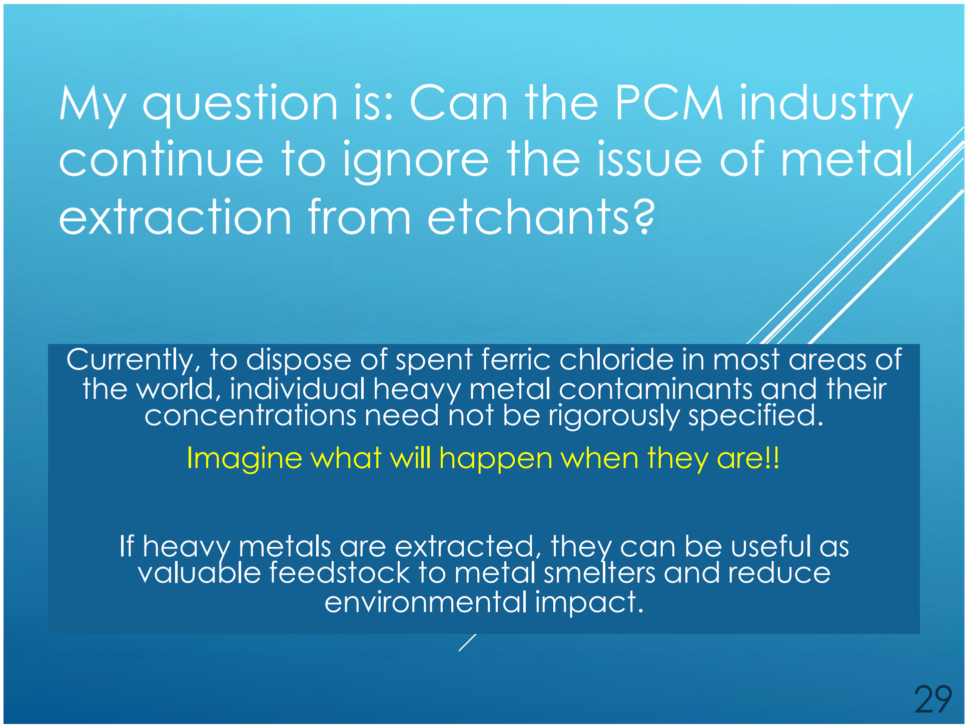
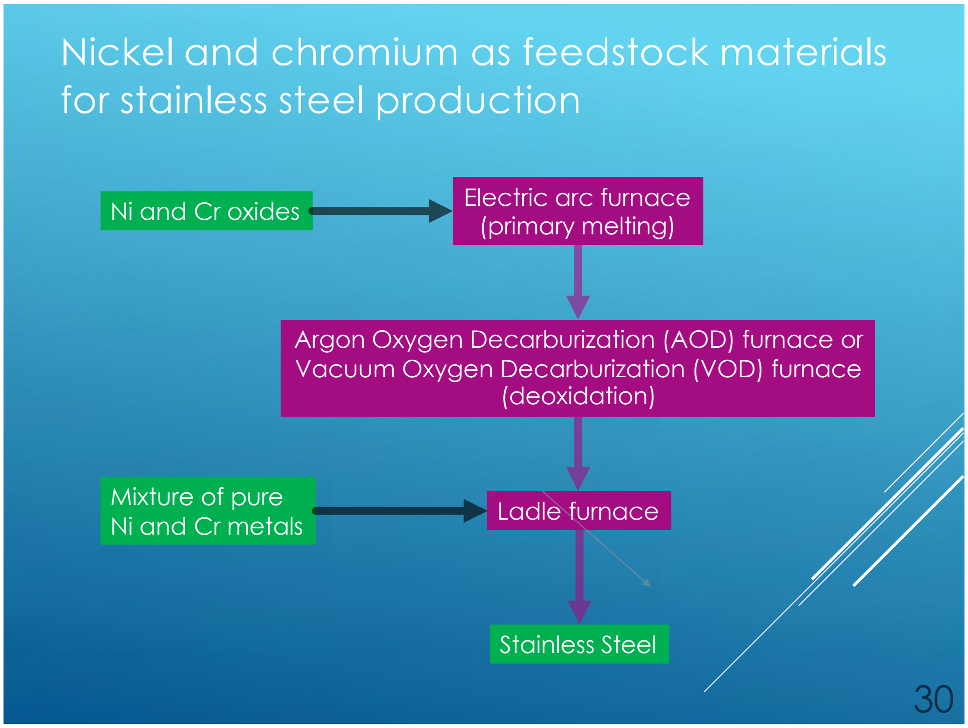
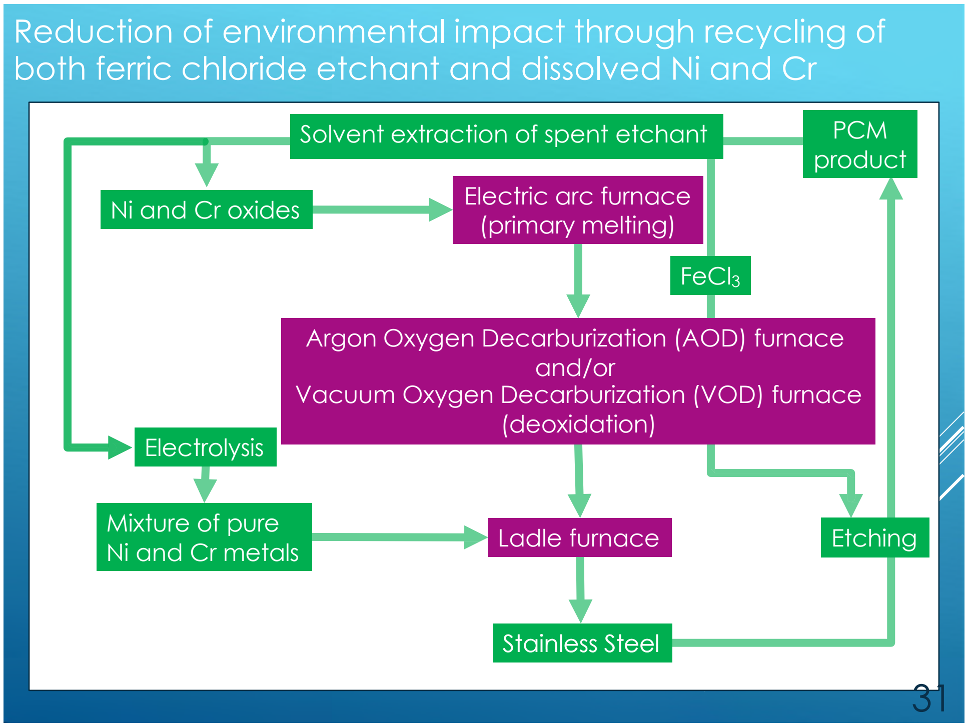
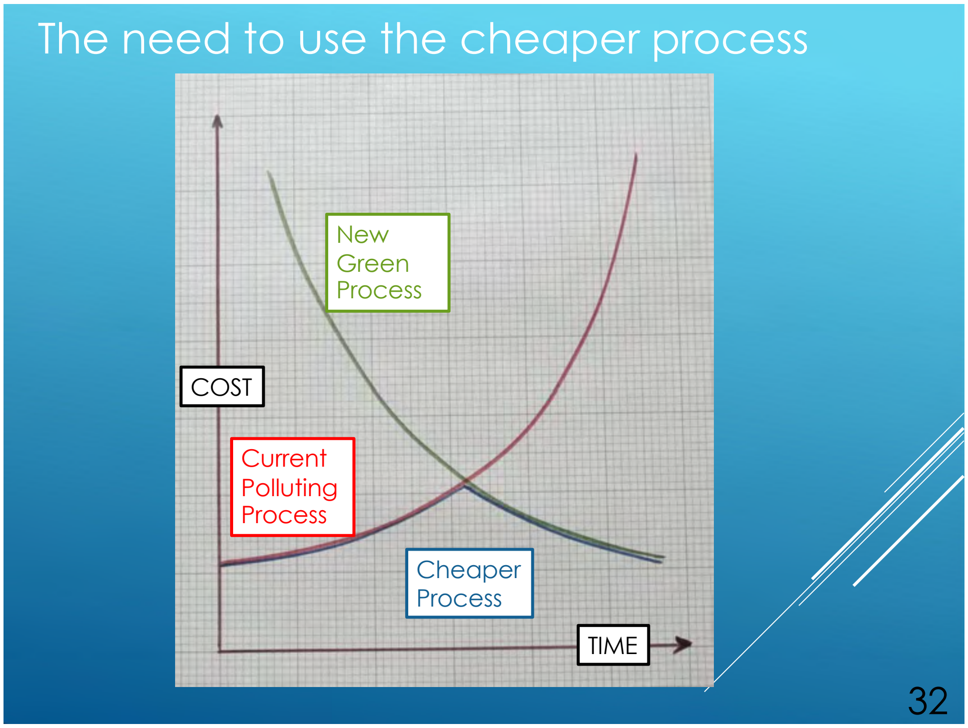
Cost of a glass-lined mixer-settler system to extract 415,000 litres of etchant per week?
Approximate cost of £250,000 to £300,000 based on initial enquiries with De Dietrich Process Systems Ltd., UK
27

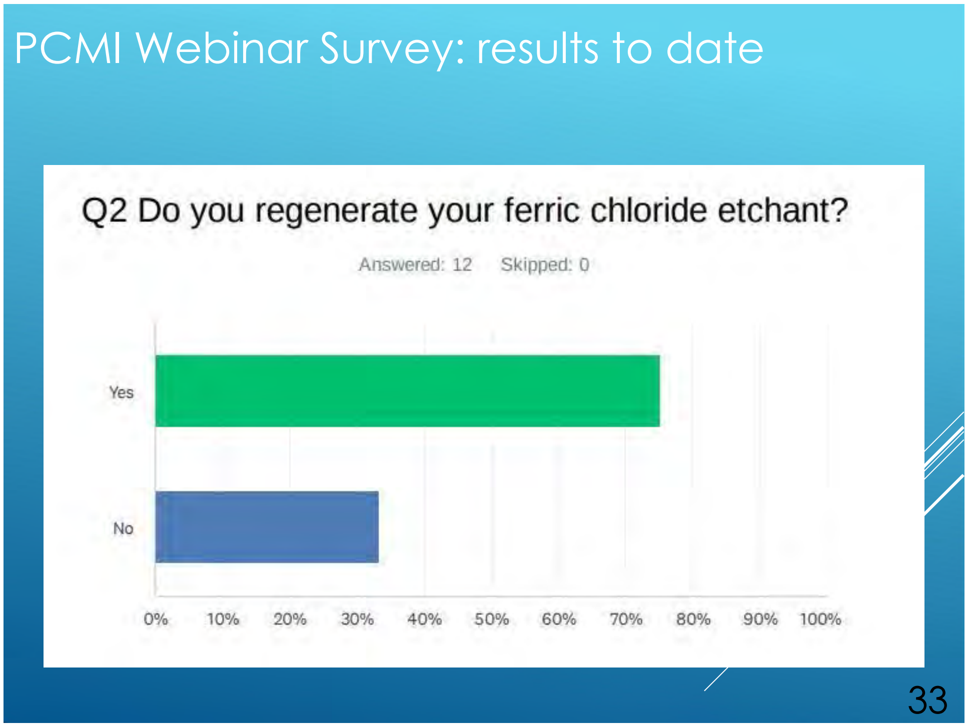

What is the cost of the extraction process and who will carry it out?
Plant costs amortised over 20 years
Solvent and extractant costs
VOC compliance costs
Collection and delivery costs (dependent on location)
Electrodeposition equipment costs to obtain pure Ni electroplate (and what effect does chromium have on the deposit value as it was valued at $65,250 per tonne on 4th March 2022)
Electricity costs for electrodeposition (dependent on location)
Who will make the profits?
Etchers in-house?
A centre financed by a consortium of etchers with % profit based on spent etchant volumes and dissolved %Ni supplied for processing?
External ferric chloride manufacturers? Probably not!
28

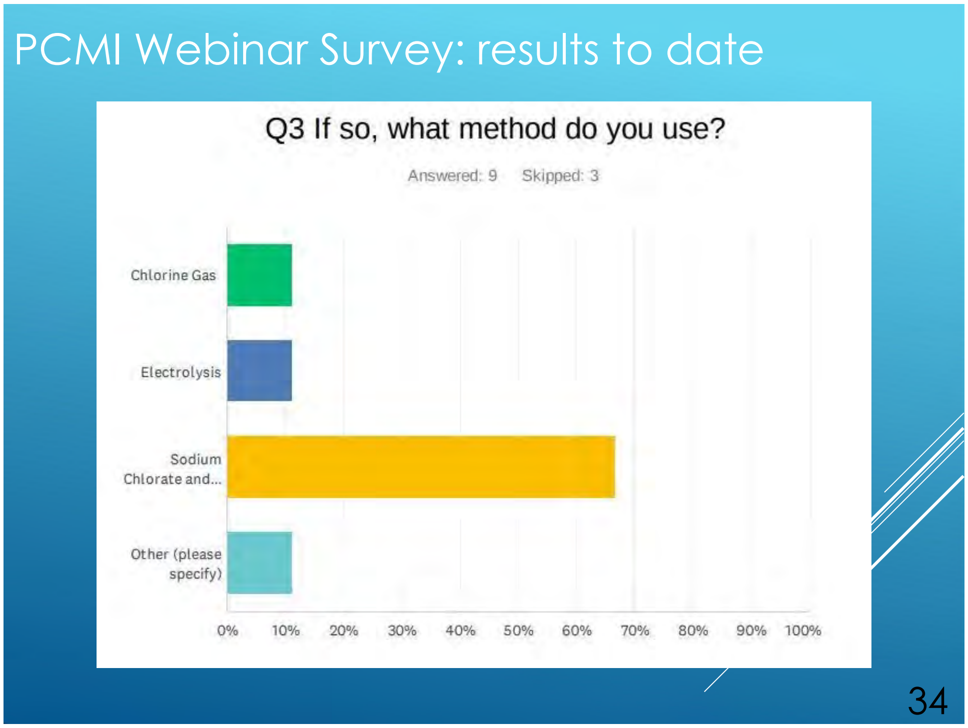

My question is: Can the PCM industry continue to ignore the issue of metal extraction from etchants?
Currently, to dispose of spent ferric chloride in most areas of the world, individual heavy metal contaminants and their concentrations need not be rigorously specified.
Imagine what will happen when they are!!
If heavy metals are extracted, they can be useful as valuable feedstock to metal smelters and reduce environmental impact.
29

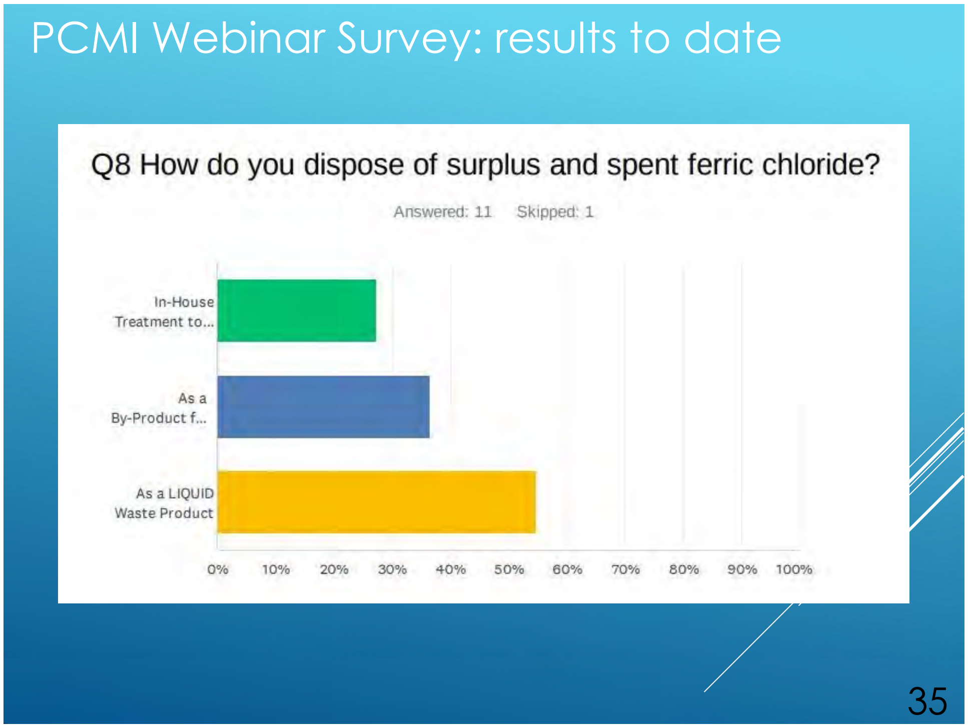

Nickel and chromium as feedstock materials for stainless steel production
Ni and Cr oxides
Electric arc furnace (primary melting)
Argon Oxygen Decarburization (AOD) furnace or Vacuum Oxygen Decarburization (VOD) furnace (deoxidation)
Mixture of pure Ni and Cr metals
Ladle furnace
Stainless Steel
30


Reduction of environmental impact through recycling of both ferric chloride etchant and dissolved Ni and Cr
Solvent extraction of spent etchant
PCM product
Ni and Cr oxides
Electric arc furnace (primary melting)
FeCl3
Argon Oxygen Decarburization (AOD) furnace and/or Vacuum Oxygen Decarburization (VOD) furnace (deoxidation)
Electrolysis
Mixture of pure Ni and Cr metals
Ladle furnace
Etching
Stainless Steel
31


The need to use the cheaper process
New Green Process
COST
Current Polluting Process
Cheaper Process
TIME
32


PCMI Webinar Survey: results to date
Q2 Do you regenerate your ferric chloride etchant?
Answered: 12 Skipped: 0
Yes
No
0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%
33


PCMI Webinar Survey: results to date
Q3 If so, what method do you use?
Answered: 9 Skipped: 3
Chlorine Gas
Electrolysis
Sodium Chlorate and...
Other (please specify)
0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%
34



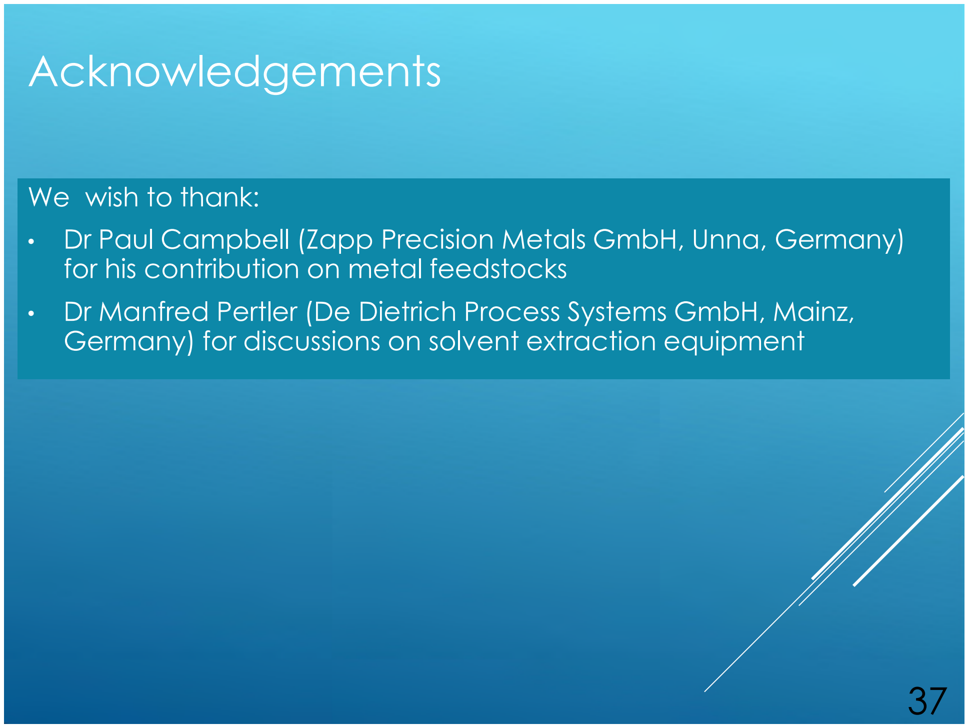
World survey costs of disposal of waste ferric chloride compared to its purchase price on 4th March 2013 (D M Allen, PCM and PEF, 2015)

Country	% of disposal cost compared to purchase price
Italy	104.0
Germany	66.7
Denmark	81.5
Sweden	106.4
Switzerland	53.8
UK	24.9
USA	66.4
USA	**146.8**
USA	**13.4**
Average	73.8

Key:
Lowest value
Highest Value

Can you help to supply us with current costs some 9 years later? We need this data to show the financial benefit of solvent extraction of dissolved Ni and Cr.

36


Acknowledgements
We wish to thank:
• Dr Paul Campbell (Zapp Precision Metals GmbH, Unna, Germany) for his contribution on metal feedstocks
• Dr Manfred Pertler (De Dietrich Process Systems GmbH, Mainz, Germany) for discussions on solvent extraction equipment
37


metaq
Präzisionsteile nach Maß


Hans

Spring 2022 Conference Photo Gallery

Emeritus Professor David Allen started his career as a chemist (BSc, 1968) and moved into photochemistry research (PhD, 1972) while studying at Cardiff University. Following post-doctoral research at Warwick University and imaging technology development in industry, David joined Cranfield University in 1976. He was appointed a Technical Liaison Member to the Photo Chemical Machining Institute (PCMI) in 1981 and is currently on the Board of Directors of PCMI responsible for education. David became Professor of Microengineering at Cranfield University in 1998 and was elected as a Fellow of The International Academy for Production Engineering (CIRP) in 2006.

David has published:

- Two PCM books: "The Principles and Practice of Photochemical Machining and Photoetching" (1986) and "Photochemical Machining and Photoelectroforming" (2015, reprinted 2016, 2017 and 2019)
- Five book chapters on non-conventional machining and contributed the chapter on 'Etching' to the on-line CIRP Encyclopedia of Production Engineering
- Seven confidential industrial PCM consortium reports
- 202 journal and conference papers and was awarded the higher doctoral degree of DSc from Cranfield University in 2013 for his thesis entitled "Contributions to Photochemical Machining and Photoelectroforming".

David retired from academia in 2011 and he now carries out consultancy and staff training in PCM companies across the world. He has worked with 26 different companies over the past 10 years.

Strengthening the weakest links in the PCM process chain: #4 Factors affecting photoresist adhesion

By

David M. Allen

Emeritus Professor of Microengineering, Cranfield University, UK

(This paper was presented at the PCMI Conference, Köln, Germany on 9th May 2022)

Abstract

Strong adhesion of a photoresist stencil to a metal surface is essential for production of quality parts fabricated by the PCM process. Photoresist adhesion is affected by many variables and good adhesion is only achieved by strict control of the processes involved in the PCM process chain leading to the formation of the photoresist stencil, especially metal cleaning, chemical and physical surface preparations, photoresist composition, photoresist processing and chemical etching. Clean stripping of the photoresist stencil after etching is also affected by the nature of the photoresist adhesion.

The various ways in which photoresist adhesion can be increased are discussed together with process recommendations. However, a quantitative figure of merit to describe adhesion strength is difficult to achieve although several qualitative adhesion tests have been proposed in the past to measure adhesion strength. These various tests are appraised for fitness of purpose.

Photoresist adhesion testing

I have received frequent complaints from PCM companies relating to poor photoresist adhesion affecting product quality but there appears to be no simple, rapid, quantitative test available in these companies to determine adhesion strength. This is both surprising and frustrating as the general coatings industry is large and needs to maintain standards to ensure product quality.

A literature search has found various standard tests for measuring adhesion strength of paints and varnishes coated on metal such as ASTM D4541: *Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Testers* and ISO 4624: *Paints and Varnishes — Pull-off test for adhesion* using equipment (Figure 1) as described below.

A quantitative test for adhesion is the pull-off test where a loading fixture, commonly called a dolly or stub, is affixed by an adhesive to a coating. By use of a portable pull-off adhesion tester, a load is increasingly applied to the surface until the dolly is pulled off. The force required to pull the dolly off or the force the dolly withstood, yields the tensile strength in pounds per square inch (psi) or mega Pascals (MPa). Failure will occur along the weakest plane within the system comprising the dolly, adhesive, coating system, and substrate, and will be exposed by the fracture surface.

Figure 1. The PosiTest AT Measures adhesion of coatings to metal, wood, concrete and other substrates featuring a manual hydraulic pump designed to apply smooth and continuous pressure with a single stroke [1].

The Standard leaves a lot to be desired as:

- a 2-part epoxy glue needs to be used that can vary in composition after curing
- the glue needs a 24-48 hour curing time before the test can be initiated
- an area of resist equal to the dolly base area needs to be isolated by cutting through the resist with a special tool
- the area may or may not contain developed features if the stencil is tested after exposure and development and
- the test is obviously a destructive test.

This test method maximizes tensile stress as compared to the shear stress applied by other methods, such as scrape or knife adhesion, and results may not be comparable. Further, pull-off strength measurements depend upon the instrument used in the test. Results obtained using different devices or results for the same coatings on substrates having different stiffness may not be comparable.

The topic of photoresist adhesion is complex and very little technical literature exists to help the PCM community. A useful reference that I have found is a thesis by Daniel Tomicic from the Department of Science and Technology, Linköping University, Sweden [2] but, unfortunately, the thesis concentrates solely on a sputtered aluminium film coated on a silicon wafer and a liquid, positive-working photoresist. The thesis indicates that perhaps 30 separate "tests for adhesion" exist but few give useful information.

PCM companies that carry out adhesion tests, usually test the resist after coating, exposure and development have been carried out. Various qualitative and subjective adhesion tests can then be applied to the stencil, such as a

- tape pull test
- resist undercut test and
- quantitative abrasion test.

Tape pull test

Tomicic [2], states: "The tape method uses an adhesive tape to lift the film off the substrate. This method gives only qualitative results and no numerical results. A direct measure of adhesion may be obtained by applying a force normal to the interface between film and metal." and "The techniques to apply the forces give inconsistent results of the adhesion due to the interface morphology."

In discussing tape pull tests with Kirk Lauver (Chemcut Corp., USA), he commented: "…many variables influence the results, e.g. angle of pull, type of tape adhesive, length of time the tape has been in contact with the surface, cleanliness of the surface before the tape is applied, pull across developed lines or in the direction of the developed resist lines etc."

Resist Undercut Test

By printing a "line and space" resolution test pattern into the photoresist and etching for specific times, it can be determined when sufficient undercut occurs to completely lift off the test pattern at a particular resolution. As etching time increases, it will be noted that the lines lifted from the metal interface become increasingly larger. Thus, for a fixed time of etching and a fixed etchant composition, the degree of undercut can be assessed. Increased adhesion will thus allow greater resolution to be attained for a fixed etching time.

Abrasion test

Tomicic [2] states: "Abrasion testing gives results that depend on both the hardness and the adhesion of the films and are affected by the burnishing action of the abrasive head." Therefore, this poses the question as to whether this test is indeed a true test for adhesion.

<u>Quantitative adhesion test procedures</u>

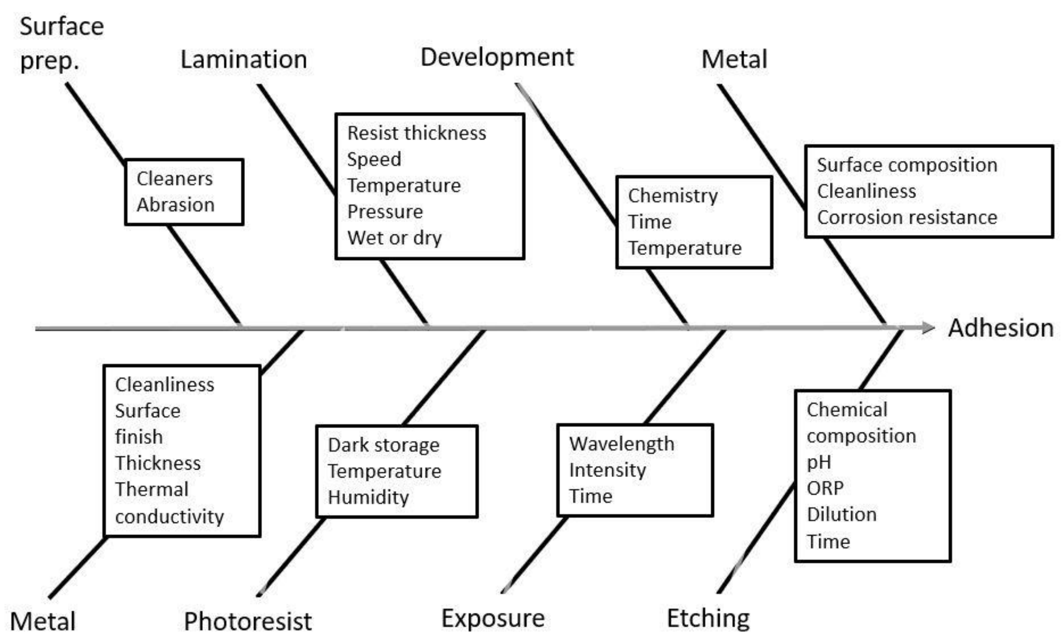
It appears from the analysis of the tests presented above that there is no standard, quantitative test for assessing photoresist adhesion and no means of assessing variables affecting adhesion. As an aside, in a period of over 80 man-years working with PCM companies, neither Kirk Lauver nor I have ever seen a quantitative test for adhesion used in a PCM company!

In summary, the current situation of adhesion testing appears to be unacceptable and I believe PCM companies need a completely different strategy to measure and monitor photoresist adhesion. Therefore, in this paper, I will attempt to emphasise which *aqueous* *negative-working dry film resist (DFR) processing techniques* are fit for purpose in achieving the required level of adhesion.

Lacombe [3] states "Adhesion is a property of surfaces". For optimum adhesion, an aqueous processable DFR must thoroughly "wet out" the surface to be coated. To wet out a metal surface the photoresist must flow and cover the surface, thus allowing for maximum contact area between the photoresist and the metal surface. It should also be noted that surfaces are difficult to study and examine. It is informative to note the quotation from the Austrian theoretical physicist, Wolfgang Pauli (1902-1959), who said: "God made the bulk; surfaces were invented by the devil."

Furthermore, the cause of weak adhesion is complicated by the large number of variables in the PCM process chain that can affect adhesion as shown in Figure 2.

Figure 2. Ishikawa (Fishbone) diagram showing factors affecting adhesion of photoresist.



We must also bear in mind the comments made by the British physicist Lord Kelvin (1824-1907) who stated:

- "Can you measure it? Can you express it in figures? Can you make a model of it? If not, your theory is apt to be based more upon imagination than upon knowledge."

and

- "If you cannot measure it , you cannot control it."

Therefore, all processes in the chain need to be rigorously controlled for optimum control of adhesion strength [4,5].

Cleaning of metal

Metal cleaning has been changed considerably over the past three decades to reduce environmental impact with organic solvent cleaners replaced by aqueous cleaners [6]. There is also a vast range of different aqueous cleaners used across the world's PCM companies. This provokes questions such as:

- Which cleaning system is best?

and

- How does one select cleaning process chemistry without quantitative evidence?

DFR Lamination

DFRs are formulated to be aqueous processable to reduce environmental impact [6]. The process of DFR lamination necessitates the need to melt dry film. When the melted photoresist fails to wet out the metal surface, ***some*** resists may be helped by the addition of water to the lamination process. This is known as wet lamination of DFRs and is an additional process causing potential control challenges in the yellow clean room.

In consideration of the question "What makes good adhesion?", it is known that mechanisms for adhesion rely on a chemical contribution (van der Waal's forces) and a physical contribution (keying into the metal microstructure).

Chemical adhesion promoters are rarely used as their use gives potential processing challenges when etching [7] although adhesion promoters have been reported as being a constituent within the photoresist formulation itself [8].

Process procedures for surface preparation include the use of:

- Scotchbrite®,
- fixed abrasives attached to rollers and discs,
- pumice sprays and
- suspensions of loose abrasives

with abrasion modifying the surface structure of the metal to provide a physical "key" for the photoresist to lock into. These processes are difficult to control consistently and can result in particulate contamination of the atmosphere and a potential contamination of the metal surface to be coated with photoresist.

There are significant differences between high-volume, reel-to-reel (R2R) PCM processing and low-volume single sheet PCM processing. It is much easier to clean a reel of thin metal with a specific composition and thickness quickly and consistently in highly-automated R2R processing because the metal is being moved continuously forward into the next integrated process (photoresist coating/lamination) under safelight conditions. In contrast, a wide variety of metal sheets with different compositions in different thicknesses require changes to cleaning regimes and thus sheets tend to stand around in stacks after cleaning, waiting for the lamination process to start, usually in a stand-alone yellow clean room. The lamination of thick sheets may also require a preliminary heat treatment to offset any undesirable heat-sink effects lowering the lamination temperature.

Surface free energy

Surface free energy (SFE) is the work that would be necessary to increase the surface area of a solid phase. SFE has a decisive influence on the wettability of solids by liquids. Every system strives for a state of free energy that is as low as possible. Liquids therefore take the smallest possible surface area at a given volume due to the surface tension (SFT); in weightlessness they form spherical droplets. However, solids cannot minimize their surface by deformation, but they can form an interface with a liquid to reduce free energy, i.e. they can be wetted. Therefore, the SFE of a solid is closely related to its wettability.

The terms SFE and SFT are physically equivalent. SFE is usually used for solid surfaces and SFT for liquid surfaces. SFE has the unit J/m^2 (Joule per square metre) as the energy per area, and STF has the equivalent unit N/m (Newton per metre) but, as industrial users favour whole numbers, units of mJ/m^2 and mN/m area usually used.

As N = J/m, $mN/m = mJ/m^2$

As $1J = 10^7$ dyne.cm then

$mJ/m^2 = 10^{-3} \times 10^7$ dyne.cm$/10^4$ cm^2 = dyne/cm

Thus, SFE and SFT can be expressed as the same number in mJ/m^2 , mN/m and dyne/cm.

For a liquid to achieve wet out on a surface and ultimate adhesion, one must understand the surface energy of the substrate. Table 1 lists typical surface energies of commonly used substrates derived from tables of published data [9-11].

Tests for wettability and measurement of surface free energy (SFE)

1. Water-break test (somewhat subjective).

Pouring water on your metal is an easy way to test its surface energy. In this test, water is representative of the aqueous processable DFR. After applying water to the metal, take notice of how the water reacts. If it pools, it means the water is more attracted to the metal surface than it is to itself. This means the surface has high surface energy. If it beads, the water is more attracted to itself than the surface, i.e. your metal has low surface energy. If you're having trouble picturing this, consider pouring water on aluminium (840 dyne/cm) as opposed to a Teflon® coated pan (18 dyne/cm). Water on aluminium pools whereas water on Teflon® beads[6]. Alternatively think of a bead of water on a car. On a freshly waxed car, the water beads up and covers a smaller surface area. On an unwaxed car, the water spreads more across the surface. By waxing the car, the surface energy of the car's surface has changed and does not allow the bead of water to cover as much area.

PCM companies that do carry out a water-break test often use tap water rather than DI water due to cost. *However, tap water contains dissolved contaminants and should not be used.*

Table 1. Published Surface Free Energy Values

Material	mN/m [9]	mN/m [10]	mN/m [11]
Platinum			2,672
Copper	1,103	1,650	1,360 *
Nickel			1,770 *
Silicon (111) plane		1,240	
Stainless Steel	700-1,000		
Silver			890 *
Aluminium	840		
Zinc	753		
Tin	526		
Glass	250-500	83.4	
Nylon	46		
Polyester (PET)	43		
ABS Plastic	42		
Polycarbonate	42		
PVC	39		41.5
Acrylic	38		
Polyethylene (PE)	31		32.4
Polypropylene (PP)	29		33
PTFE Fluoropolymer (Teflon®)	18	19	19.1
			*theoretical value

2. Dyne pens [12]

Dyne pens comprise a range of pens containing liquids of different surface tensions. When the Dyne level test pen is applied to the surface, the liquid will either form a continuous film on the surface or pull back into small droplets. If the Dyne test fluid remains as a film for 3 seconds or more, the substrate will have a minimum surface energy of that ink value, expressed in mN/m (dyne/cm).

3. The Krüss Mobile Surface Analyser (MSA)

The MSA involves the measurement of individual liquid droplet contact angles and thus allows a quantitative value of SFE to be determined on individual metal sheets and in reel-to-reel (R2R) systems.

In summary, Young's equation takes into consideration the thermodynamic equilibrium between the three phases of matter in contact: **S**olid, **L**iquid and **G**as.

Table 2. Surface tension of test liquids

Surface Tension component	Total Surface Tension	Dispersive Component	Polar Component	Acid Component	Base Component
Test Liquid	**Dyne/cm**				
Formamide	58.0	39.0	19.0	2.28	39.6
Diiodomethane	50.8	50.8	0	0	0
Water	72.8	26.4	46.4	23.2	23.2
α-bromonaphthalene	44.4	44.4	0	0	0

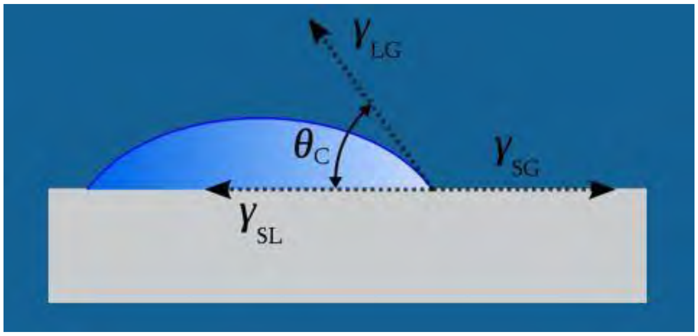
Regarding a schematic of a liquid drop on a metal surface (Figure 3) then

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta_C \text{ and } \gamma_{LG}(1+\cos\theta_C) = \Delta W_{SLG}$$

where ΔW_{SLG} is the solid-liquid adhesion energy per unit area.

Therefore, as $\theta_C \rightarrow 0$, adhesion energy maximises and the surface wets out.

Figure 3. Droplet contact angle measurement



Details of the techniques used have been presented by Frese [13]. Larger scale equipment to measure contact angle is also marketed by Biolin Scientific [14] and GBX Scientific.

<u>Case study</u>

Using contact angle measurement technology, Kim *et al* [15] demonstrated a time-dependent wettability of polished stainless steel and showed the surface became hydrophobic as time passed. Oxygen was identified as the dominant factor in the wettability transition.

This research indicates that materials such as stainless steel should be coated with DFR as soon as possible after metal cleaning and that contact angle measurement can be useful to assess cleaning methods for performance.

Photoresist processing

Photoresist exposure is required to cross-link polymer chains. This process can produce stresses within the resist structure and the correct exposure for optimum resolution is essential. Photoresist development control is also essential as vertical sidewalls are required for ultimate resolution plus excellent adhesion to underlying metal to prevent seepage of etchant under the resist film.

Both processes need very tight control, otherwise defects are difficult to attribute to either of the two processes. Careful microscopic evaluation of the resultant stencil can be informative. This is rarely carried out in production as it is time-consuming. However, as product specifications become more demanding rigorous process control is essential.

Post-exposure baking is generally regarded as a way of toughening the stencil and increasing adhesion but it can induce more stress in the film [8]. Is this process merely an excuse (a "bandage") for inadequate cleaning?

Post-development baking has also been recommended to increase adhesion but this raises the potential problem of lifting any "foot" formed in processing [6].

To attain the highest resolution with vertical sidewalls in dry film photoresist it has been demonstrated that, in the photoresist processing chain, the significant factor to control is exposure energy. Photoresist development, post-exposure baking and post-development baking are not significant [16].

Etching

In the etching process, any metal-resist interface weakness is affected by etchant ion size and DFR permeability. For example, etching in HF (with a small F^- ion) produces more attack at the interface than etching with ammonium bifluoride, $NH_4F.HF$ (with a larger HF_2^- ion).

Good adhesion is necessary for high-quality etching but most parts need the resist to be stripped at the end of the process chain, so the strong adhesion forces then need to be broken!

Conclusion

Recommendations for adhesion control include:

(1) Testing for clean metal surfaces is a preferred strategy in comparison to performing destructive adhesion pull tests on processed photoresist stencils.

(2) MSA and Dyne Pen wettability tests are very quick tests (performed in seconds) whereas standard adhesion tests are lengthy (often taking several days).

(3) Quantitative measurement of water contact angles on "cleaned" metal surfaces is extremely useful in comparing different cleaning processes, the efficiency of the chemical formulations used and the degradation of the chemistry during use.

(4) There should be minimum lag time between metal cleaning and metal coating.

Tight control of the PCM process chain is at the heart of good adhesion. A lack of photoresist adhesion is symptomatic of loss of overall process monitoring and control within the chain.

The overall % yield of product depends on the number of processing steps in the chain and the % yield at each step, as illustrated in Table 3, should be maximised. Note also that the lower the overall process yield, the higher the process cost will be.

Table 3. % Process yield dependency on the number of processing steps and yield per step.

Number of processing steps	% Yield per step	Overall process yield	% Process yield	Comment on % process yield
10	95%	$(0.95)^{10}$	59.9	Unacceptable
10	99%	$(0.99)^{10}$	90.4	Unacceptable
10	99.9%	$(0.999)^{10}$	99.0	Acceptable ?
15	95%	$(0.95)^{15}$	46.3	Unacceptable
15	99%	$(0.99)^{15}$	86.0	Unacceptable
15	99.9%	$(0.999)^{15}$	98.5	Acceptable ?

Acknowledgements

I wish to acknowledge help and useful comments from Kirk Lauver (Chemcut, State College, PA, USA), Dr Daniel Frese (Krüss, Hamburg, Germany), Jackie Sharkey (Dyne Testing Ltd., Lichfield, UK) and Dr Araz Barani (Zapp GmbH, Unna, Germany) in preparing this paper.

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How Contact Angle Measurements Can Help To Optimize Photoresist Adhesion

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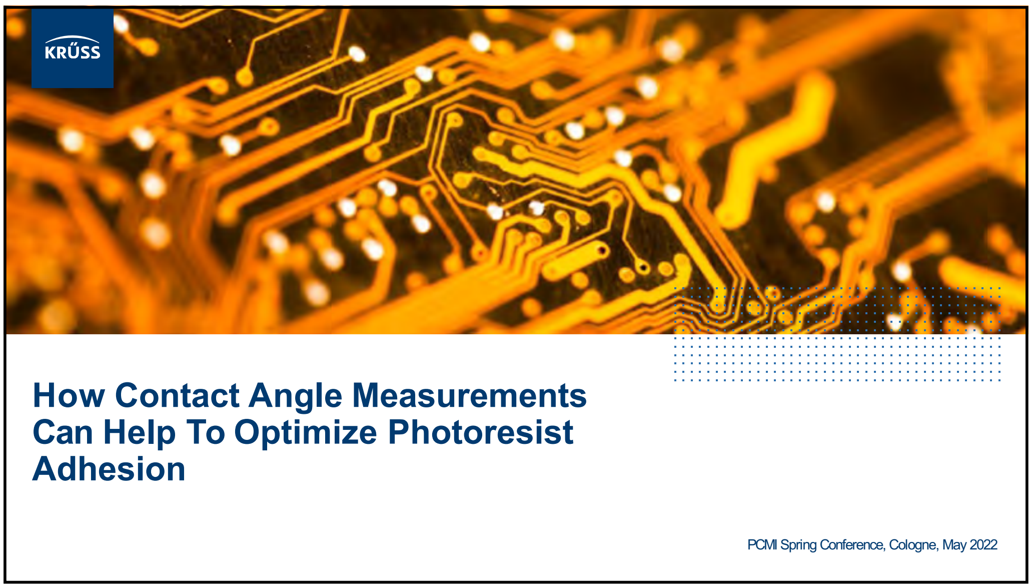
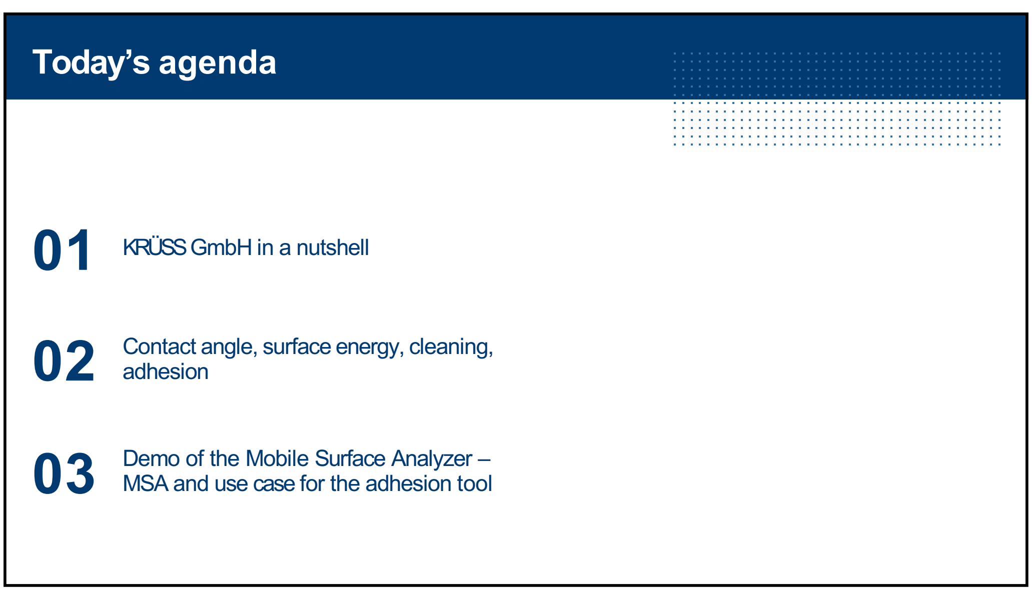
Dr. Frese has been working together with key companies and research centers in the field of coating technology, surfactant research, adhesives, personal care, just to name a few, building solid experience in surface and interface science.





01

KRÜSS GmbH in a nutshell

Global market leader and family-owned business since 1796

- Headquartered in Hamburg, Germany (≈ 200 employees)
- Daughter-companies in Charlotte, NC, USA and Shanghai, CN
- Invented the first Digital Tensiometer in the 1980s
- Main current product lines: Tensiometers, Contact Angle Meters, Foam Analyzers

We serve many different industries and applications – but today I want to focus on where we can serve photochemical machining

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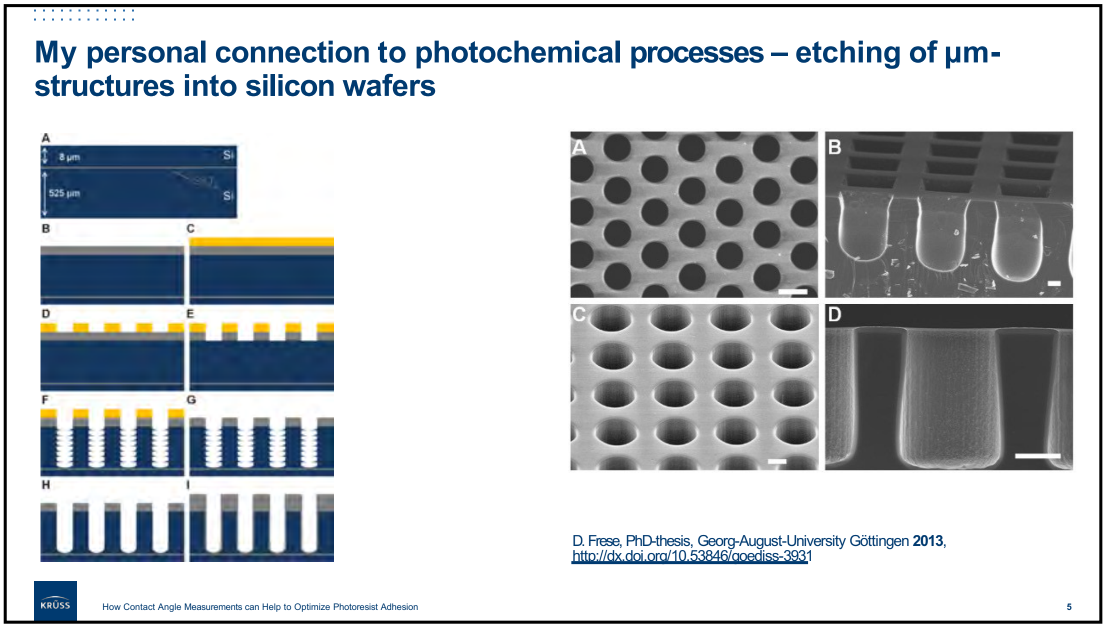
My personal connection to photochemical processes – etching of µm-structures into silicon wafers
A
8 µm
525 µm
Si
Si
B
C
D
E
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D. Frese, PhD-thesis, Georg-August-University Göttingen 2013,
http://dx.doi.org/10.53846/goediss-3931
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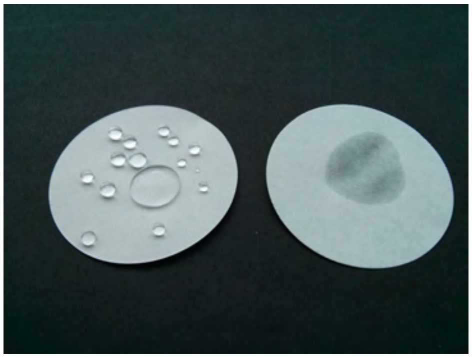
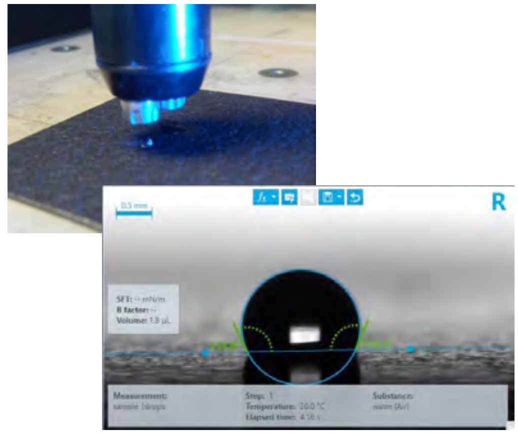
02
The concept of contact angle and SFE
And how it affects adhesion

The shape of a drop – simple as it seems – can tell us a lot about the surface and its properties



Membranes. Left: hydrophobized, right: untreated



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The Young equation describes this drop shape based on physical parameters

$$\cos\theta = \frac{\sigma_s - \sigma_{ls}}{\sigma_l} \iff \sigma_s = \sigma_{ls} + \sigma_l \cos\theta$$

σ_l = Liquid's surface tension (SFT)
σ_s = Solid's surface free energy (SFE)
σ_{ls} = Liquid/solid interfacial tension (IFT)
Θ = Contact angle

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So much for contact angle basics – now let's have a look at adhesion!

=> In all cases, improper surface preparation was the reason for poor coating adhesion

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There are some widespread measures that typically are taken when adhesion fails

1) *„Cleaning": Solvent-wipe, spray cleaning, CO_2-snowblasting, laser, plasma, corona*
2) *„Activating": plasma, corona, primer, laser, conversion coating*
3) *„Roughening": sandblasting, abrasive grinding, etching, conversion coating*
4) *„Blame coating": switch to different coating, adjust formulation*

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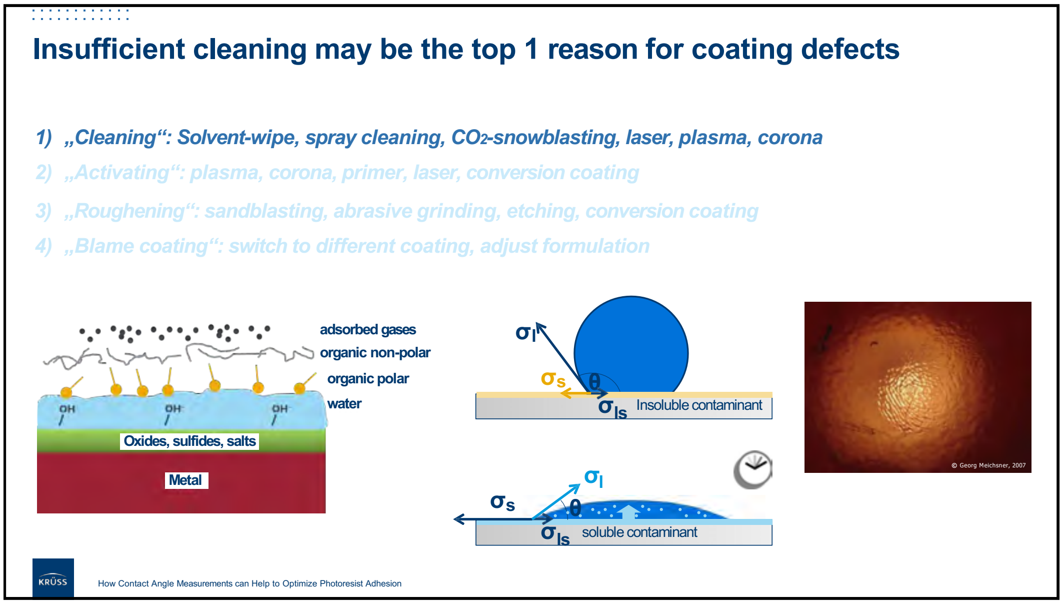
Insufficient cleaning may be the top 1 reason for coating defects
1) „Cleaning“: Solvent-wipe, spray cleaning, CO2-snowblasting, laser, plasma, corona
2) „Activating“: plasma, corona, primer, laser, conversion coating
3) „Roughening“: sandblasting, abrasive grinding, etching, conversion coating
4) „Blame coating“: switch to different coating, adjust formulation
adsorbed gases
organic non-polar
organic polar
water
OH
Oxides, sulfides, salts
Metal
σl
σs
θ
σls
Insoluble contaminant
soluble contaminant
© Georg Meichsner, 2007
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At what point can we consider something to be „clean enough“? What‘s invisbile to the eye can be measured, though!
Surface free energy as a parameter for cleanliness control
• Experimental setup:
Contaminated steel plates
Cleaning in a ultrasonic bath, 3% Mucasol; variation of dwell time
Analysis of steel plate surfaces
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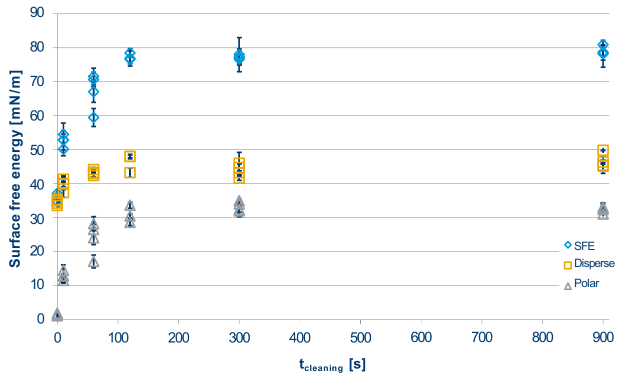
After 120 s an optimum cleaning is reached – further cleaning doesn't show any effect

After only 10 s of cleaning, significant differences in surface free energy can be observed



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Once the dwell time has been optimized, the method can be used for quality control

Controling the cleanliness of processed parts

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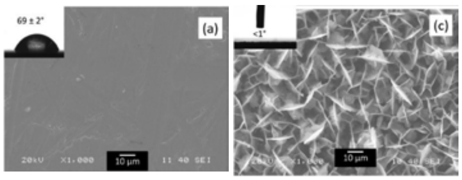
Changing the surface chemistry can help a coating to spread and adhere properly

1) „Cleaning": Solvent-wipe, spray cleaning, CO_2-snowblasting, laser, plasma, corona
2) „Activating": plasma, corona, primer, laser, conversion coating
3) „Roughening": sandblasting, abrasive grinding, etching, conversion coating
4) „Blame coating": switch to different coating, adjust formulation



J D Brassard, Nano-micro structured superhydrophobic zinc coating on steel for prevention of corrosion and ice coating, *J Colloid Interface Sci* **2014**, in press.

Step:	Target SFE:	Actual SFE:
Raw sample before cleaning	≥ 34 mN/m	30 mN/m
Sample after cleaning	≥ 42 mN/m	45 mN/m
Sample after etching	≥ 48 mN/m, ≥ 10 % polar	52 mN/m, 11 % polar
Finished sample after phosphating	≥ 58 mN/m, ≥ 20 % polar	61 mN/m, 24 % polar

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Roughness can help, but only when wetting is good

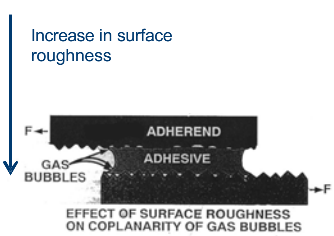
1) „Cleaning": Solvent-wipe, spray cleaning, CO_2-snowblasting, laser, plasma, corona
2) „Activating": plasma, corona, primer, laser, conversion coating
3) „Roughening": sandblasting, abrasive grinding, etching, conversion coating
4) „Blame coating": switch to different coating, adjust formulation

- Adhesive bonding of Ni-samples:

Roughness [microinches]	Shear strength [g]
1.7	90
2.5	105
4.5	135
6.0	180
9.0	250

- Maplewood, bond with urea-formaldehyde resin

Surface	Shear force [PSI]
smooth	3 120
sand blasted	2 360
sawn	2 690
patterened	2 400



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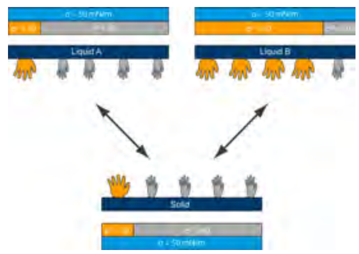
But for good adhesion both surface and coating must match

1) *„Cleaning“: Solvent-wipe, spray cleaning, CO_2-snowblasting, laser, plasma, corona*
2) *„Activating“: plasma, corona, primer, laser, conversion coating*
3) *„Roughening“: sandblasting, abrasive grinding, etching, conversion coating*
4) ***„Blame coating“: switch to different coating, adjust formulation***

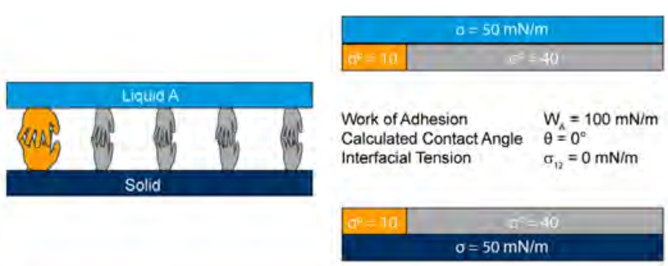


KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

The best connection between coating and surface can be obtained when the polarity ratios match

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2 \times \left(\sqrt{\sigma_1^d \sigma_2^d} + \sqrt{\sigma_1^p \sigma_2^p} \right)$$

Work of adhesion W_A



KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

A polarity mismatch can cause poor adhesion despite "good" overall numbers

$$\sigma_{12} = \sigma_1 + \sigma_2 - 2\times\left(\sqrt{\sigma_1^d\sigma_2^d} + \sqrt{\sigma_1^p\sigma_2^p}\right)$$

Work of adhesion W_A

KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

Physical parameters that describe adhesion can be derived from contact angle analysis

Spreading coefficient:

$$S = \sigma_s - \sigma_l - \sigma_{sl}$$

Work of adhesion:

$$W_A = 2\sqrt{\sigma_s^d\sigma_l^d} + 2\sqrt{\sigma_s^p\sigma_l^p}$$

Interfacial tension:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^d\sigma_l^d} - 2\sqrt{\sigma_s^p\sigma_l^p}$$

Parameter	Effect	Critical value
S	Spontaneous wetting	≥ 8 mN/m
W_A	Initial bonding strength	≥ 65 mN/m
σ_{sl}	Long term stability	≤ 1 mN/m

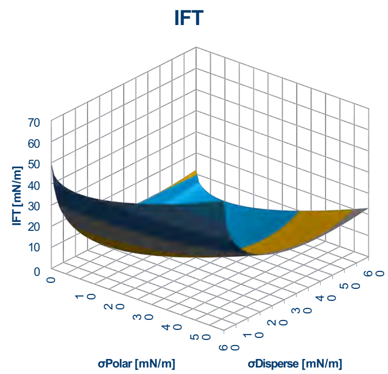
According to: KRÜSS AR 260 *Optimizing Automotive Coatings* **2007**.

Test inks / dyne pens do not deliver any information on this!

KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

Based on the results for either the coating or the substrate, wetting can be predicted

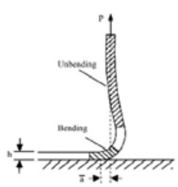
Minimize interfacial tension



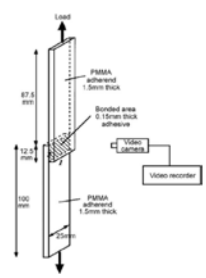
$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s^d\sigma_l^d} - 2\sqrt{\sigma_s^p\sigma_l^p}$$

There are different direct methods to test a coating‘s adhesion

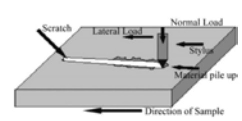
Some examples from international norms/standards



Peel Test, ASTM D1876



Tensile Lap shear test, ISO 4587:2003



Scratch test, ASTM C1624

F Awaja *et al.*, *Prog Polym Sci* **1988**, *34*, 948.

How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

Contact angle measurements are a proven, quick alternative for those destructive and time consuming methods

Some examples where contact angle can predict the outcome of other tests

Table 2
Combination of direct and indirect techniques used by researchers for the adhesion investigations.

Direct technique	Indirect technique	Polymer system	Reference
Lap Shear test	XPS	Plasma treated PP system	[133]
	FTIR	Epoxy–amine system, Polyimide (PI) films	[183,240,125]
	EDS, Contact Angle	DC glow discharge treated HDPE	[91]
	SEM, XPS	Maleic anhydride-grafted pp in PP	[116]
	XPS, Contact Angle	PE, PEEK	
Pull out test	SEM, XPS, Contact Angle	Ozone treatment of PET and poly(hydroxyethyl methacrylate	[186]
Pull off/Stud test	XPS	144 I/O Film-BGA	[201]
	XPS, SEM	Copper metallised glass fibre reinforced epoxy	[198]
	XPS, Contact Angle	Flame treated PP	[236]
	XPS, SEM	PP–copper compound	[241]
Nanoindentation/Scratch test	XPS, Contact Angle	Plasma polymerized hexane films	[188]
		Plasma treated PET	[189]
		Acrylic coated polymers	[192]
	SEM, Contact Angle, Raman Spectroscopy	Ion implanted PC surface	[206]
Peel test	FTIR-ATR	Oxygen and pulse plasma of polypropylene and poly(tetrafluoroethylene)	[242]

F Awaja *et al.*, *Prog Polym Sci* **1988**, *34*, 948.

How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

In literature, you can find several examples for improved adhesion based on matching polarity ratios

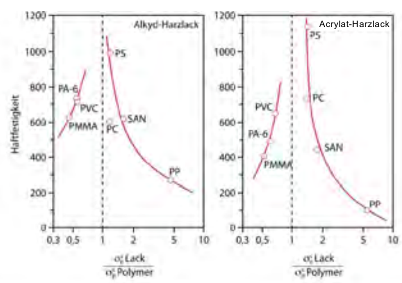
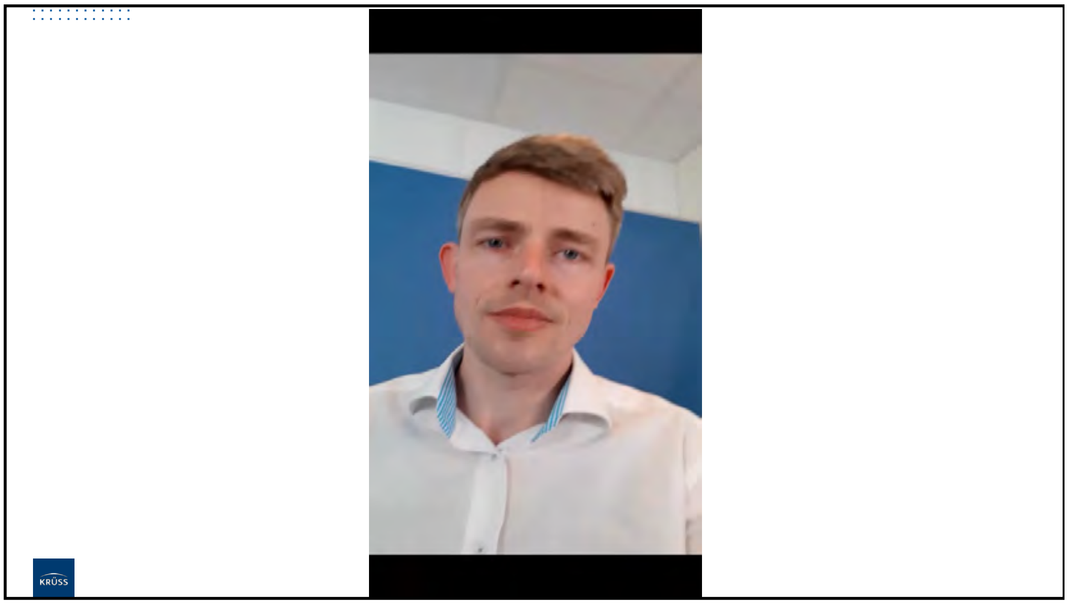


Bild 40 Haftfestigkeit als Funktion der polaren Oberflächenspannungsanteile beim Alkyd-Harzlack und beim Akrylat-Harzlack auf verschiedenen Thermoplasten (Potente)

From: Kunststoff-Schadensanalyse, gez. Ehrenstein, G. W.; Universität Erlangen; LKT

How Contact Angle Measurements can Help to Optimize Photoresist Adhesion


03
Check adhesion potential with a click
The Mobile Surface Analyzer - MSA
KRÜ
Mobile Surface Analyzer


KRÜSS

Here's a use case for our adhesion analysis workspace of our ADVANCE software

Sample name	σ [mN/m]	$σ^D$ [mN/m]	$σ^P$ [mN/m]	Polarity [%]
Kevlar-based Fishing Line	34.52	33.41	1.11	3.22

Sample name	σ [mN/m]	$σ^D$ [mN/m]	$σ^P$ [mN/m]	Polarity [%]
Organic Coating	26.53	23.20	3.33	12.55

- The coating gives color and reduces friction
- Problem: 40-50 casts and the coating was worn off
- ADVANCE allows for direct calculation of adhesion parameters:

		Kevlar-based Fishing Line	
Organic Coating	W_A	59.53	mN/m
	$γ_{SL}$	1.52	mN/m
	S	6.47	mN/m
	$θ$	0.00	°

KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

First idea on customer side was to do a plasma activation to increase adhesion

That turned out to be a bad idea

Sample name	σ [mN/m]	$σ^D$ [mN/m]	$σ^P$ [mN/m]	Polarity [%]
Kevlar-based Fishing Line	34.52	33.41	1.11	3.22
Plasma-treated Kevlar Line	39.25	34.37	4.88	12.45

		Kevlar-based Fishing Line			Plasma-treated Kevlar Line	
Organic Coating	W_A	59.53	mN/m	W_A	64.54	mN/m
	$γ_{SL}$	1.52	mN/m	$γ_{SL}$	1.24	mN/m
	S	6.47	mN/m	S	11.48	mN/m
	$θ$	0.00	°	$θ$	0.00	°

- Plasma treatment, a typical measure to improve adhesion, made the coating wear off after only <10 casts!

  => What went wrong?

KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

Plasma treatment made water feel much more confortable at the interface

Activating the solid was not the right step to take

Sample name	σ [mN/m]	σ^D [mN/m]	σ^P [mN/m]	Polarity [%]
Kevlar-based Fishing Line	34.52	33.41	1.11	3.22
Plasma-treated Kevlar Line	39.25	34.37	4.88	12.43

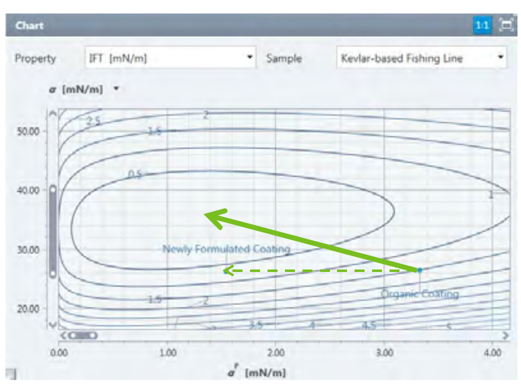
		Kevlar-based Fishing Line			Plasma-treated Kevlar Line	
Organic Coating	W_A	59.53	mN/m	W_A	64.54	mN/m
	γ_{SL}	1.52	mN/m	γ_{SL}	1.24	mN/m
	S	6.47	mN/m	S	11.48	mN/m
	θ	0.00	°	θ	0.00	°
Water	W_A	69.02	mN/m	W_A	86.30	mN/m
	γ_{SL}	38.30	mN/m	γ_{SL}	25.75	mN/m
	S	-76.58	mN/m	S	-59.30	mN/m
	θ	92.97	°	θ	79.32	°

- The ratio, by which a coating-line interface is preferred over a water-line interface decreased from 25.2 to only 20.8!

KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

Looking at the iso-line plot gives clear directions how the coating should be changed

Adhesion analysis workspace in ADVANCE software



KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

Re-formulation of the coating resulted in the desired improved coating stability

The result shows: it works!

Sample name	σ [mN/m]	σ^D [mN/m]	σ^P [mN/m]	Polarity (%)
Organic Coating	26.53	23.20	3.33	[illegible]
Water	72.80	21.80	51.00	70.05
Newly Formulated Coating	26.40	24.85	1.55	[illegible]

	Kevlar-based Fishing Line		
Organic Coating	W_A	59.53	mN/m
	γ_{SL}	1.52	mN/m
	S	6.47	mN/m
	θ	0.00	°
Water	W_A	69.02	mN/m
	γ_{SL}	38.30	mN/m
	S	-76.58	mN/m
	θ	92.97	°
Newly Formulated Coating	W_A	60.25	mN/m
	γ_{SL}	0.67	mN/m
	S	7.45	mN/m
	θ	0.00	°

- The new formulation increases the ratio of IFT coating-line vs. water-line from 25.2 to 57.2!

=> Now the coating survived >250 casts!

KRÜSS How Contact Angle Measurements can Help to Optimize Photoresist Adhesion

KRÜSS

Thank you for your attention!

How can we enable YOU to change the world?

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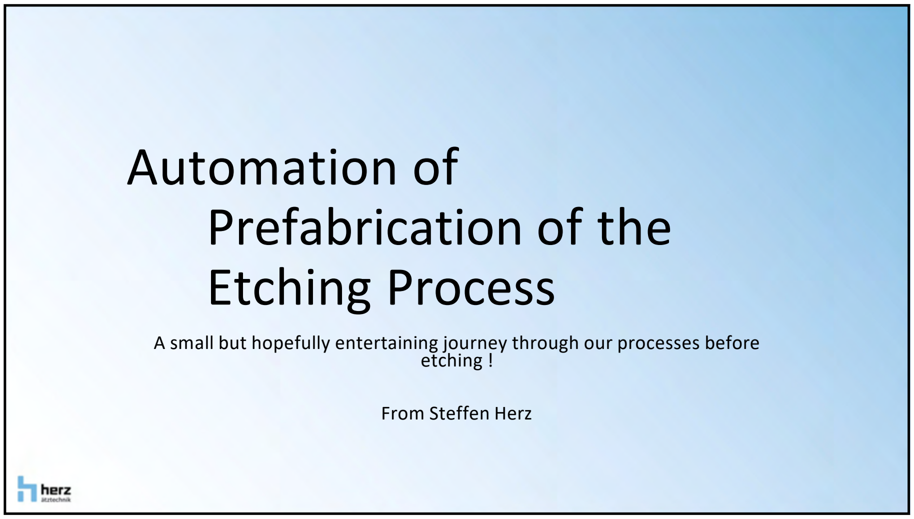
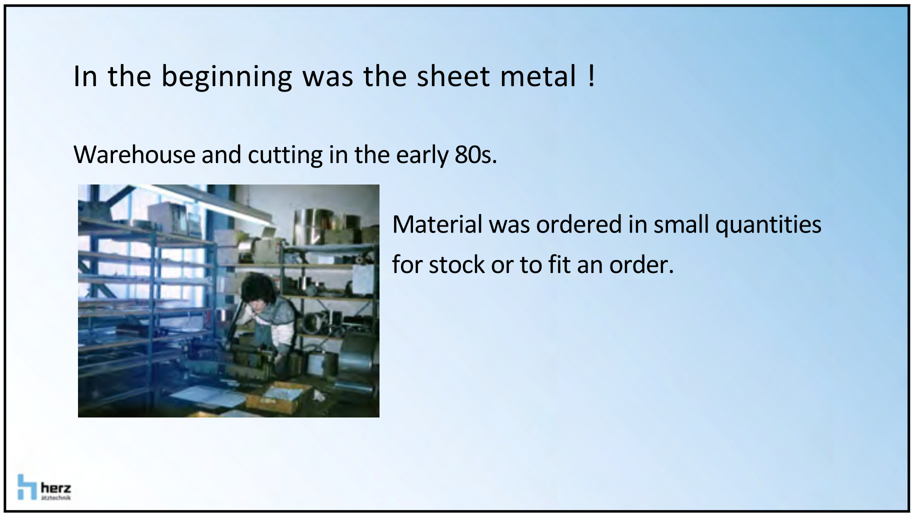
Steffen Herz has been the CEO for Ätztechnik Herz since 1999. He has also served as the Chemical Technical Assistant.

As a university student, Steffen worked at Daimler Chrysler and studied physics and project management. He received his diploma in 1999. Steffen received the McKinsey Startup award 2001 for Herz-Automotive GmbH.
He also served in the German armed forces from 1989-1990.

Steffen is a member of the PCM Board of Directors, Membership Committee and Germany Conference Committee.

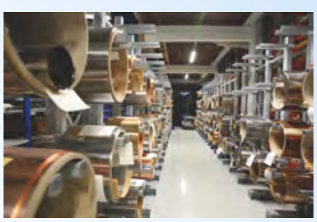




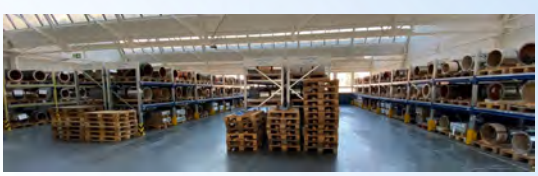
In the beginning was the sheet metal !

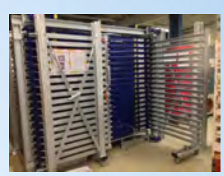
Over time, the storage develops. Larger quantities and a greater number of types of materials are stocked.

In the beginning was the sheet metal !



Today : manual cutting for small quantity and sheet material.
Automatic slitting and cut-to-length line for cuts from coil.





In the beginning was the sheet metal !

Cleaning :

First there was the hand cleaning , ATA and sheet metal so bad luck !
ATA is a scouring paste ! Unpopular activity , picture from 1974 !

Cleaning :

Unfortunately there are almost no pictures from the intervening period. We have tried everything.

Electrolytic dip degreasing , brushing , plasma and many substances banned today !

Work safety and environmental protection became popular and so did things like ROHS , REACH .....

Cleaning :

Today, pretreatment only takes place by machine. Monitored systems equipped with metering systems reliably clean the surfaces and then transfer them for lamination.

Lamination :

Solid or liquid ? In the beginning, we used both. We still mourn the ammoniacal developable red resists from DuPont. Eternally storable and always good adhesion ! But already very long history !

Since then, many resists have come and gone. Etching companies are always looking for new optimal resist .

Lamination :

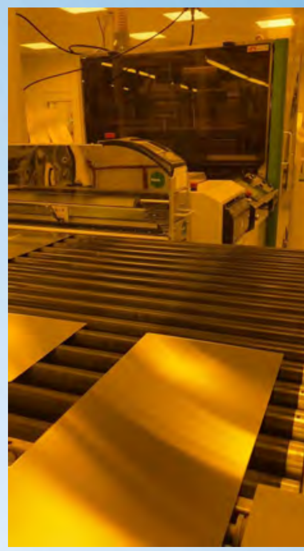
Equipment was purchased and operated as part of capacity expansion and automation. Unfortunately, many of them are only for large series and standard formats. So nothing for a service provider in the field of etching technology !

Some things went as fast as they came !

Lamination :

Of course, today we have equipment that covers our needs. Larger quantities are laminated today largely fully automatically.

As an example, a gauge converter between cleaning and laminator. Laminator is twice as fast as pretreatment. The converter allows us to run two lanes through the cleaning and make full use of the laminator.



Lamination :

Liquid resist :

For special applications we still use liquid resists. Today, however, in compliance with regulations in an explosion-proof container because of the solvents.

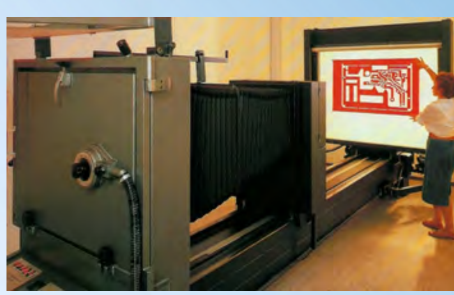
Picture as example from AHK !

Phototools :

A long time ago :

Drawing on the drawing board and first steps in IT.
This Unix computer cost the equivalent of a midsize car !

Phototools :



Cutting plotter and repro camera ! Downsizing for film tolerance minimization.

Filmtools :

In the mid-80s, the first Gerber flatbed plotter came into the house. With it, everything changed . Films could be produced quickly in a flexible and repeatable manner. But each film was still loaded individually and then developed !

This changed in 2001 when plotters with attached developers became standard until today. In mass production, film tools still have a right to exist. Automatic printers with films are cheap and have high throughput.

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Imaging :

Workhorses from days gone by ! We still use printers for some jobs !

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Imaging :

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17

Imaging :

Of course, we also use DI systems. At the moment, however, mainly for samples, special products and tests. This can change of course , we follow the market closely !

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Developing :

Surprisingly, we have almost no pictures of developing ! There have been no significant changes here either. Certainly the machines have become bigger and faster. But technically it has remained the same.

This is just changing !

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Developing :

Developers so far !

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Developing :

Since the quantities in the benefit area are also constantly increasing, we have ordered an automation system for one of our three developers as a pilot project. (Supplier is present, gladly take percentages :-) . The goal is to develop the plates coming from the printer without a man. Realization still in this year! With success this is also duplicated on the other plants. However, there will still be the possibility for samples / prototypes and special material to insert by hand !

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Conclusion :

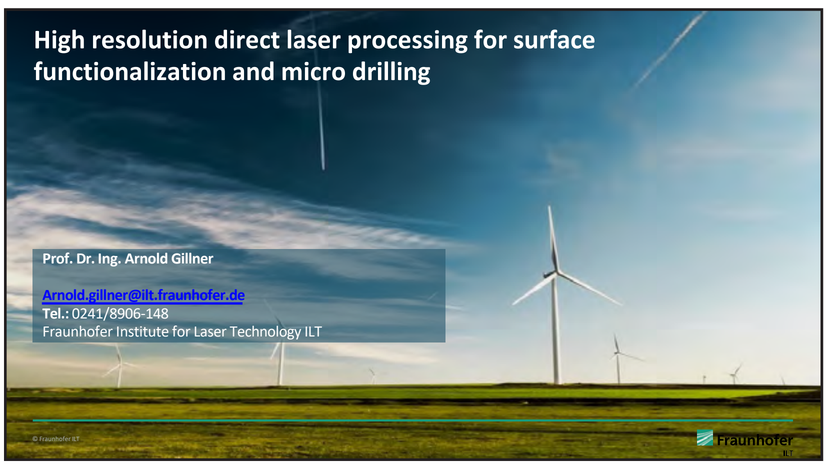
I have deliberately spoken only about benefit production. Roll-to-roll is an area that is easier to automate because of the webs. In addition, we have only been manufacturing webs for 25 years! It may be astonishing for some what and how we deal with it, but that is due to our structure of customers. We have omitted the confusions along our history such as screen printing ! Although this technique in the form of inkjet printers is just again very interesting!

Now to what we do best !

herz ätztechnik

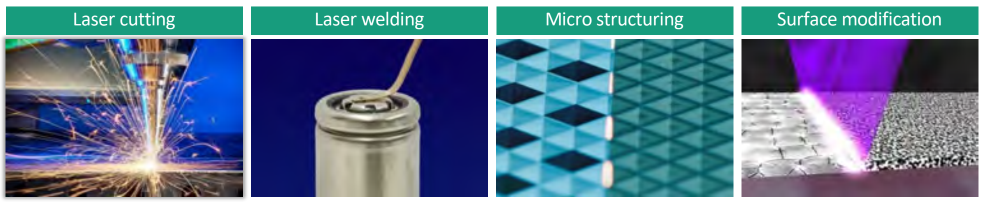
Dr. Arnold Gillner, studied Physics at the University of Darmstadt and made his PHD in Mechanical Engineering at the RWTH Aachen in 1994. Since 1985 he has worked as a scientist at the Fraunhofer-Institut for Laser Technology. In 1992, he started the Department for Micro Technology at the ILT and since 2010 he has headed the Department of Joining and Ablation. Together with more than 65 scientists he is developing industrial laser processes for macro and micro joining, packaging, laser cutting and ablation, micro and nano structuring, polymer applications, and life science applications.

He is a member of the RWTH and gives lectures on Lasers in Life Science and Lasers in Micro- and Nanotechnology. He is also the Managing Director of the Fraunhofer Group on Light and Surface and Head of the advisory board of MedLife. In his scientific field, he coordinates with numerous national and European R&D-projects on welding, cutting, process control, and biofabrication.



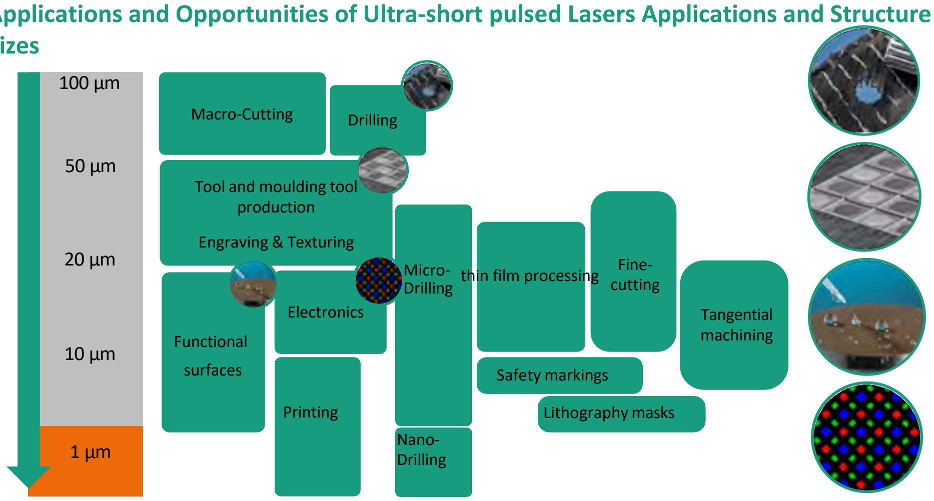
Functional surfaces by laser structuring

Overview laser processes



Source: [9]

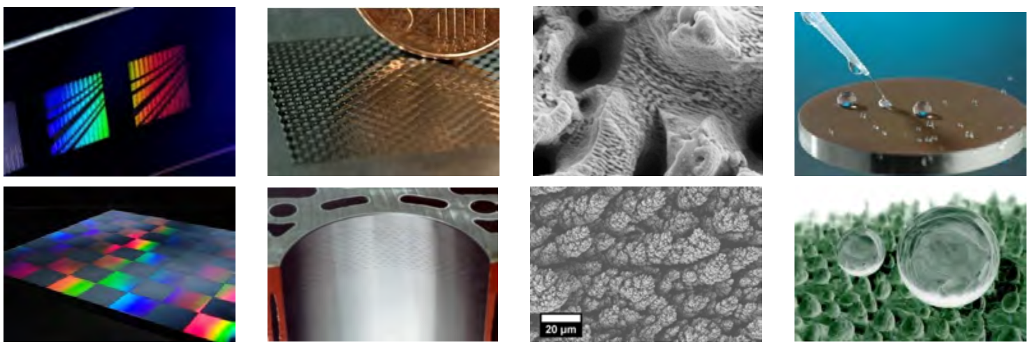
Applications and Opportunities of Ultra-short pulsed Lasers Applications and Structure Sizes



Functional surfaces

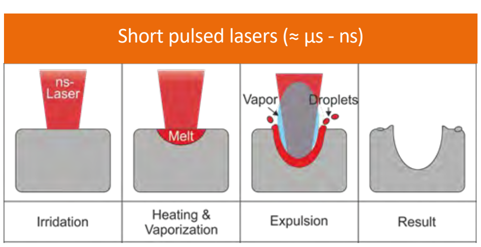
Functional surfaces and applications

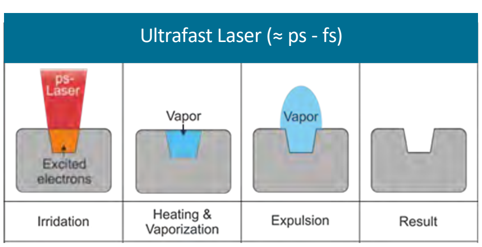
Optical properties	Tribology	Electro-Chemical	Surface effects



Functional surfaces

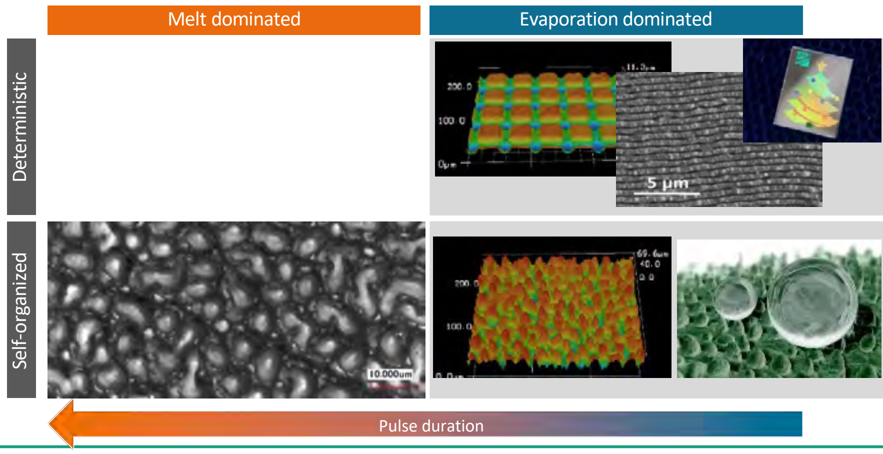
Short pulse and ultra short pulse laser processes





Functional surfaces

Classification of surface structures

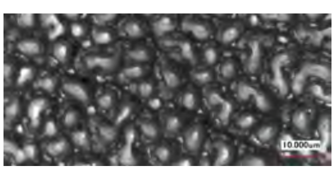


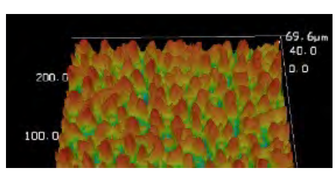
Fraunhofer ILT

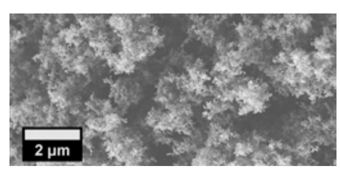
Functional surfaces

Typical properties of surface structures

Remelting	Evaporation	Redeposition







- **SOMS**
  Self organizing melt structures
- Typical scale: 5-20µm
- Increase in surface area ~10x

- **CLP**
  Cone like protrusions
- Typical scale: 1-10µm
- Increase in surface area ~10-100x

- **LINF**
  Laser induced nano foam
- Typical scale: 100nm
- Increase in surface area ~1000x

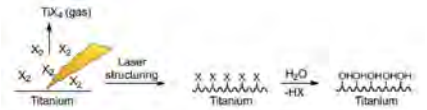
Fraunhofer ILT

Functional surfaces

Chemical modifications

Reactive gas assisted texturing

- Influence of the process gas on the formation of microstructures
- Formation of chemical compounds
  - ➔ Change in topology
  - ➔ Change of surface chemistry
  - ➔ High feed rates



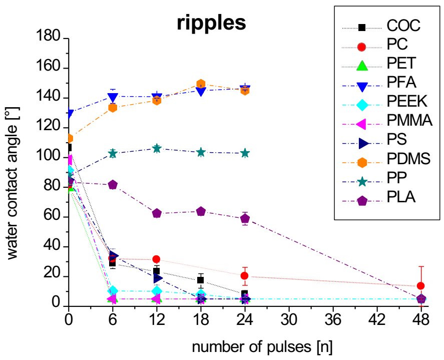
Fraunhofer ILT

Laser surface modification for changing wetting properties

Survey of laser treated polymers

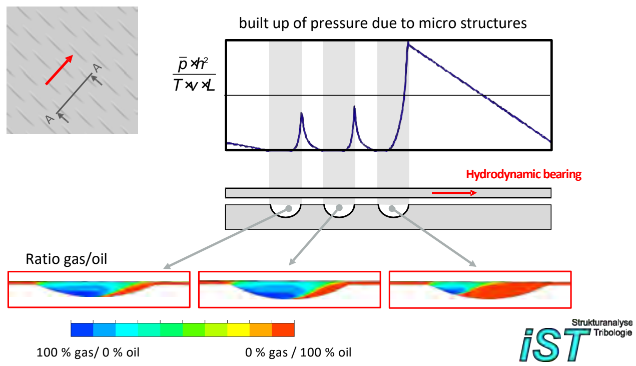
- increase of hydrophobic properties for PDMS, PFA, PP
- PEEK, PS, COC etc. are hydrophilized
- Enhanced roughness and chemical changes of the polymer surface are relevant

► **laser induced "lotus" or "anti-lotus" effect**



Fraunhofer ILT

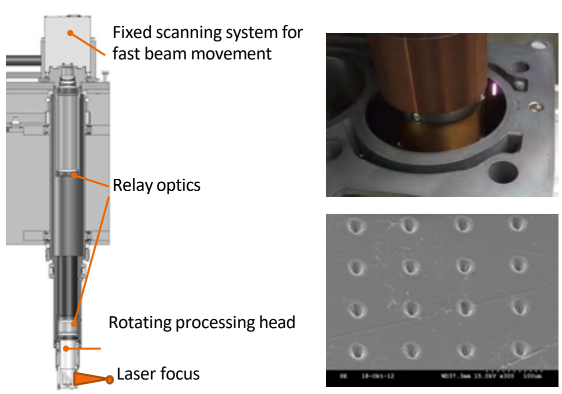
Surface structuring for friction reduction



SMARTSURF

Fraunhofer ILT

Machining technology: Development of scanning systems & processing heads for cylinder liner processing



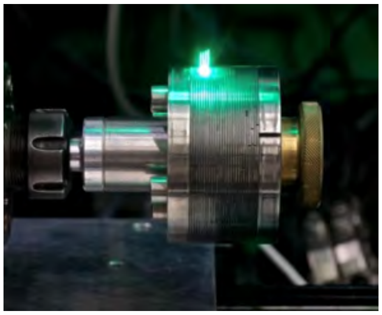
Gehring

SMARTSURF

Fraunhofer ILT

Tailored surfaces

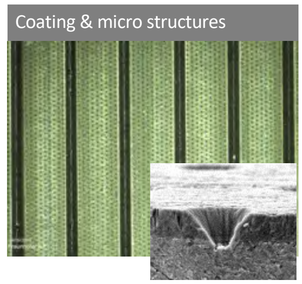
Reduction of friction by micro structuring

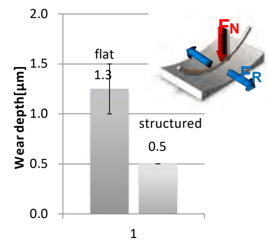


Parallel structuring of piston rings with multiple beams

Laser: ultrafast laser 6 ps

Pulse energy: up to 300 µJ





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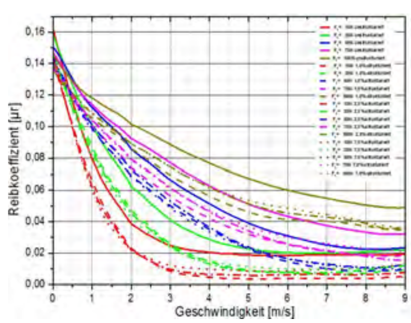
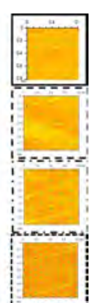
Tailored surfaces

Reduction of friction by micro structuring





- Friction partners:
- Laser structured liner surface segments
- Unstructured piston ring
- Test parameters:
- Temp: 110°C
- Low lubrication

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Tailored surfaces

Process chain for the production of tailored surfaces

Design of surfaces

- Macro structure
- Micro structure
- Nano structure
- Chemical composition

Laser processing

- Micro structuring
- Periodic structures
- Cone like protrusions
- Interference structuring
- Laser polishing

Embossing

- Process parameters
- Reproduction of small structures
- Energy distribution

Measurement

- Geometric accuracy
- Contact angle
- Activation energy
- Roughness
- Adhesion / Friction
- etc…

Model prediction

- Prediction of reproducibility
- Prediction of contact angle/adhesion/friction

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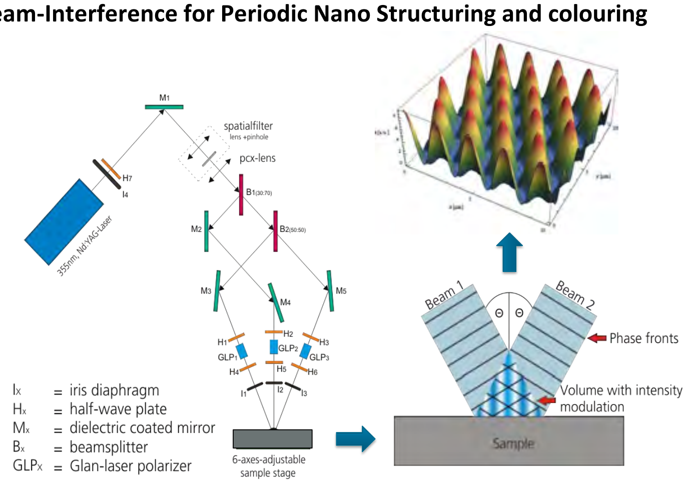
Multi-Beam-Interference for Periodic Nano Structuring and colouring



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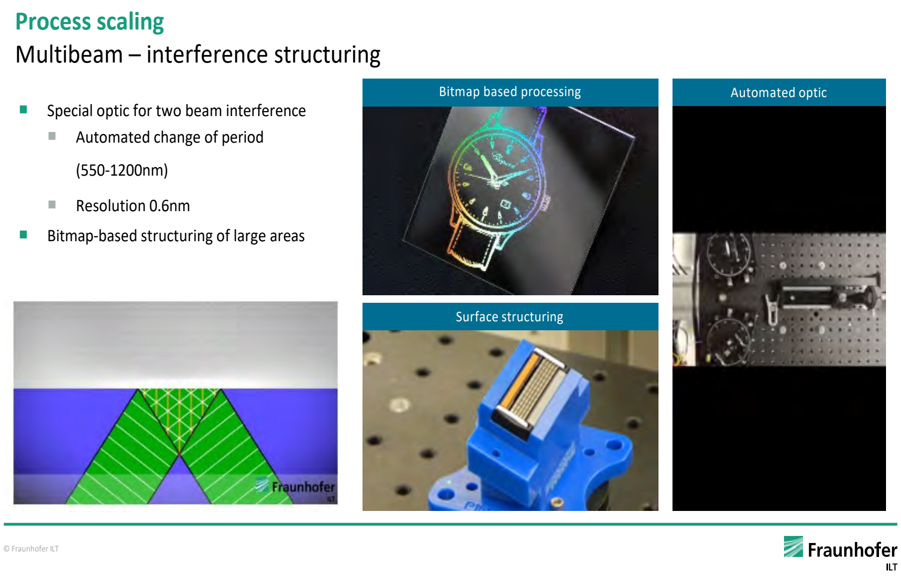
Process scaling
Multibeam – interference structuring
Special optic for two beam interference
Automated change of period
(550-1200nm)
Resolution 0.6nm
Bitmap-based structuring of large areas
Bitmap based processing
Automated optic
Surface structuring
Fraunhofer
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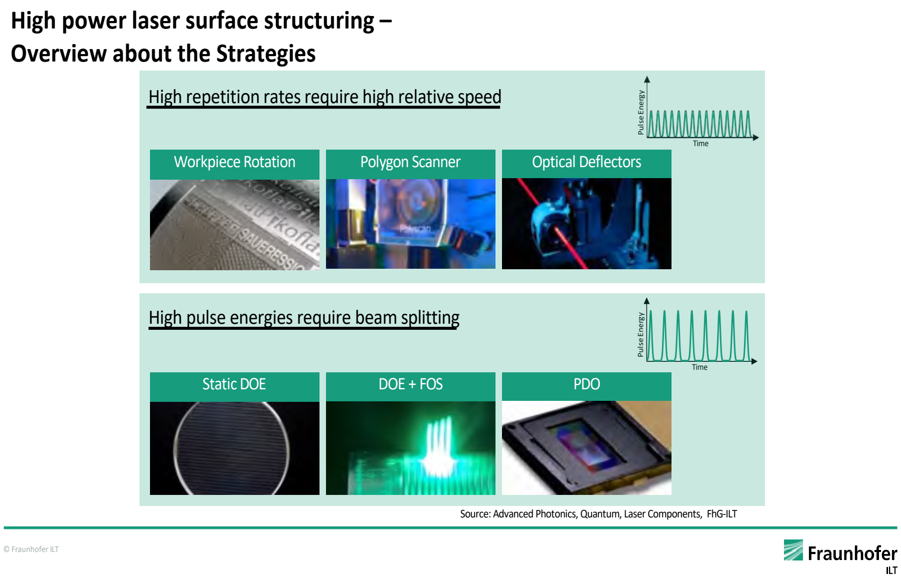
Fraunhofer
ILT


High power laser surface structuring –
Overview about the Strategies
High repetition rates require high relative speed
Pulse Energy
Time
Workpiece Rotation
Polygon Scanner
Optical Deflectors
High pulse energies require beam splitting
Pulse Energy
Time
Static DOE
DOE + FOS
PDO
Source: Advanced Photonics, Quantum, Laser Components, FhG-ILT
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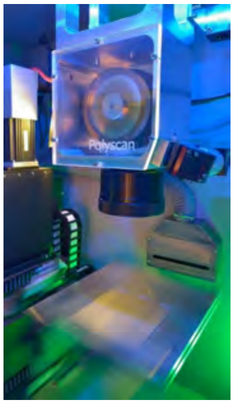
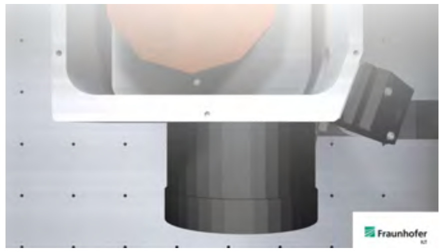
ILT

Process scaling

Fast beam deflection with polygon scanner



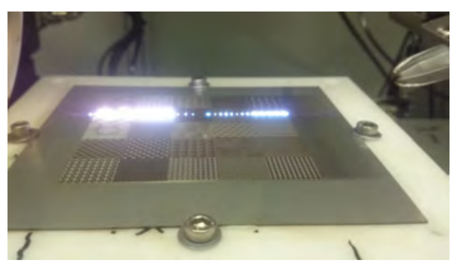


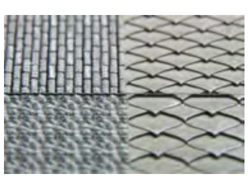
- Fast spinning polygon mirror
- One fast scanning direction with up to 1000 m/s
- Synchronization of facets and laser beam by FPGA
- Manufacturing deviations of polygon mirror have to be considered / balanced

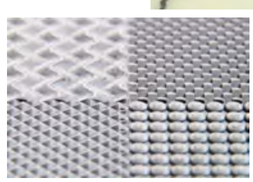
Process scaling

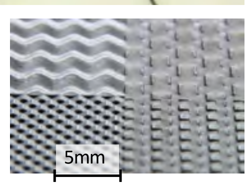
Fast beam deflection with polygon scanner

- Processing area: 100 x 200mm^2
- Spot size: 25-45 µm (for 1064nm)
- Scan speed: 20-360m/s
- Average power: 30-330W



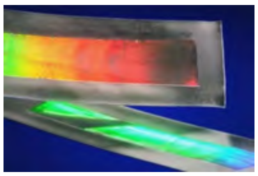




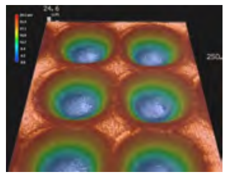


Process scaling

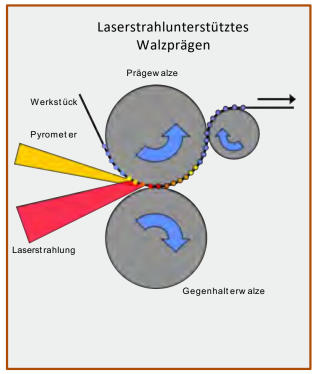
Large area embossing of micro-& nano-structures

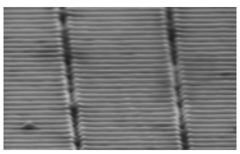


Nano embossed aluminium stripe

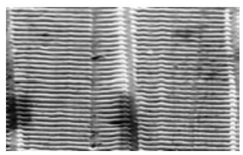


Polished tool surface (ra<100nm)





Tool



Embossing result

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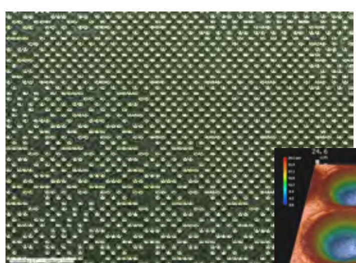
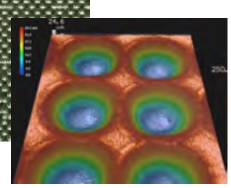
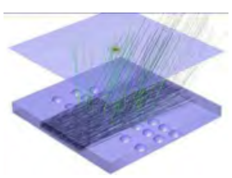
Light guiding and light scattering structures by micro injection moulded lens arrays in PMMA



Micro moulding tool for lens array



After tool polishing sufficient part quality with surface accuracy better than 100 nm



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Micro-Structuring and Polishing for Lightguides

- Micro-structuring with ps-lasers, Ablation of micro lenses, 30 x Ø 150 µm
- High repeatability and accuracy (< 5 µm)
- Machining time for one lense approx. 0,3 Sec.
- Up to 250.000 lenses per mold > 20 h machining time
- Polishing of structured surface with ns-lasers
- **>> 100 laser structured and laser polished tool inserts in production**
  (at different companies)

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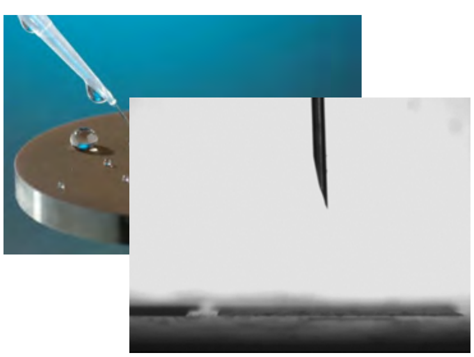
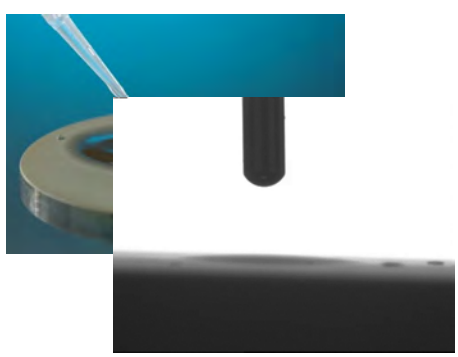
Tailored surfaces

Extreme enhancement of the surface area

Hydrophobic coating



Hydrophylic coating



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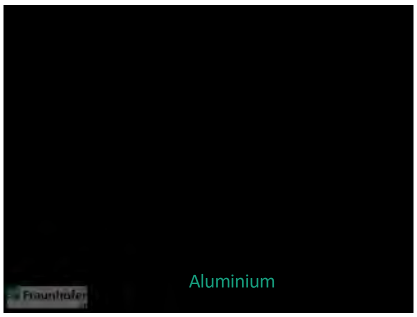
Statistical surface texturing of metals for wetting property setting



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Superhydrophobic surfaces form laser structured molding tools

Hydrophobic bowl

- Shape of the molding tool: ball scraper
- Plastic: PEEK

In Cooperation with the following RWTH Aachen institutes

- Institute for Plastic Processing
- Surface Engineering Institute

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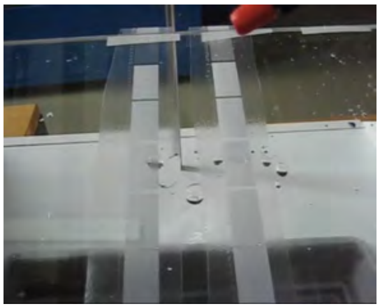
Wettability of embossed foils with laser generated micro and nano structures



Hydrophobic plastic foil

- Continuous embossing process for large scale production
- Left side: unstructured normal material (backside of structured foil)
- Right side: Structured material with hydrophobic properties

In Cooperation with the following RWTH Aachen institutes

- Institute for Plastic Processing
- Surface Engineering Institute

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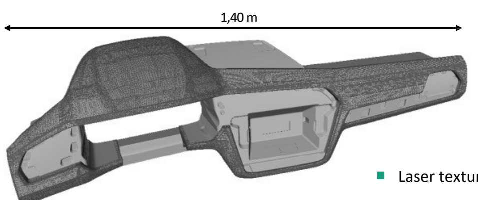
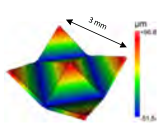
Micro structured tools
for design applications in automotive interieurs



Serien-Instrumententafel VW Tiguan



- Laser textured tools
- Natural and technical surfaces
- S.o.A: ns-Lasers
- New developments: Combined ns-ps-Ablation
- Advantages:
  - Higher ablation rate
  - Higher Precision
  - Improved design capabilities

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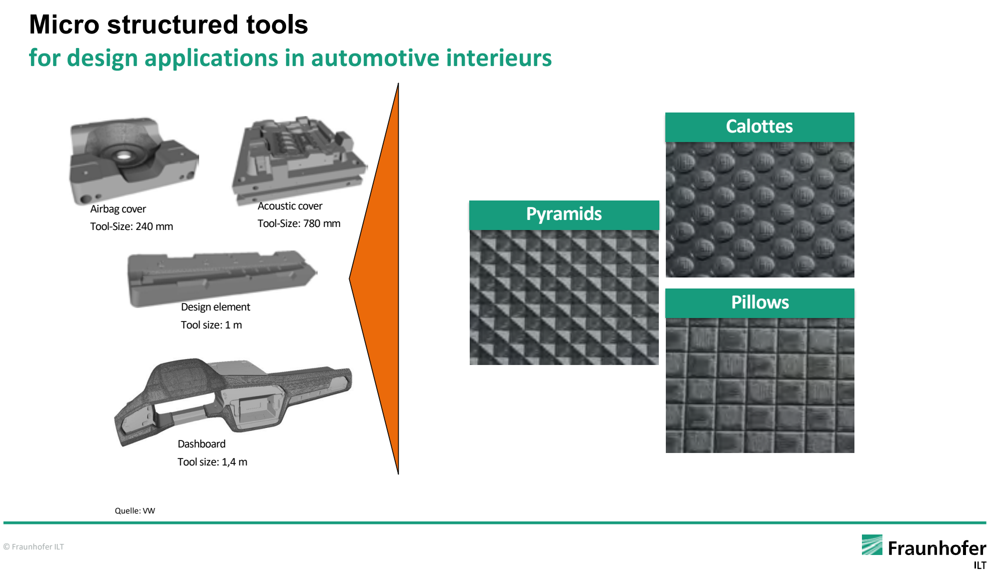
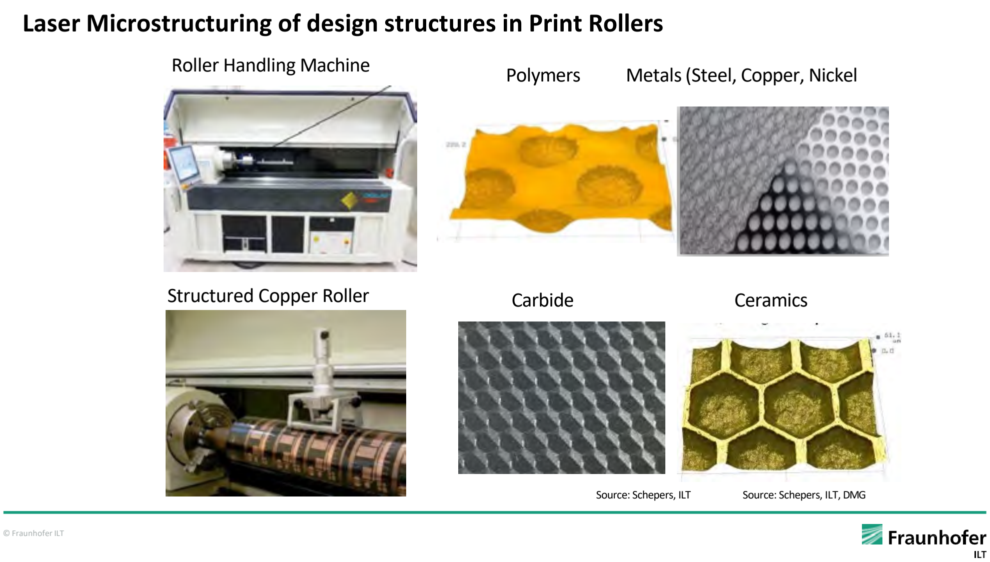

Micro structured tools
for design applications in automotive interieurs
Airbag cover
Tool-Size: 240 mm
Acoustic cover
Tool-Size: 780 mm
Design element
Tool size: 1 m
Dashboard
Tool size: 1,4 m
Quelle: VW
Calottes
Pyramids
Pillows
© Fraunhofer ILT
Fraunhofer
ILT


Laser Microstructuring of design structures in Print Rollers
Roller Handling Machine
Polymers
Metals (Steel, Copper, Nickel
Structured Copper Roller
Carbide
Ceramics
Source: Schepers, ILT
Source: Schepers, ILT, DMG
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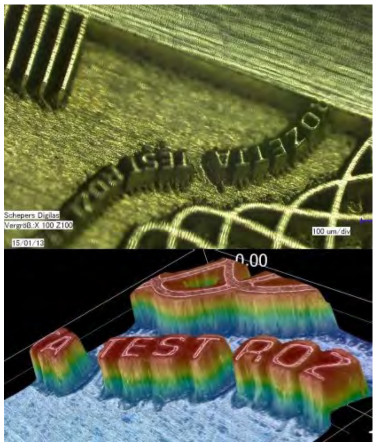
ILT

Laser Microstructuring of Print Rollers



Exemplary Process Parameters

Pulse duration 10 ps

Power 30 W @ 4 MHz

Wavelength 1064 nm

Ablation depth per pulse 1 µm

Surface speed 30 m/s

Machining Result

Ablation Depth: 200 µm

Line Width: 50 µm

Surface Roughness Ra 0,5 µm

Machining Time (Ø100x150mm) 48h

Source: Schepers

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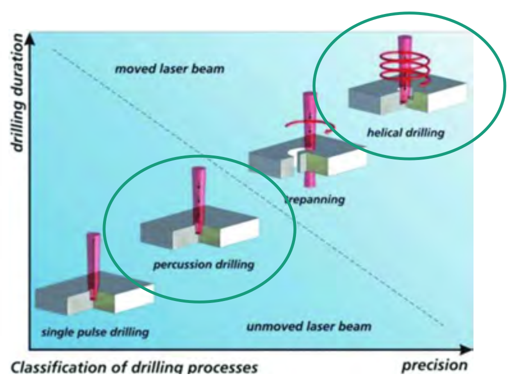
Laser Drilling: Types of Laser Drilling

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

Laser drilling strategies

Fraunhofer ILT

Drilling strategies



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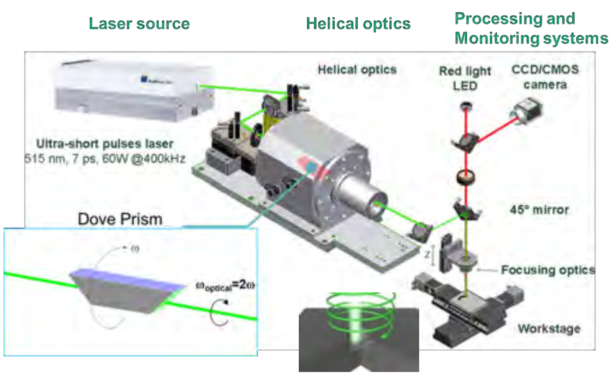
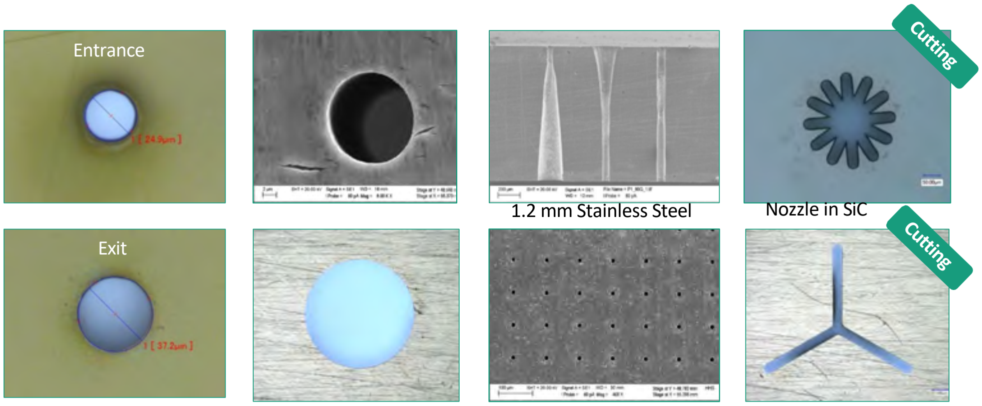
Helical Optic (WEBO): System Technology



Drilling & Cutting

- Electronic Vias
- Microfilter
- Ceramic & glass machining
- Microtechnology

Helical drilling: Different materials to be drilled



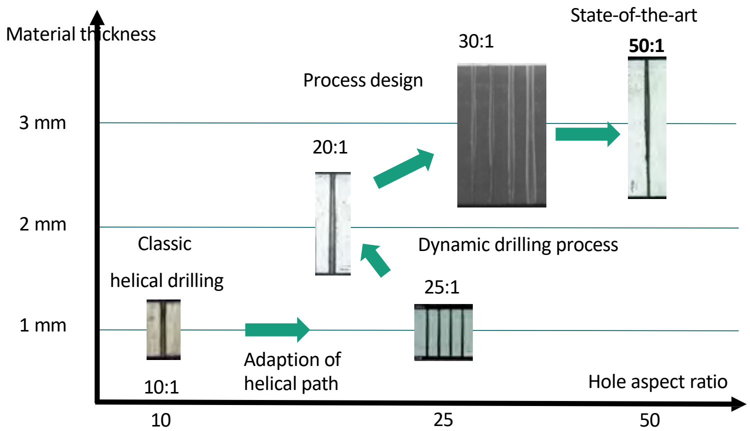
1.2 mm Stainless Steel

Nozzle in SiC

50 µm Polyimide Foil | 10 µm Titanium Foil | 10 µm Titanium Foil | 50 µm copper-nickel alloy

Helical drilling: Increase of aspect ratio

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook



WEBO

Productivity	< 10/sec
Aspect ratio	≤ 50:1
Precision	≥10 µm, Taper

- How deep can we get?

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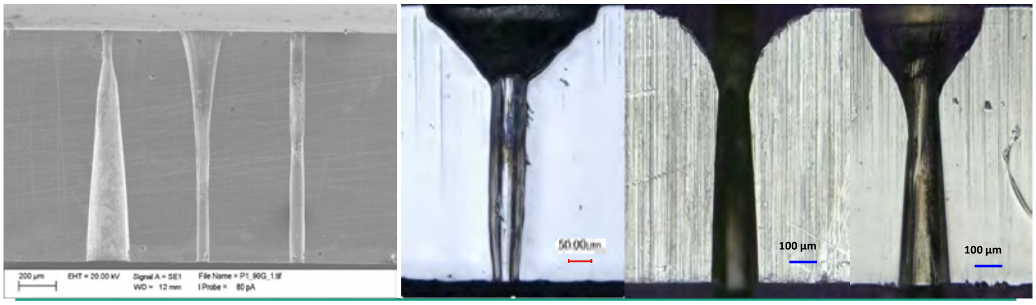
Helical drilling: Cross-section

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

- Machining of negative, positive and cylindrical holes with high aspect ratio
- Shaping of tailored cross-sections by dynamic helical drilling process
- Material: 1mm thick stainless steel

funnel-like hole trophy form



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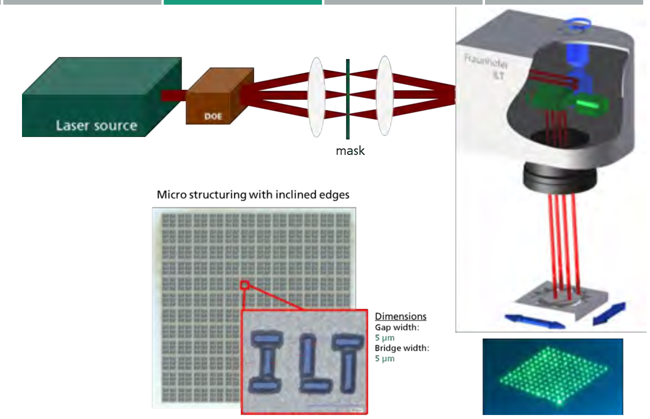
Multibeamscanner: System Technology

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

Parallel Processing of Metals

- Multibeam > 100 beamlets
- Pulse duration 1 -10 ps
- Wavelength 300 – 1000 nm
- Spot size 7 - 30 µm



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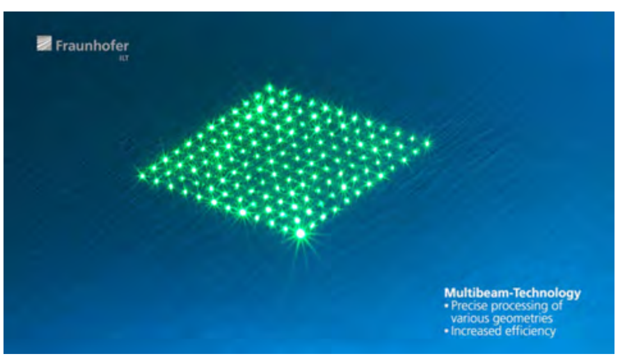
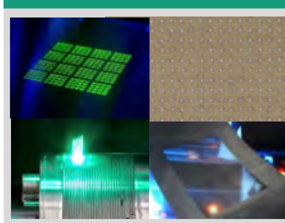
Multibeamscanner

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

Multibeam processing with more than 100 beams in parallel



Drilling & Ablation



- Consumer electronics
- Microfilter
- Sensor technology
- Embossing tools

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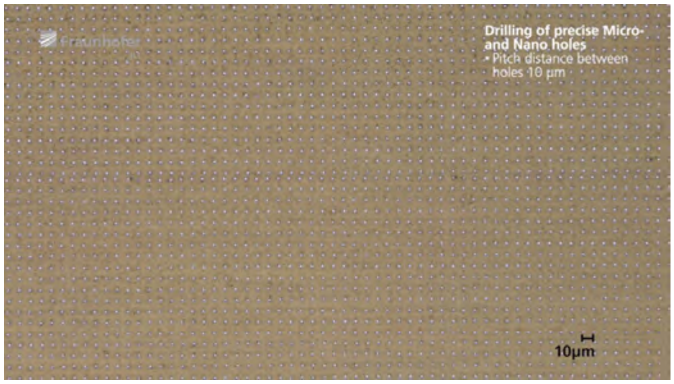
Multibeamscanner: Drilling results

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook



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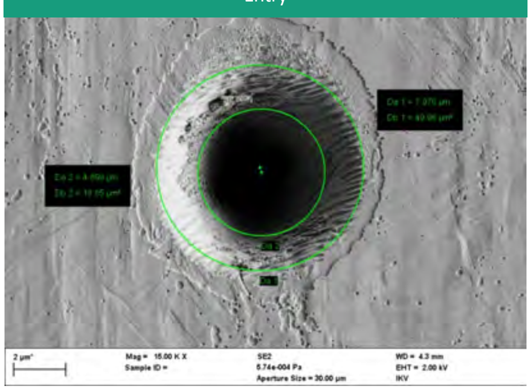
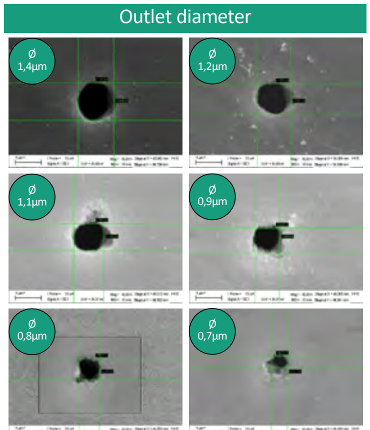
Multibeamscanner: Drilling results

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

Entry



Outlet diameter



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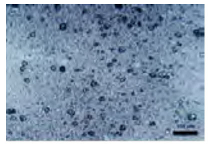
Multibeamscanner: Summary

Motivation | Laser drilling | Helical Optic (WEBO) | **Multibeamscanner** | Microscanner | Summary & Outlook

Application possibilities:

- Water Filtration
- Bio-technology
- Pharmaceutical technology
- Medical technology
- Food production
- Microreactor technology
- Gas sensors
- Fine dust filter
- others



Micro Plastics
< 10 µm

MRSA
0.8 -1.2 µm

MBS

Productivity	> 10.000/sec
Aspect ratio	~ 10:1
Precision	≤ 10 µm

- How fast can we get?

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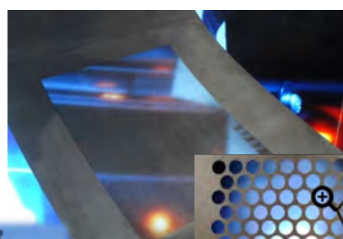
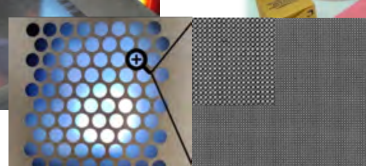
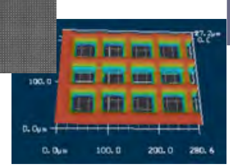
Micro perforation of water filters





SimConDrill



Metallic micro sieves for Cyclone filter

Hole diameter < 10 µm

60 Mio holes in self cleaning filter

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Evaluation of the Prototype

Sludgewater outlet

Cleanwater outlet

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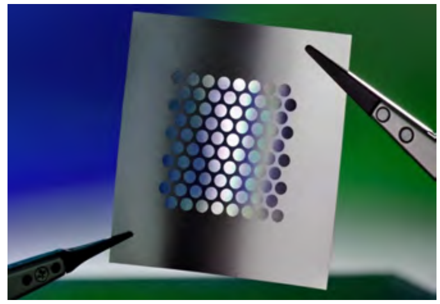
Fraunhofer ILT Portfolio for Water Treatment

- Manufacturing of **metallic micro filter by laser drilling**
  - Hole diameter:
    - State of the art: > 0,8 µm
    - Potential: < 0,4 µm
  - **Quality assurance** of laser processing
  - Materials: Polymers, Glasses, Ceramics, Metals
- **Surface functionalizing** by laser structuring
  - Hydrophobic / -philic surfaces
  - Antibacterial & Antifouling surfaces
  - Functional surfaces (Encymatic coating)
- **Photochemical Water Treatment**
  - UV-Treatment
  - Plasma Treatment



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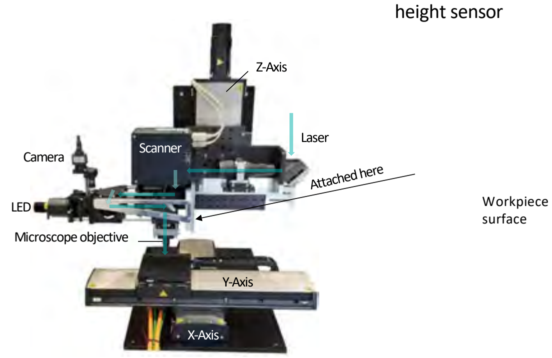
UV-Microscanner: System Technology

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

- Wavelength = 343 nm (ultraviolet)
- Pulse duration = 1 ps
- Max. average power = 17 W
- Focus diameter d = 0.5 – 5 µm
- Accuracy of height sensor and axes = 0.3 µm
- Live process monitoring



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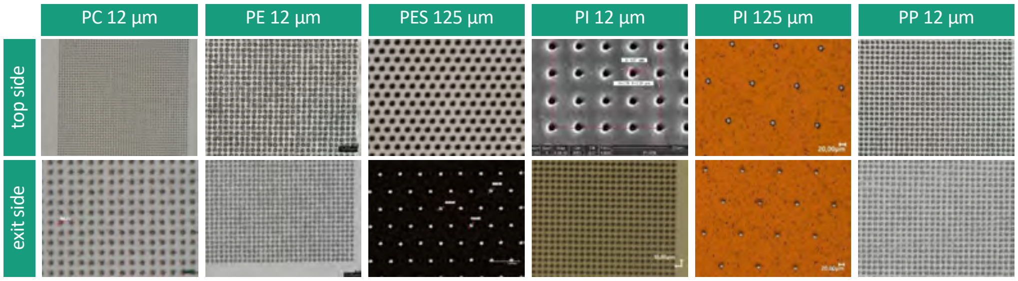
Fraunhofer ILT

UV-Microscanner: Polymer Materials for Laser-drilling

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook



- Holes of 1–5 µm diameter with extremely high reproducibility
- No thermal damage of the membranes
- All kinds of polymer processable

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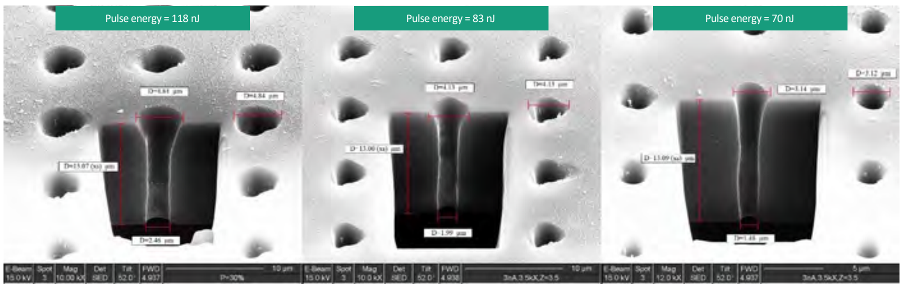
Fraunhofer ILT

UV-Microscanner: Cross-section of laser-drilled Polymer

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook

Laser-drilled 12.5 µm PI cross-sectioned using FIB



- Hole shape mostly cylindrical unlike metals
- Research on processing strategy to make defined taper angles ongoing

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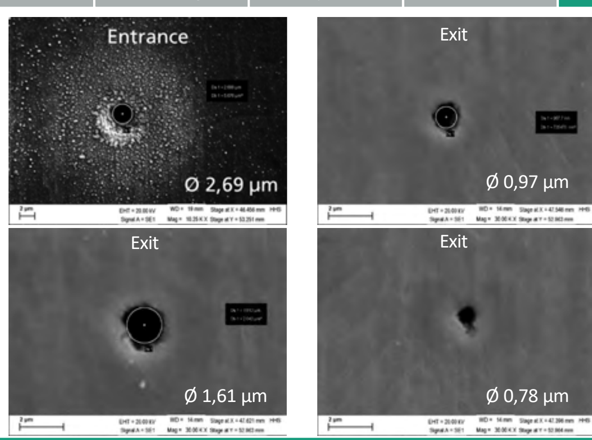
Fraunhofer ILT

IR-Microscanner: Drilling of 10 µm stainless steel foils

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook



Micro-scanner

Productivity	> 100/sec
Aspect ratio	~ 10:1
Precision	≤ 2 µm

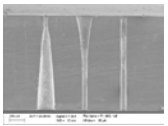
- How small can we get?

Seite 48 Fraunhofer ILT

Fraunhofer ILT

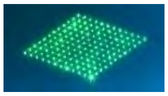
Conclusion

Motivation | Laser drilling | Helical Optic (WEBO) | Multibeamscanner | Microscanner | Summary & Outlook



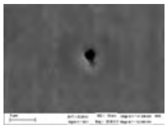
WEBO

Productivity	< 10/sec
Aspect ratio	≤ 50:1
Precision	≥10 µm, Taper control



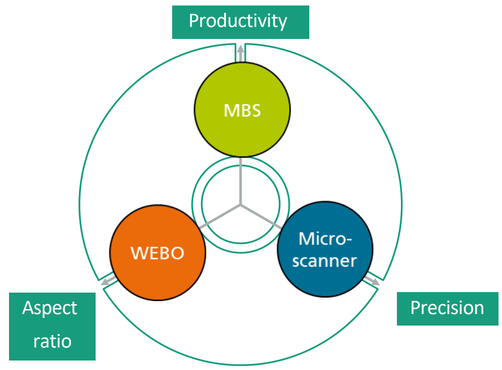
MBS

Productivity	> 10.000/sec
Aspect ratio	~ 10:1
Precision	≤ 10 µm

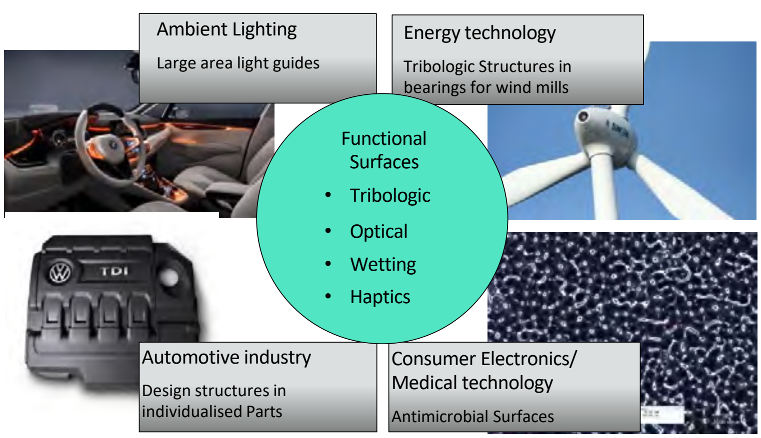


Micro-scanner

Productivity	> 100/sec
Aspect ratio	~ 10:1
Precision	≤ 2 µm

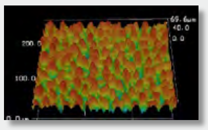
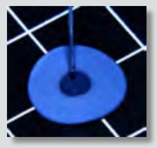


High Laser Power with adapted system technology will allow large area processing for functional surfaces



Process scaling

Fraunhofer objectives – Closing the gap between research and industry

Process development	Proof of effectiveness	Upscaling
		
▪ Fundamental research ▪ Proof of concept ▪ Process validation ▪ Feed rates <1mm/min	▪ Characterization of surfaces and their properties ▪ Feed rates <100mm/min	▪ Process scaling ▪ Integration/Automation ▪ Feed rates >1m/min

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Source: [18,16]

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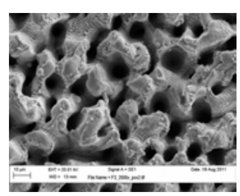
Large Area structuring with laser radiation

Quelle:phereclus

Quelle:fos4x

Micro structuring of wind rotors

- Anti icing
- Anti sticking of insects
- Structur size < 10 µm



- Micro- and nano structures to generate functional surfaces

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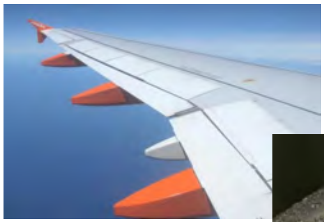
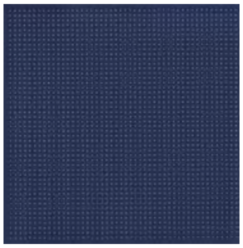
Large Area structuring with laser radiation


Quelle:Airbus

Micro holes in airfoils for interface designing

- Hole diameter < 200 µm
- Variable hole pattern Bohrungssequenzen
- Shaped holes for improved gas flow



- Drilling rate > 10.000 holes /sec
- Different drilling techniques
  - Single Pulse
  - Percussion
  - Helical drilling

THANK YOU VERY MUCH FOR YOUR ATTENTION!

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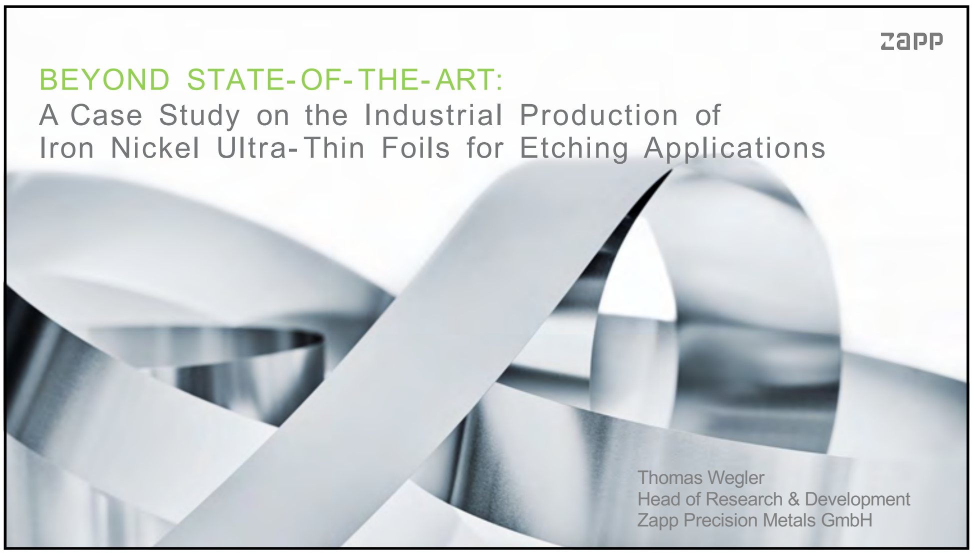
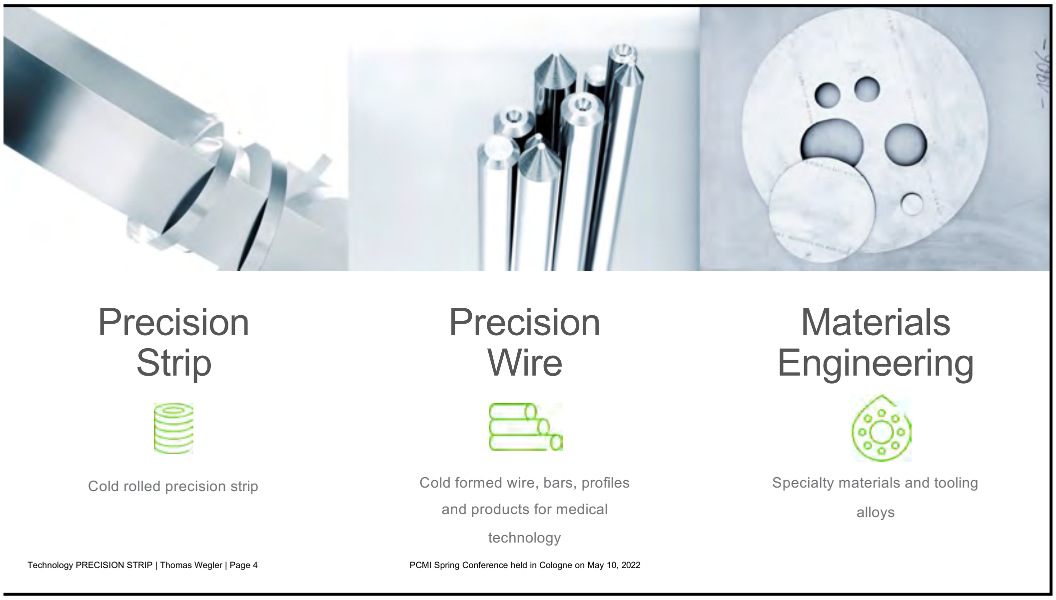
Fax: +49 241 8906 -121
Email: Arnold.gillner@ilt.fraunhofer.de

Thomas Wegler was born on 14, July 1966. From 1987- 1992, he studied metallurgy at the TU Freiberg in Germany with a Dipl. Ing.

From 1992 – 1999, he was the Lab. Manager at the ZAPP Ergste plant in Germany. From 2000 – 2002, he was an assistant production manager precision strip (ZAPP) plant in Dartmouth, MA, USA. From 2003-2009, he was the production manager precision strip at the ZAPP plant in Ergste, Germany. Since 2010, he has been the R&D Manager Precision Strip at the ZAPP plant in Unna, Germany.




zapp
>300
Years
15
Locations
1,350
Employees
~$500m
Sales
Solutions


Precision Strip
Cold rolled precision strip
Precision Wire
Cold formed wire, bars, profiles and products for medical technology
Materials Engineering
Specialty materials and tooling alloys
Technology PRECISION STRIP | Thomas Wegler | Page 4
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zapp
Sandviken
Sheffield
Ratingen
Unna
Schwerte
Pforzheim
Pleasant Prairie
Dartmouth
Stratford
Santa Fe Springs
Summerville
Pearland
Seoul
Taicang
Hong Kong
Pune
Service Centers
Production
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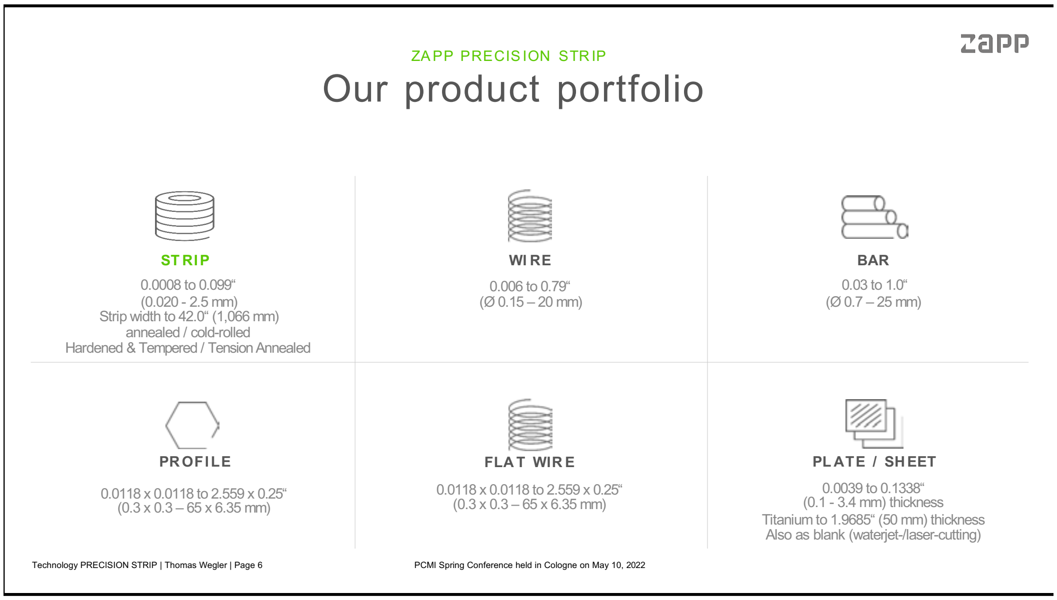
zapp
ZAPP PRECISION STRIP
Our product portfolio
STRIP
0.0008 to 0.099“
(0.020 - 2.5 mm)
Strip width to 42.0“ (1,066 mm)
annealed / cold-rolled
Hardened & Tempered / Tension Annealed
WIRE
0.006 to 0.79“
(Ø 0.15 – 20 mm)
BAR
0.03 to 1.0“
(Ø 0.7 – 25 mm)
PROFILE
0.0118 x 0.0118 to 2.559 x 0.25“
(0.3 x 0.3 – 65 x 6.35 mm)
FLAT WIRE
0.0118 x 0.0118 to 2.559 x 0.25“
(0.3 x 0.3 – 65 x 6.35 mm)
PLATE / SHEET
0.0039 to 0.1338“
(0.1 - 3.4 mm) thickness
Titanium to 1.9685“ (50 mm) thickness
Also as blank (waterjet-/laser-cutting)
Technology PRECISION STRIP | Thomas Wegler | Page 6
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ZAPP PRECISION STRIP

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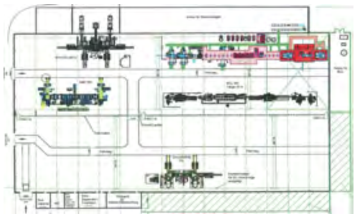
Precision Strip production facility Unna, Germany

- Modern plant, equipped with state-of-the-art production facilities
- Raw material inspection line, precision rolling mill, tension leveling line and bright annealing; including tension annealing line & special tempering processes
- Facility layout designed to optimize material flow, reduce handling and shorten internal lead-times
- Unique online quality inspection and response systems enable optimum geometry (flatness) and surface finish condition



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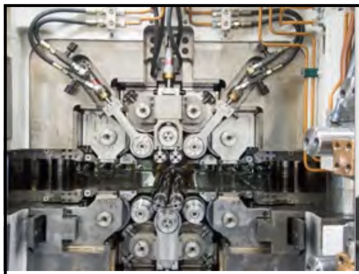

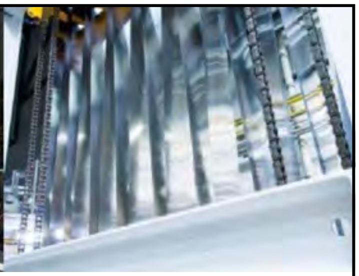

ROLLING MILL

0.020 - 1.00 mm
up to 750 mm wide

- State of the art measuring and steering systems
- Extremely tight thickness tolerances, via x-ray equipment
- Extreme flatness due to flatness measurement rolls

TENSION LEVELLING

0.020 - 0.60 mm

- Optimized shape and flatness control, via integrated measuring and steering system
- Thickness measured along the complete length of the strip
- Possibility of surface inspection/control on both sides of the strip via integrated inspection system

TENSION ANNEALING

0.020 - 0.25 mm*

- Complete removal of residual stress due to special heat treatment process, eliminates deformation during etching and ensures thermal stability at elevated temperatures.

*Super Stress Relieved (SSR) process developed for gauges up to 0.60 mm

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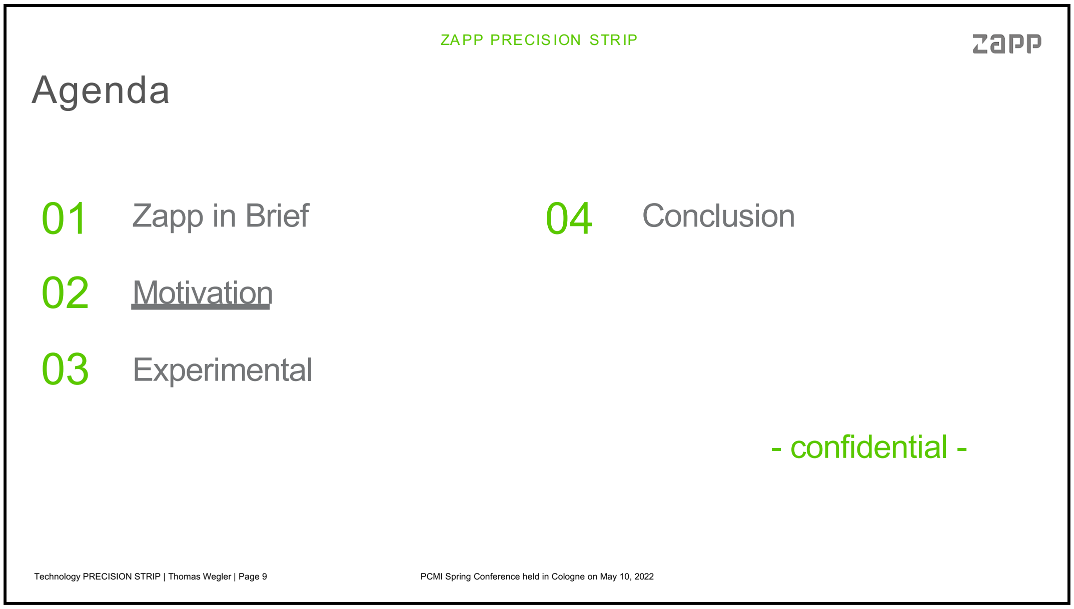
ZAPP PRECISION STRIP
zapp
Agenda
01 Zapp in Brief
02 Motivation
03 Experimental
04 Conclusion
- confidential -
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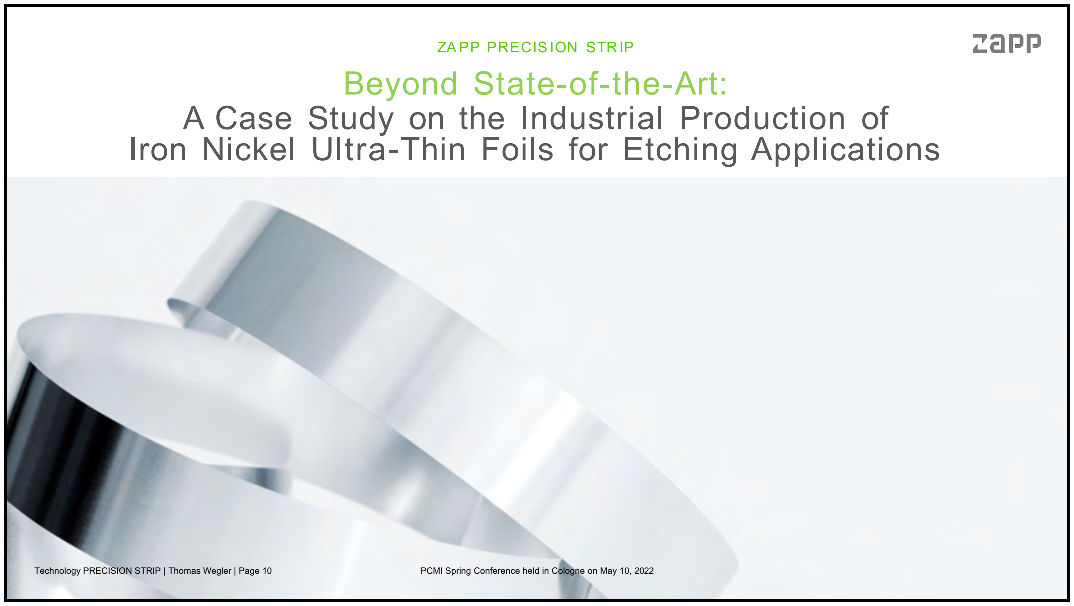
ZAPP PRECISION STRIP
zapp
Beyond State-of-the-Art:
A Case Study on the Industrial Production of
Iron Nickel Ultra-Thin Foils for Etching Applications
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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

zapp

Abstract

For the mass production of OLED-displays, used within mobile phones and other consumer electronics, so called "**fine metal masks**" (FMM) are produced via reel-to-reel **etching** processes.
The required tolerances for properties such as through-hole size, contour form and pitch or periodicity, in both the rolling and transverse directions, in turn demand almost impossible tolerances within the continuous production of the foil material. Some of the inherent challenges and their practical solutions are presented and discussed within this case study.

Allen DM et al 2005 CIRP Annals 54 Issue 1 187-190

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ZAPP PRECISION STRIP

zapp

Agenda

01 Zapp in Brief

02 Motivation

03 Experimental

04 Conclusion

- confidential -

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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Methods of thickness determination

IMS: https://www.ims-experts.com

Mitutoyo https://shop.mitutoyo.de/

Mahr: https://metrology.mahr.com

Vollmer: https://www.vollmergmbh.de/de/produkte-kontaktmessgeraete.html

Heidenhain:
https://product.heidenhain.de

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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Thickness measurement and inline control

Tactile inline measurement of foil thicknesses can affect the surface

Non-contact measurement of thickness like a laser is possible, but not accurate enough:

Influences of temperature, position and fluctuations

Difficulty:

- Which tolerances can be safely met for thicknesses below 30 µm in an industrial process?
- How is the process regulated during continuous production, e. g. during cold rolling?
- How can we define process standards, accompanied by measurements, in the laboratory under standardized conditions (temperature)?

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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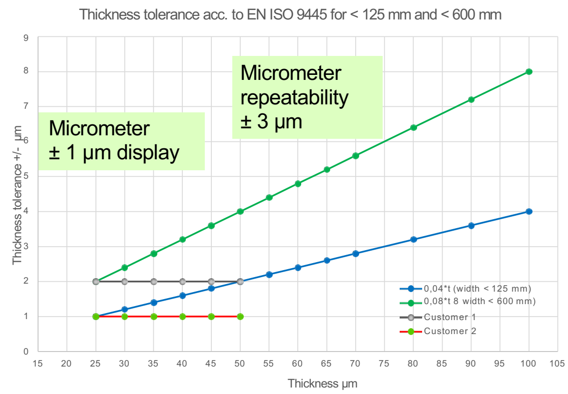
Thickness and tolerance

	Repeatability
750 mm wide mill	± 0.21 µm
ULM	± 0.25 µm
Hand held micrometer	± 3 µm

- The requirements for thickness are very tight.
- Repeatability of a hand held micrometer gauge is not capable for the required tolerances.
- Even our ULM and the X-Ray gauges are not capable of measuring the required tolerances.

Note:

Customers require tolerances for narrow strip defined for thicker gauges (red and black graph)



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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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Influence of roughness to thickness tolerance

Comparison of the roughness standards ISO 4287 and ASME B46.1

ASME B46.1-2009

Z_n = the vertical distance between the highest and lowest points of the profile within a sampling length segment labeled (ln)

Rmax (maximum roughness depth) = the largest of the successive values of **Z_n** calculated over the evaluation length

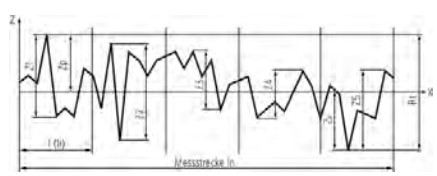
Rt (maximum height of the profile) = the vertical distance between the highest and lowest points of the profile within the evaluation length

Rz (average maximum height of the profile) = the average of the successive values of Rz_n calculated over the evaluation length. $\mathbf{Rz} = \frac{1}{n}(Z1+Z2+...Zn)$

ISO 4287

Rt, Rz = the same definition as the ASME standard

Rmax = not defined in the standard



Source: ISO-4287

$$\text{Ra} = \frac{1}{l}\int_0^l |Z(x)|\,dx$$

arithmetic mean of the magnitudes of the ordinate values Z(x) within a single measurement section

Technical advice:

The surface quality should be described with Ra; Rt and Rz.
A definition of Rmax offers no added value.

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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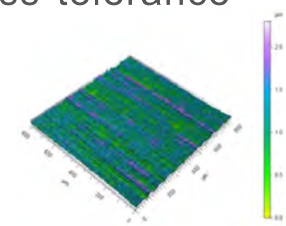
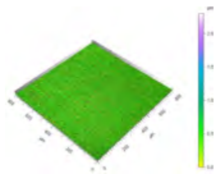
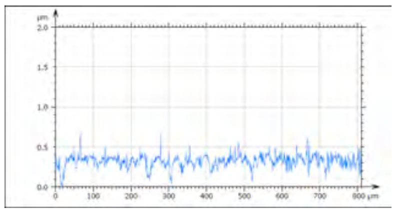
Influence of roughness on thickness tolerance

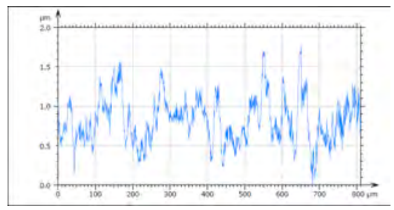
ISO 25178

Height Parameters	Measuring surface: mirror fin.	bright fin. fine	bright fin. medium	bright fin. rough			Gauge length 5.8 mm — Comparable to
Sa µm	0.045	0.094	0.126	0.2443	µm	Arithmetical average height	Ra
Sz µm	0.650	0.951	1.113	2.209	µm	max. height (pit + tip)	Rt
S10z µm	0.565	0.593	0.705	1.426	µm	ten tip height / 5% cut	Rz









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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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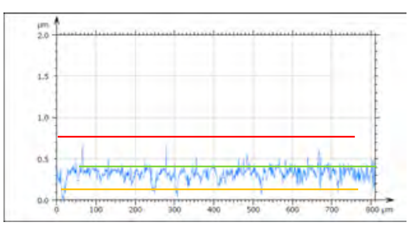
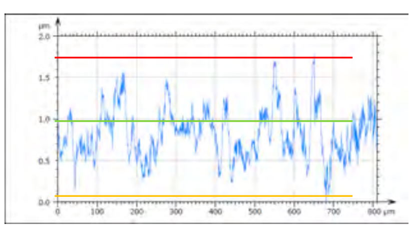
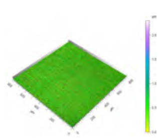
What is the thickness on a microscopic level? Red, Green or Yellow?



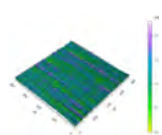


What do you think? Which line is the right one?



Conclusion

- One should agree on the exact surface characteristics beforehand, when considering less than +/-3µm and/or thinner than 60µm
- The precise measurement method or system to be used should be determined/agreed upon in advance



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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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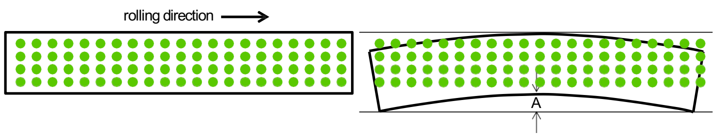
Camber affects processing and the resolution

- The greatest deviation of a coil edge from a straight line is called camber
- Excessive camber does not allow for the efficient processing of reel-to-reel product, as steering through a continuous line is difficult and in some cases impossible
- To achieve the desired pattern on a strip exhibiting camber, the material has to be put under tension during exposure. This can lead to form deviation from centre to edge, after the release of tension.



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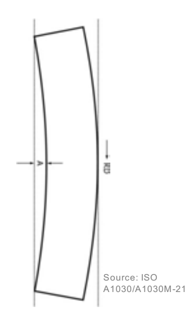
Camber



25 µm thick strip, 6 m sample > Different operators record different readings
Not a problem for a 250 µm thick strip.
The material is stiff enough during handling and the repeatability is ok.

A1030/A1030M − 21
Standard Practice for measuring flatness characteristics of steel sheet products1

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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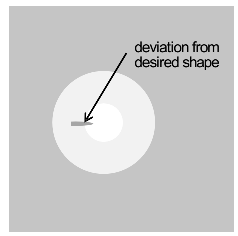
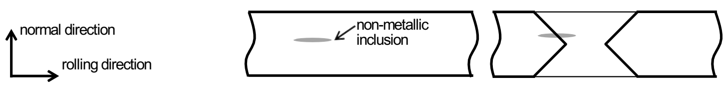
Metallic strips contain non-metallic inclusions and in some cases precipitations

- Non-metallic inclusions cannot be avoided in production of metallic materials
- In some alloy families precipitates, like carbo-nitrides, are present
- To ensure the desired resolution and shape accuracy of through-holes, or even the function of the edges, the size of the particles must be controlled
- Clean steel and precise heat treatment for fine dispersion of precipitates are the prerequisites for fulfilling the most demanding requirements





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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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Cleanness determination for micrometer scale is not standardized

Usually, the degree of purity is determined by light microscopy.

A minimum area of a few square millimeters is checked.

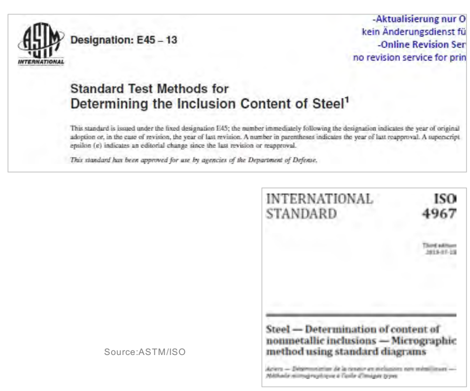
On the basis of comparative images, the degree of purity of a cold strip is characterized at magnifications of 100 x (sometimes higher).

Difficulty:

- Inclusions of a few micrometers are at the resolution limit of light microscopy.
- Only a small part of the volume, about 1 ppm, is characterized.
- However, customers test the material 100 %, either by forming, during processing or by complex testing techniques...

> **Due to lack of standard for micrometer inclusions a Zapp testing standard was established for highest purity material.**

> **Suitable process controls in metallurgy and casting are necessary.**



Designation: E45 – 13

Standard Test Methods for
Determining the Inclusion Content of Steel[1]

INTERNATIONAL STANDARD ISO 4967

Steel — Determination of content of nonmetallic inclusions — Micrographic method using standard diagrams

Source:ASTM/ISO

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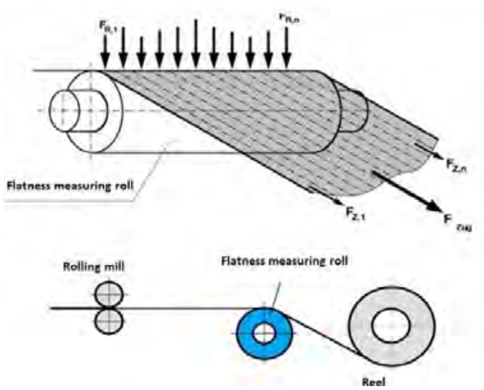
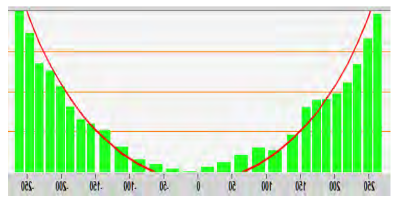
Inline flatness measurement





A lot of tension is necessary during strip cold rolling

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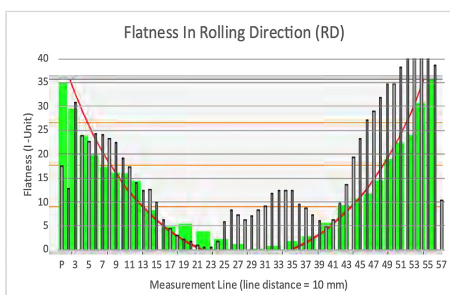
Flatness measurement
Inline v laboratory

The customer's requirements for precise stencils and masks can be below 1 to 2 I-Unit.

Difficulty

- The available flatness measurements (optical or with force sensors) are not precise enough.
- The inline measurements take place under tension stress.
- Laboratory measurements on foils are subject to certain fluctuations and do not allow for assessment along the entire strip length (sometimes a several kilometers!)

> **Lengthy development and preliminary testing to determine the right strategy and best practice.**



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PCMI Spring Conference held in Cologne on May 10, 2022

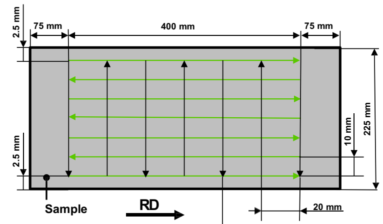
BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

zapp

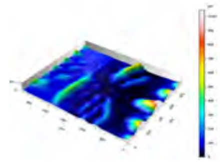
Laboratory flatness measurement

- **Standard:**
  Internal Standard (based on ASTM A1030)
- **Test equipment:**
  - Excel 661HC Micro-Vu
  - Measurement range (width, length, height): 650 x 680 x 160 mm
  - Measurement accuracy - length, width: 2.5 + L/200 µm
  - Measurement accuracy – height (laser): 0.5 µm
- **Measuring procedure:**
  - A triangulation laser measures the heights on defined lines
  - For each line an I-Unit value is calculated
  - With the results a topographic picture of the sample can be generated

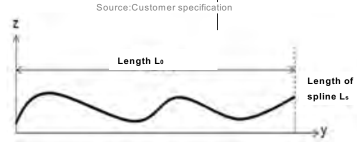
Source: Micro-Vu



Source:Customer specification



Measurement result



$$l_! \ (\mathrm{I-Unit}) = \frac{L_s - L_0}{L_0} * 10^{"}$$

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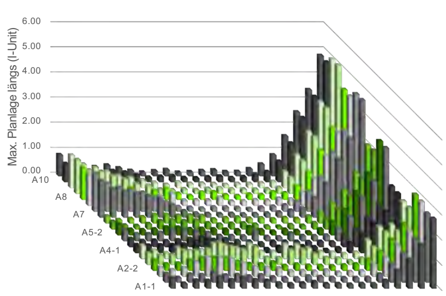
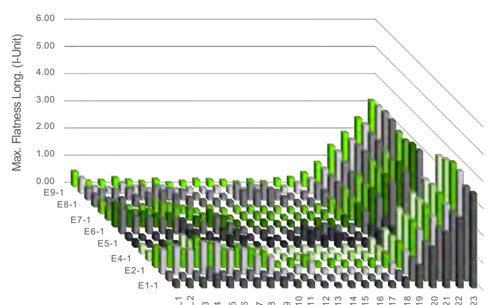
Laboratory flatness measurement variation





Influence of the sample

- To analyze the influence of the sample, 9 samples were taken at the beginning and end of a coil and the flatness were measured.
- Within the samples the max. spread is ≈ 1.0 I-Unit

	Max. Flatness RD (I-Unit)	Max. Flatness TD (I-Unit)
Standard Deviation	1,00	0,28

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

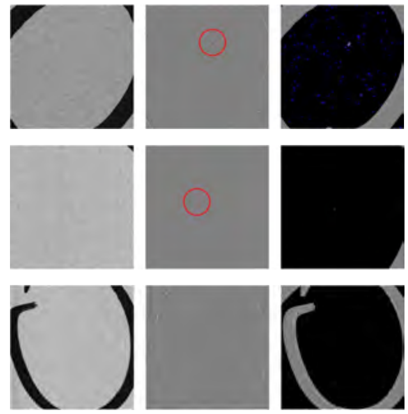
Surface defects with depths below 1 µm & diameters less than 500 µm hardly detectable

For highly demanding applications in electronics, or for dynamically stressed springs, defects with a depth >0.5 µm or >1 µm are not permitted.

Difficulty:

- No automatic system currently available that can detect such defects inline and with the related height differences.
- Visual recognition depends not only on lighting and inspection techniques, but also on the inspector's capabilities.
- Only the ends of foils can be visually assessed.

> It is essential to define and agree on inspection techniques and standards with the customer.



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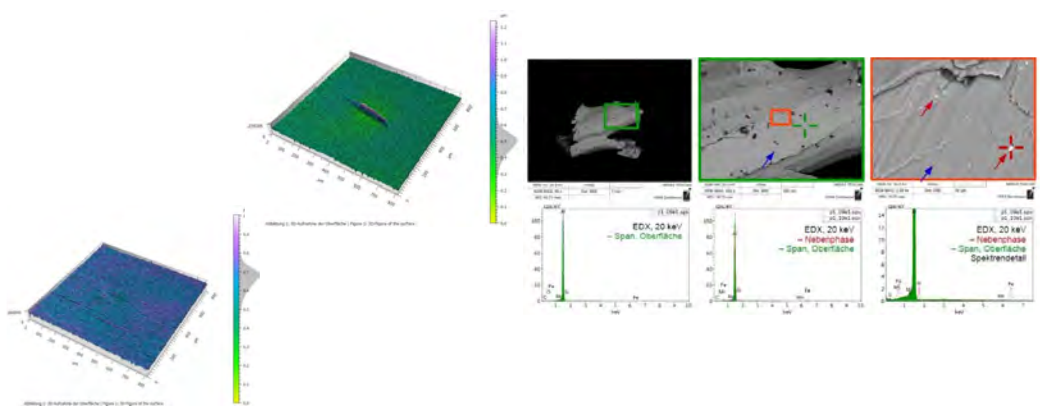
BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

Avoidance of surface defects



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ZAPP PRECISION STRIP

zapp

Agenda

01 Zapp in Brief

02 Motivation

03 Experimental

04 Conclusion

- confidential -

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BEYOND STATE-OF-THE-ART - INDUSTRIAL PRODUCTION OF IRON NICKEL ULTRA-THIN FOILS

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Conclusions

- The requirements for thin foils for the electronic industry are currently beyond the known / established standards for precision strip products.
- Many of the required tolerances are at the very limit of measurement equipment capability.
- Specially configured equipment is necessary to carry out the measurement tasks successfully.
- In order to organize successful serial production, finely tuned standards are required.
- A strict set of procedures must be defined and followed in order to meet the requirements of the customer specification.

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STRESS FREE PRECISION ETCHING WITH
ZAPP SUPER-ETCH AND ZAPP MICRO-ETCH
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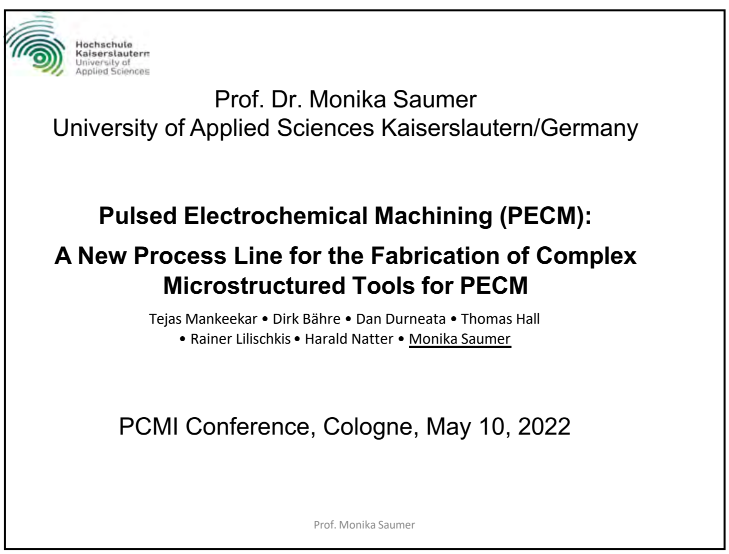
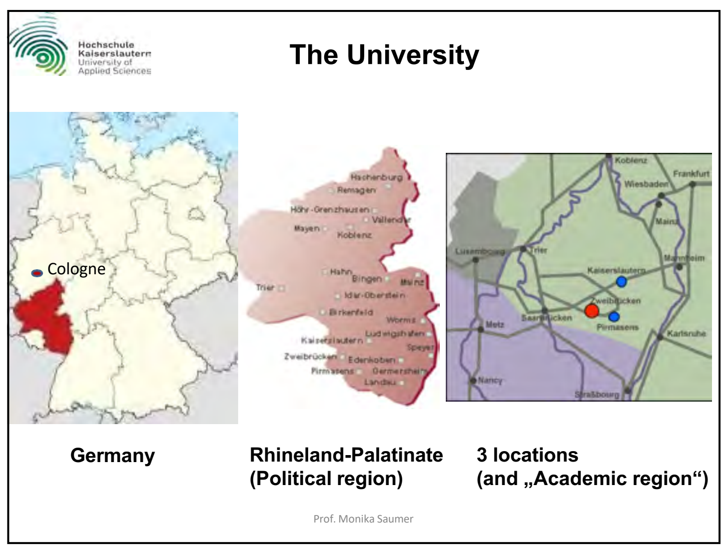
SCHMID
Our special rolling and heat treatment processing takes the
stress out of our precision strip as well as your working day.
www.zapp.com

Prof. Monika Saumer, Dr. rer. nat., chemist, is Professor for Chemical Microfabrication at the University of Applied Sciences Kaiserslautern/ Zweibrücken (Germany), head of cleanroom with microfabrication facilities, spokeswoman of the research center "Integrated Miniaturised Systems", and leads the research team Chemical Processes in Micro- and Nanotechnology.

From 1992 to 1998 she was a postdoctoral research fellow at the Institute of Microstructuring Technology (IMT) at the Karlsruhe Institute of Technology, Germany (KIT). From 1990 to 1992 she worked as research fellow at the Institute of Instrumental Analysis (IFIA) at KIT. In 1993, she received her doctoral degree in chemistry at the University of Karlsruhe, Germany.

She is an expert in micro- and nanostructured bio-interfaces and electrochemistry. A particular focus is on 2D and 3D nanostructuring with wet chemical (etching, electrochemical deposition) and nanoimprint technologies. She is a co-author of several high impact papers in journals like Advanced Functional Materials, Small, Advanced Materials Technologies and ACS Biomaterials Science & Engineering.





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The University

3 locations

- Kaiserslautern
- Pirmasens
- Zweibrücken

5 faculties / departments

- Computer Sciences and Microsystems Technology
- Business Administration
- Mechanical and Electrical Engineering;
- Architecture
- Logistics and Polymer Technology

25 Bachelor courses / 15 Master courses

6000 students

400 staff

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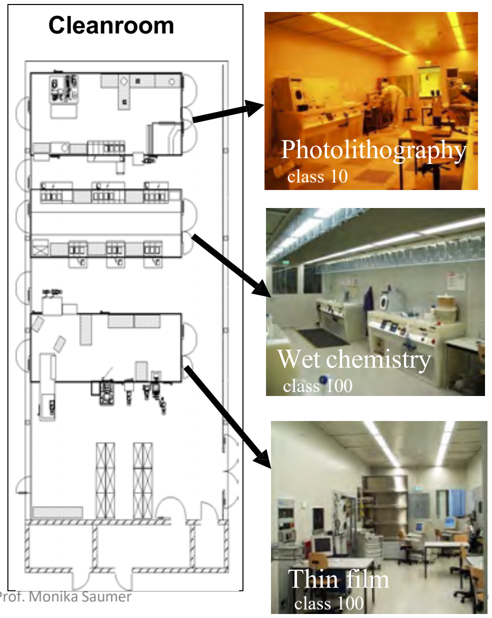
The University

Location Zweibrücken

Microsystems Technology Centre



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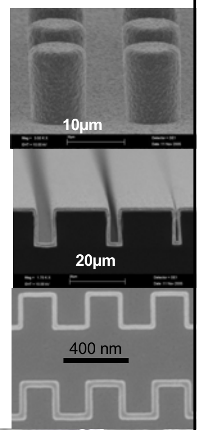
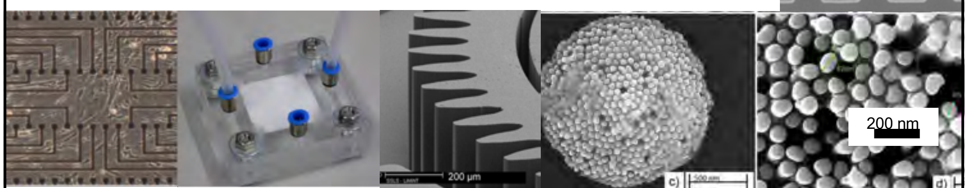
Research topics

Micro/nano devices via (electro-)chemical methods

Applications e.g.

- **Magnetic sensors and actuators (NiFe and CoP based alloys)**
- **„Surfaces“ and interfaces for technical/biomedical applications**
- **Gold-Electrodes for neuronal cell activity measurements**
- **Bio-reactor for cell culturing**
- **Lab on chip and electrochemical sensors**





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Funding of our research

Funding:
- Regional (by Rhineland Palatinate)
- German Ministries
- European Union
- Direct from industry

Cooperation with industry
- Research with public funding
- Direct contracts with mutual research interest
- „Pure“ contract research
  (industry is „owner“ of the intellectual properties)

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Microstructured Tool Fabrication for PECM

A New Process Line for the Fabrication of Complex Microstructured Tools for PECM

Tejas Mankeekar[1] • Dirk Bähre[2] • Dan Durneata[3] • Thomas Hall[2] • Rainer Lilischkis[1] • Harald Natter[3] • Monika Saumer[1]

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and Industry Partner

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What is Pulsed Electrochemical Machining (PECM)?

Electrochemical: electron transfer during chemical reaction (redoxreaction)

e.g. $2\ Fe^{3+} + Ni\ (s) \rightarrow 2\ Fe^{2+} + Ni^{2+}$

Machining: process in which a material is cut to a desired final shape and size by a controlled material-removal process (subtractive manufacturing)

Electrochemical Machining:

formation of soluble metal ions by releasing of electrons is the „cutting process"

e.g. $Ni\ (s) \rightarrow Ni^{2+} + 2\ e^-$ — oxidation = anodic partial reaction takes place at the anode technically: „ething"

Who captures the electrons?

e.g. $2\ Fe^{3+} + 2\ e^- \rightarrow 2\ Fe^{2+}$

e.g. $NO_3^- + H_2O + 2\ e^- \rightarrow NO_2^- + OH^-$

reduction = cathodic partial reaction takes place at the cathode

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What is Pulsed Electrochemical Machining (PECM)?

How the electrons are transferred (technical solution)?

Option 1: „**locally**" at the interface of the workpiece and the etching solution

- **Technical realisation for microfabrication:**
  photolithography–wet chemical etching („Photochemical Machining" = **PCM**)
- Pulse possible? No.

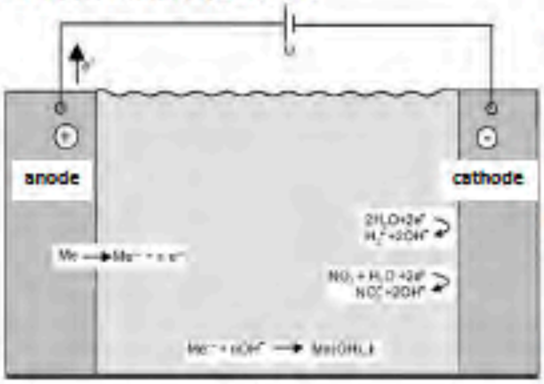
Option 2: **via an external power supply**

- **Technical realisation for microfabrication:**
  microstructured tool used as cathode („Electrochemical Machining" = **ECM**)
- Pulse possible? Yes. („Pulse Electrochemical Machining" = **PECM**)

→ **etching of difficult to etch material possible**

What is Pulsed Electrochemical Machining (PECM)?

Anodic metal dissolution:



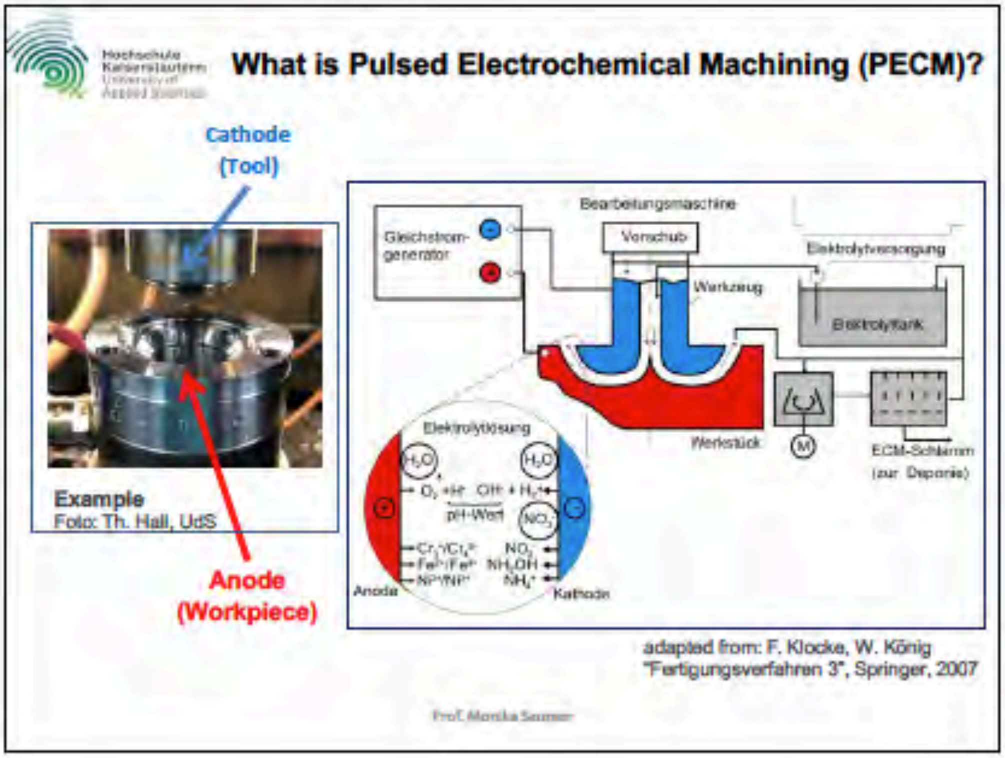
[KIK007]

Applying a DC voltage (ECM)

► Complex electrochemical reactions at the electrodes

1. **Anodic metal dissolution:**
The material to be removed passes into the electrolyte emitting electrons and metal ions

2. **Cathodic reduction:**
Hydrogen development
no material removal


What is Pulsed Electrochemical Machining (PECM)?
Cathode
(Tool)
Example
Foto: Th. Hall, UdS
Anode
(Workpiece)
Bearbeitungsmaschine
Gleichstrom-
generator
Vorschub
Elektrolytversorgung
Werkzeug
Elektrolyttank
Werkstück
ECM-Schlamm
(zur Deponie)
Elektrolytlösung
Anode
Kathode
adapted from: F. Klocke, W. König
"Fertigungsverfahren 3", Springer, 2007
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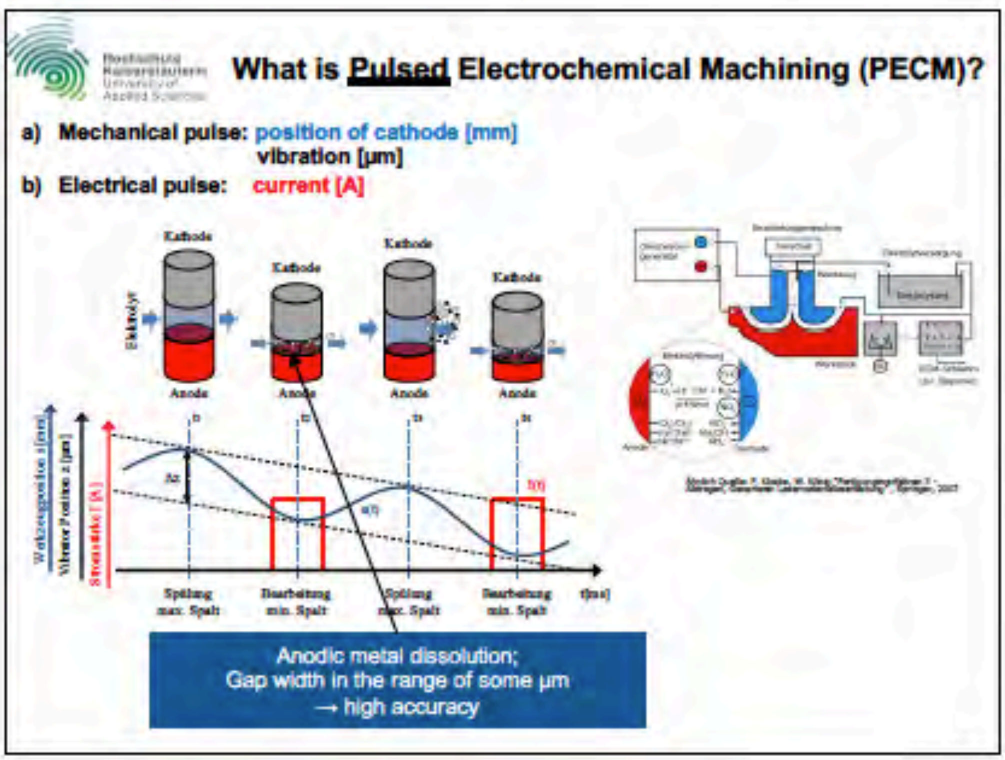
What is Pulsed Electrochemical Machining (PECM)?
a) Mechanical pulse: position of cathode [mm]
vibration [µm]
b) Electrical pulse: current [A]
Kathode
Anode
Elektrolyt
Spülung
max. Spalt
Bearbeitung
min. Spalt
t[ms]
Anodic metal dissolution;
Gap width in the range of some µm
→ high accuracy

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What is Pulsed Electrochemical Machining (PECM)?

Operating Cell

PEM Tec

Electrolyte Conditioning

Control

Generator

Source: PEMTec SNC

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Microstructured Tool Fabrication for PECM

Project demand:
Produce metallic sealing system via **PECM** whose functional surfaces are also suitable for low-pressure applications

Very high demands on metallic sealing systems: parts must be **accurate** in **shape**, **dimension**, **position** and **surface finish**

One Challenge:
Tool fabrication for PECM

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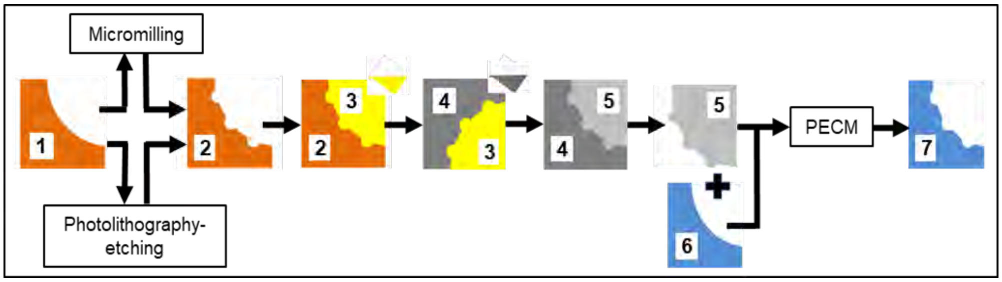
Microstructured Tool Fabrication for PECM

Process chain for micro-structuring:



1 Substrate,
2 Substrate after micro-structuring (**reusable master form**)
3 Silicone casting (**reusable**)
4 Epoxy casting
5 PECM tool (electroforming of e.g. Ni)
6 Metal workpiece
7 Metal workpiece after micro-structuring

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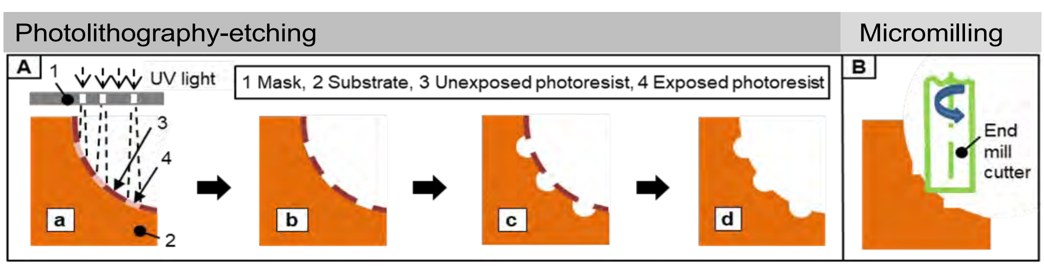
Microstructured Tool Fabrication for PECM

Initial micro-structuring processes



Substrate
- **a** during exposure
- **b** after developing the photoresist (red)
- **c** after wet chemical etching and
- **d** after photoresist stripping

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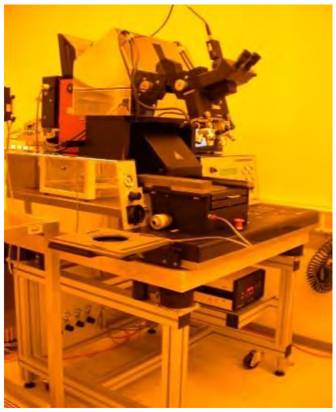
Microstructured Tool Fabrication for PECM

Photolithography:



- Positive Photoresist: AZ1514 H
- Spincoating: 2080 rpm for 90 s
- Softbake: 100°C für 10 min
- Relaxation: 22°C für 10 min
- Exposure:

  Hard contact mode: 40 s

  Hg-Lamp broadband 5.9 mW cm^{-2}
- Development:

  Alkaline solution (AZ 726 MIF), 60 s
- Resist thickness ~ 5 µm

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Microstructured Tool Fabrication for PECM

Wet chemical etching:

- Etching medium: $FeCl_3$
- Concentration: 2.33 M
- pH: 0.28 (at 32 °C)
- Temperature: 50 °C
- Etching time: 15 min
- Etching mode: Continuous agitation
- Resist stripping: Acetone followed by Ethanol

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Microstructured Tool Fabrication for PECM

Micromilling:

- Equipment: HSPC 2522; KERN Microtechnik
- No. of axes used: 3
- Micromilling cutter: Solid carbide; ø 4 mm
- Revolutions per minute: 5000
- Cutting speed: 62.83 m/min
- Vertical feed: 30 mm/min
- Horizontal feed: 60 mm/min (0.006 mm/tooth)
- Coolant: WICODRAW 1433 S;
  Wilke Kühlschmiertechnik

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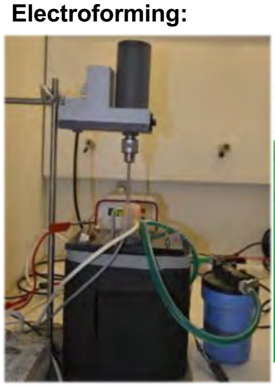
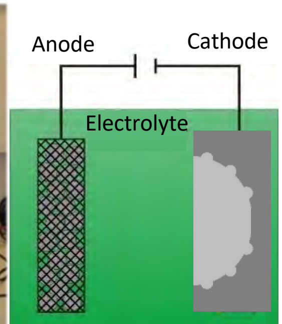
Microstructured Tool Fabrication for PECM

Electroforming:





- Volume: 3 L
- Electrolyte: Nickel Sulfamate
- pH: 5.8
- Temperature: 40 °C
- Current density: 20 mA/cm^2

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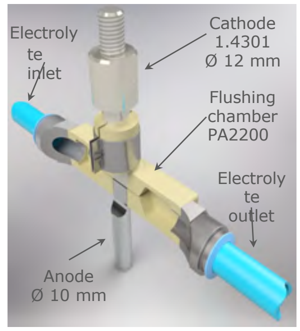
Microstructured Tool Fabrication for PECM

Pulse electrochemical machining:

Quelle: http://www.pemtec.de

Generator und Steuerung | Arbeitszelle | Elektrolyt-aufbereitung

Source: PEMTec SNC



Process Chamber

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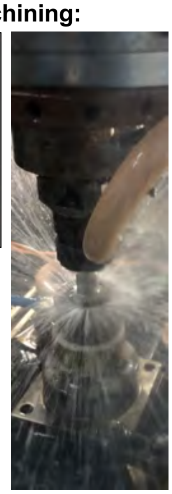
Microstructured Tool Fabrication for PECM

Pulse electrochemical machining:

PECM process chamber,
b Nickel PECM tool
c Metal workpiece after micro-structuring



Process parameters	
Process voltage U [V]	12
Pulse on-time t_{on} [ms]	2.5; 5
Feed rate v_f [mm/min]	0.05-0.35
Electrolyte conductivity σ_{el} [mS/cm]	100±5
Mechanical frequency f_{mech} [Hz]	50
Electrical frequency f_{electr} [Hz]	50
Electrolyte pressure p_{el} [kPa]	300
Electrolyte temperature T_{el} [°C]	20±1.5

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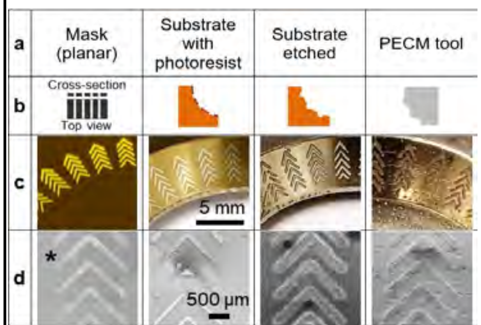
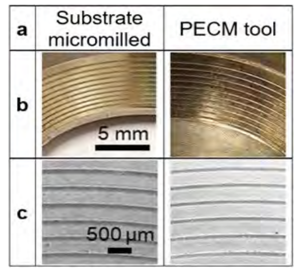
Microstructured Tool Fabrication for PECM

Micro-structures over the photolithography-etching process chain:



a Process state,
b Schematic cross-section,
c Digital camera,
d SEM, *Optical microscope

Micro-structures over the micromilling process chain:



a Process state,
b Digital camera,
c SEM

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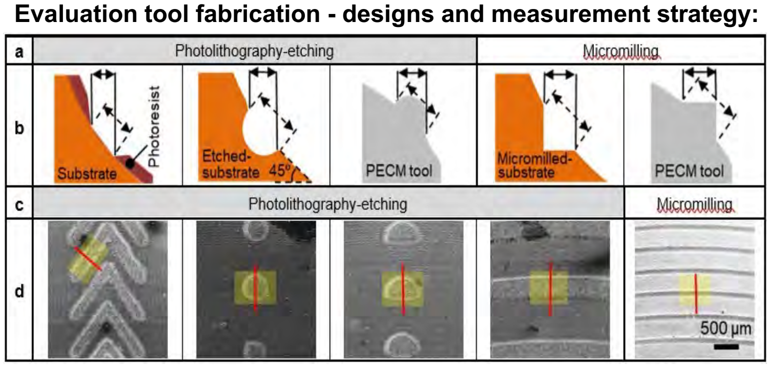
Microstructured Tool Fabrication for PECM

Evaluation tool fabrication - designs and measurement strategy:



b measurement method
Top view width: solid lines
→ calculation of real width: dotted line
d SEM pictures of the structures with measurement location

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Microstructured Tool Fabrication for PECM

Dimensional change of the micro-structures over the process chain:

A	Planar structures of the mask	Photoresist structures on the substrate		Etched structures in the substrate (reusable master form)			PECM tool with structures	n
	Top view width (µm)	Top view width (µm)	Real width (µm)	Real width (µm)	Under-etching (µm)	Etch rate (µm/min)	Real width (µm)	
Arrows	100	96 ± 8	136 ± 11	307 ± 18	86	5.7	303 ± 17	6
	150	140 ± 3	198 ± 4	380 ± 16	91	6.1	373 ± 11	6
Circles	100	89 ± 2	126 ± 3	215 ± 10	45	3.0	223 ± 8	4
	300	301 ± 9	426 ± 13	513 ± 25	44	2.9	506 ± 25	4
	500	501 ± 9	709 ± 13	808 ± 17	49	3.3	819 ± 14	4
Semicircles	100	104 ± 3	147 ± 4	231 ± 16	42	2.8	233 ± 8	4
	300	302 ± 8	427 ± 11	518 ± 25	45	3.0	503 ± 24	4
	500	497 ± 12	703 ± 17	803 ± 20	50	3.3	802 ± 14	4
Rings	50	42 ± 5	59 ± 7	177 ± 17	59	3.9	171 ± 18	4
	100	103 ± 7	146 ± 10	276 ± 10	65	4.3	264 ± 8	4
	300	296 ± 11	419 ± 16	556 ± 33	69	4.6	550 ± 33	4
B	CAD			Micromilled structures in the substrate (reusable master form)				
Rings	100			126 ± 41			124 ± 34	10

A Photolithography-etching and **B** Micromilling
(width ± standard deviation, n: number of measurements)

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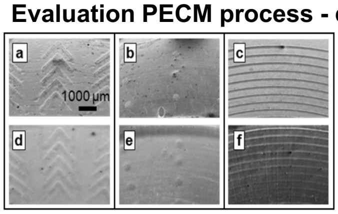
Microstructured Tool Fabrication for PECM

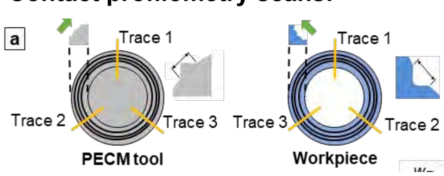
Evaluation PECM process - designs and measurement strategy:



PECM tools
(Rings: micromilled master)

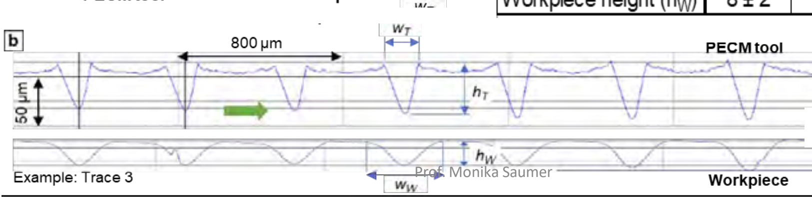
micro-structured workpieces after PECM

Contact profilometry scans:



c

Micro-structure	Trace 1	Trace 2	Trace 3
Tool width (w_T)	95 ± 9	116 ± 11	167 ± 8
Workpiece width (w_W)	303 ± 25	329 ± 26	358 ± 14
Tool height (h_T)	24 ± 4	31 ± 5	51 ± 5
Workpiece height (h_W)	8 ± 2	11 ± 1	20 ± 2



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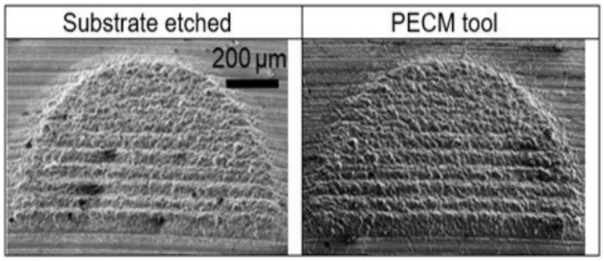
Microstructured Tool Fabrication for PECM

Potential of the tool fabrication:



Turning grooves oi the original substrate are visible:

left: etched substrate (master form) (indentations)
right: corresponding PECM tool (elevated structures)

Prof. Monika Saumer

Hochschule Kaiserslautern University of Applied Sciences

Microstructured Tool Fabrication for PECM

Conclusion:

- **Micromilling and Photolithography-Etching**
  → freely scalable structure design and dimensions in the sub mm range
- **Silicon prototype (reusable)** → cost effective tool fabrication
- **Electroforming** → a wide range of metals and alloys as tool material
- **Scalable tool size, parallel tool production**
- **A nearly unlimited number of tools from one microstructured master**
  → reproducible and cost effective

Prof. Monika Saumer

Hochschule Kaiserslautern University of Applied Sciences

Microstructured Tool Fabrication for PECM

Conclusion:

- Our proof-of-concept (sealing rings):
  - smallest dimensions on the tool (approx.):
    - 200 µm for rings, (semi-)circles
    - 300 µm for arrows
    - 124 µm for rings via micromilling
  - smallest dimension on the workpiece (approx.)
    - 330 µm
- Open Access Publication:

  Mankeekar et al, Int J Adv Manuf Technol 119, 2825–2833 (2022).

Prof. Monika Saumer

Hochschule Kaiserslautern University of Applied Sciences

Microstructured Tool Fabrication for PECM

Acknowledgement:

•Team in Zweibrücken (Precision engineering workshop, Clean room, Measurement technology)

Hochschule Kaiserslautern University of Applied Sciences

- Project partners: Saarland University and Industry partner

UNIVERSITÄT DES SAARLANDES

- Funding: Federal Ministry for Economic Affairs and Energy (Bundesministerium für Wirtschaft und Energie – BMWi)

ZIM Zentrales Innovationsprogramm Mittelstand

Bundesministerium für Wirtschaft und Energie

Prof. Monika Saumer

Emeritus Professor David Allen started his career as a chemist (BSc, 1968) and moved into photochemistry research (PhD, 1972) while studying at Cardiff University. Following post-doctoral research at Warwick University and imaging technology development in industry, David joined Cranfield University in 1976. He was appointed a Technical Liaison Member to the Photo Chemical Machining Institute (PCMI) in 1981 and is currently on the Board of Directors of PCMI responsible for education. David became Professor of Microengineering at Cranfield University in 1998 and was elected as a Fellow of The International Academy for Production Engineering (CIRP) in 2006.

David has published:

- Two PCM books: "The Principles and Practice of Photochemical Machining and Photoetching" (1986) and "Photochemical Machining and Photoelectroforming" (2015, reprinted 2016, 2017 and 2019)
- Five book chapters on non-conventional machining and contributed the chapter on 'Etching' to the on-line CIRP Encyclopedia of Production Engineering
- Seven confidential industrial PCM consortium reports
- 202 journal and conference papers and was awarded the higher doctoral degree of DSc from Cranfield University in 2013 for his thesis entitled "Contributions to Photochemical Machining and Photoelectroforming".

David retired from academia in 2011 and he now carries out consultancy and staff training in PCM companies across the world. He has worked with 26 different companies over the past 10 years.


Reclamation Opportunities / Secondary Markets for By-products
Lindner Hotel City Plaza, Köln, Germany
Tuesday 10th May 2022
Presented by:
Prof David Allen
Emeritus Professor of Microengineering, Cranfield University, UK
Dr Peter Jefferies
Innovation Technology Leader, Heatric Division of Meggitt, UK
and
Davide Toson
Plant Manager, Chimimetal, Italy
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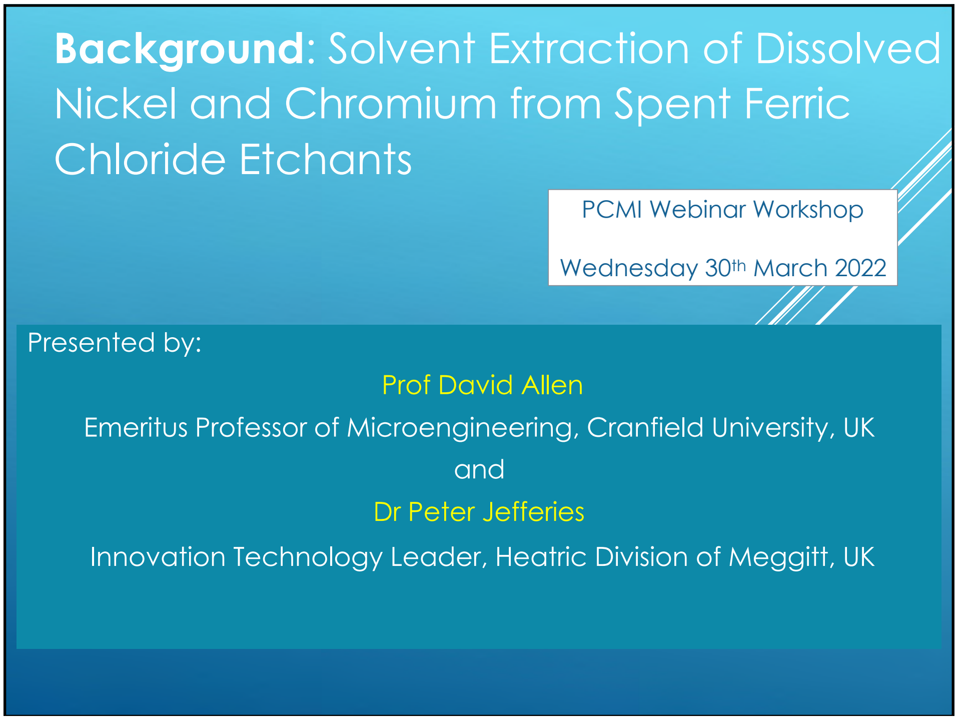

Background: Solvent Extraction of Dissolved Nickel and Chromium from Spent Ferric Chloride Etchants
PCMI Webinar Workshop
Wednesday 30th March 2022
Presented by:
Prof David Allen
Emeritus Professor of Microengineering, Cranfield University, UK
and
Dr Peter Jefferies
Innovation Technology Leader, Heatric Division of Meggitt, UK

Solvent extraction

Organic solvents have a high environmental impact due to the association of VOCs with photochemical smog, low-level ozone and "Health & Safety" concerns (volatility, low flash point and toxicological effects).

Solvent extraction is therefore a costly process requiring strict control.

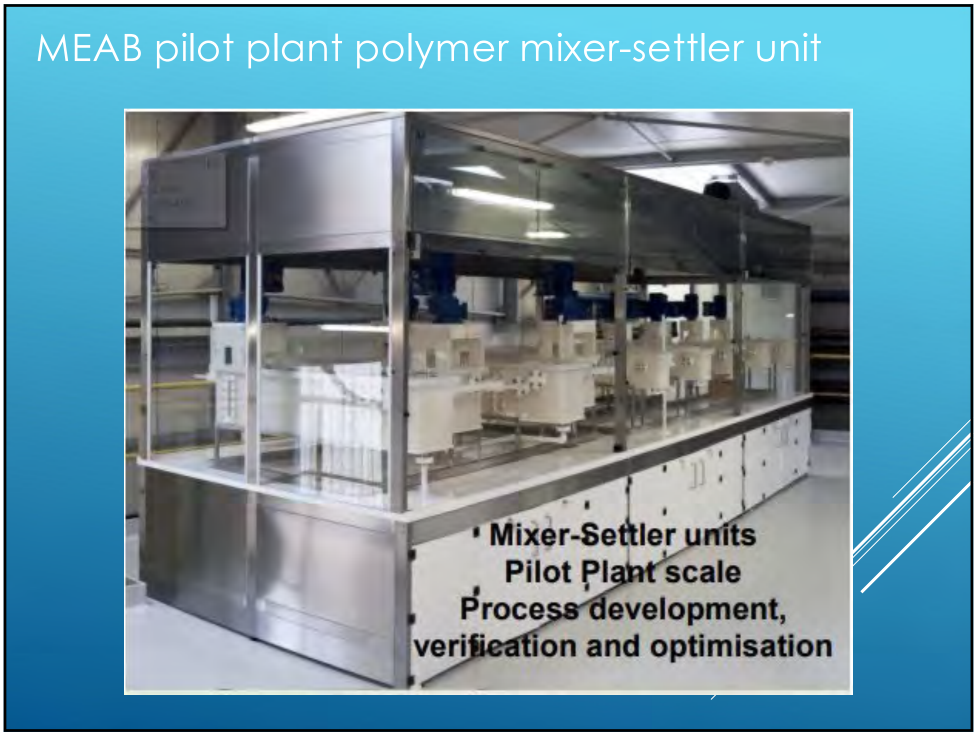
However, the process is still being investigated and might be accepted by the PCM industry if the **economics** become favourable with time.

Patents and papers have been written on separating concentrated Fe/Ni mixtures for at least 50 years!

Commercial mixer-settler design in glass

Photograph courtesy of De Dietrich Process Systems


Commercial mixer-settler design in glass
Glass is relatively expensive but transparent
Polymers are cheaper but opaque


MEAB pilot plant polymer mixer-settler unit
Mixer-Settler units
Pilot Plant scale
Process development, verification and optimisation

MEAB nickel extraction system

Nickel extraction plant with simultaneous neutralization

Photos courtesy of MEAB, Askim, Sweden and Aachen, Germany

Financial considerations for extraction of nickel from waste ferric chloride etchant

+ Value of nickel metal extracted

+ In theory, no additional purchases of ferric chloride if etchant regenerated

+ Etchant regeneration cost remains the same

+ No disposal costs for waste etchant, noting that these will always increase with time

- Cost of extraction equipment and electrolysis costs

- Labour and chemical costs

- Solvent "Health and Safety" costs

- Transport costs if extraction carried out off-site

-Note that etchant manufacturers have a vested interest to sell fresh/recycled $FeCl_3$

Economy of scale

A profitable nickel extraction process must depend on large quantities of spent ferric chloride being generated by etching. This implies large volumes of nickel-containing alloys need to be etched.

<u>Case study</u>

Consider a company such as Heatric that etches PCHEs. This company currently dissolves 400 tonnes of nickel-containing 18/8 stainless steel into ferric chloride etchant per annum. This means 32 tonnes of nickel are dissolved into solution per year.

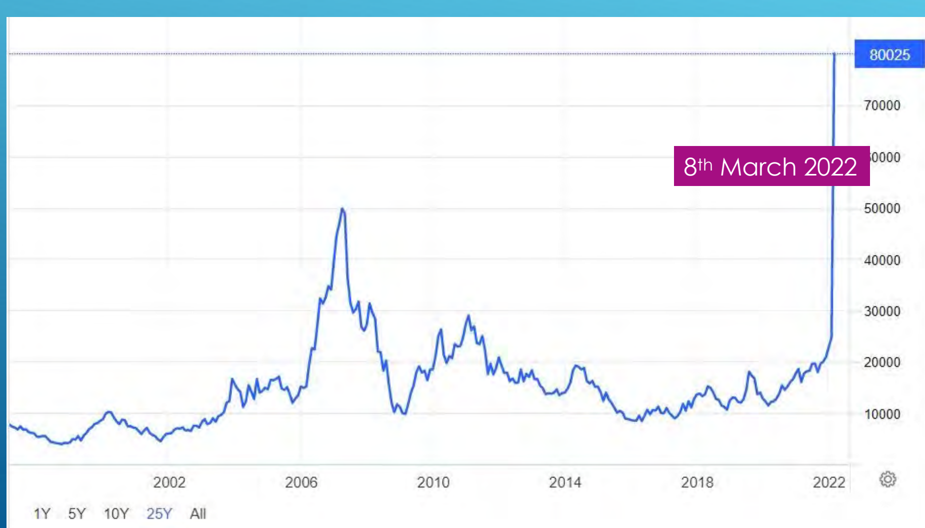
The price (4th March 2022) of nickel was approx. US$29,600 per tonne.

If all 32 tonnes of nickel can be extracted as pure nickel metal, the value of the nickel product would be $947,200 per annum.

If the price of nickel were to revert back to 2007 prices, the value of the nickel product would yield $1,764,000.

The $64 million question is "What is the cost of the extraction process?"

Nickel futures jumped more than 65% to $80,025 per tonne, having topped the $100,000 mark for the first time ever as western sanctions against Russia over its invasion of Ukraine sparked concerns over the metal supply. The unprecedented move in the nickel market led the London Metal Exchange to halt trading for the remainder of Tuesday's session. Russia accounts for about 10% of the global nickel supply, mainly for use in stainless steel and electric vehicle batteries.



Meggitt's heat exchanger plates etching facility in Birmingham

Bulk etching of stainless steel and other high-Ni alloys

Material size: 600 mm wide, ranging in length up to 1,800 mm long

Nominal etch depth: 1.1 mm

Metal removed per plate: 4 kg

5-7 tonnes of metal etched per week

Using up to 20 tonnes of chlorine liquid per week

MEGGiTT

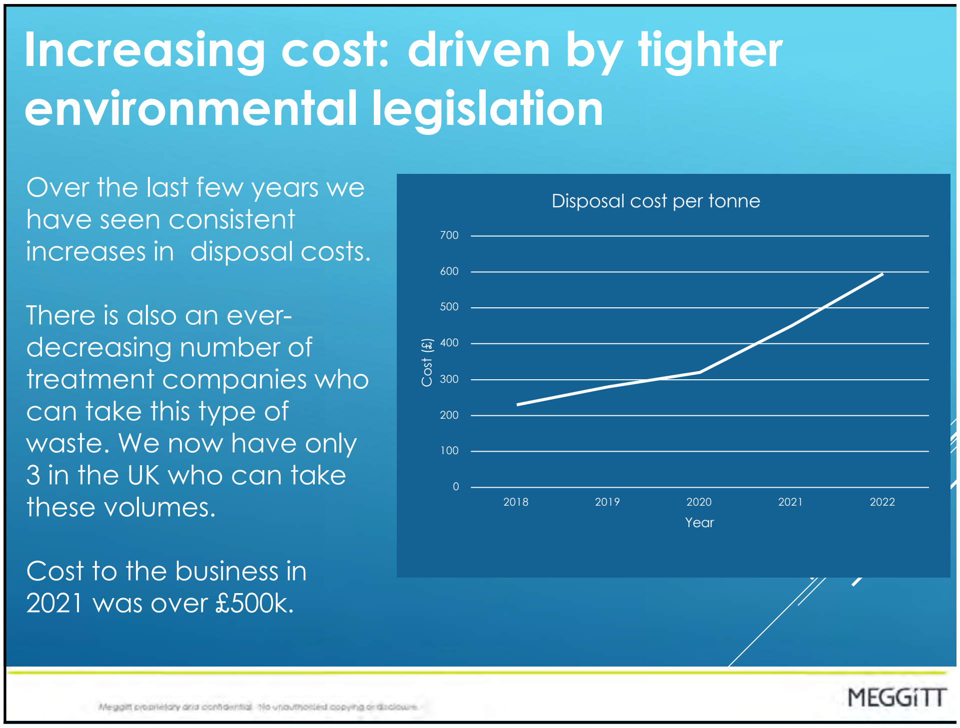
Regeneration- the scale of the problem

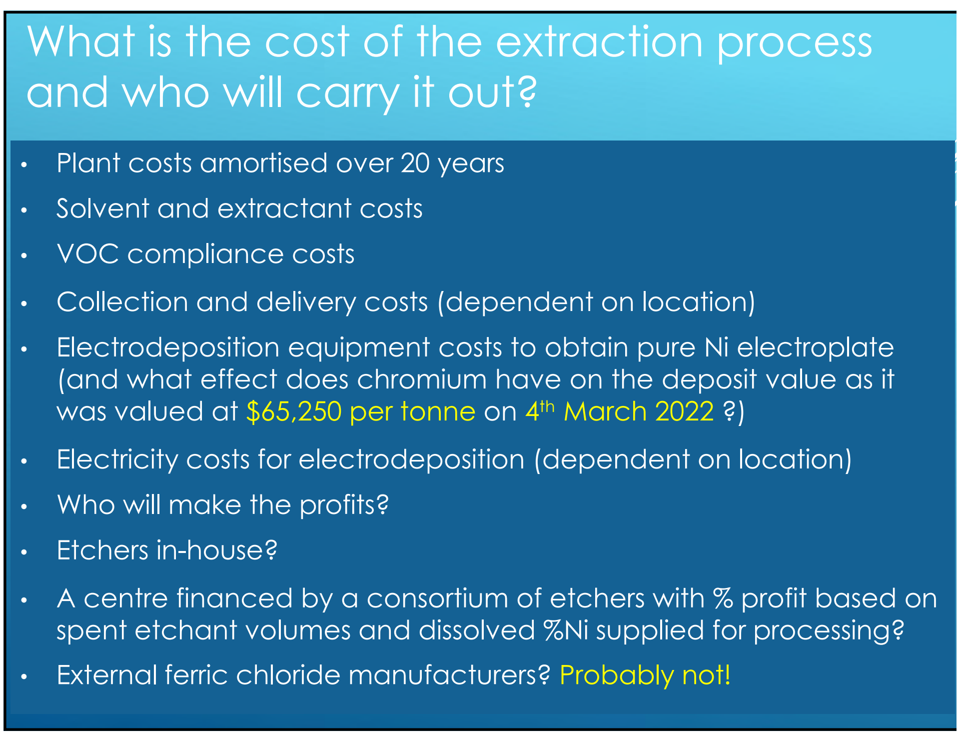
We have six 8-chamber etch lines running 24hr per day, 7 days per week and generating around 30 tonnes of waste ferric per week.

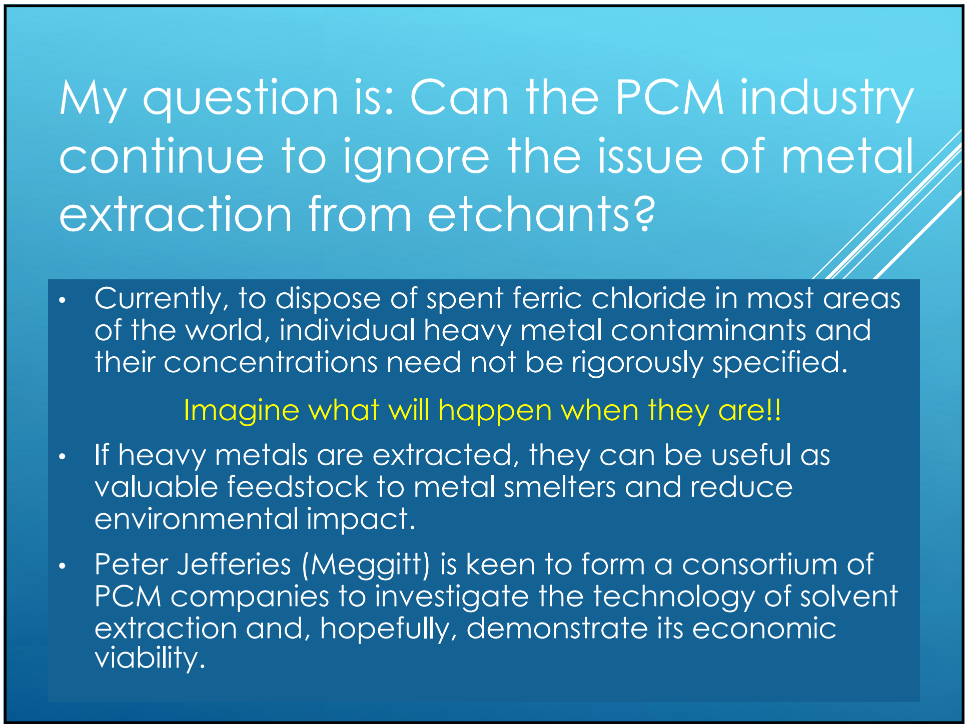
On average, 2 road tankers per week are used to dispose of this waste.

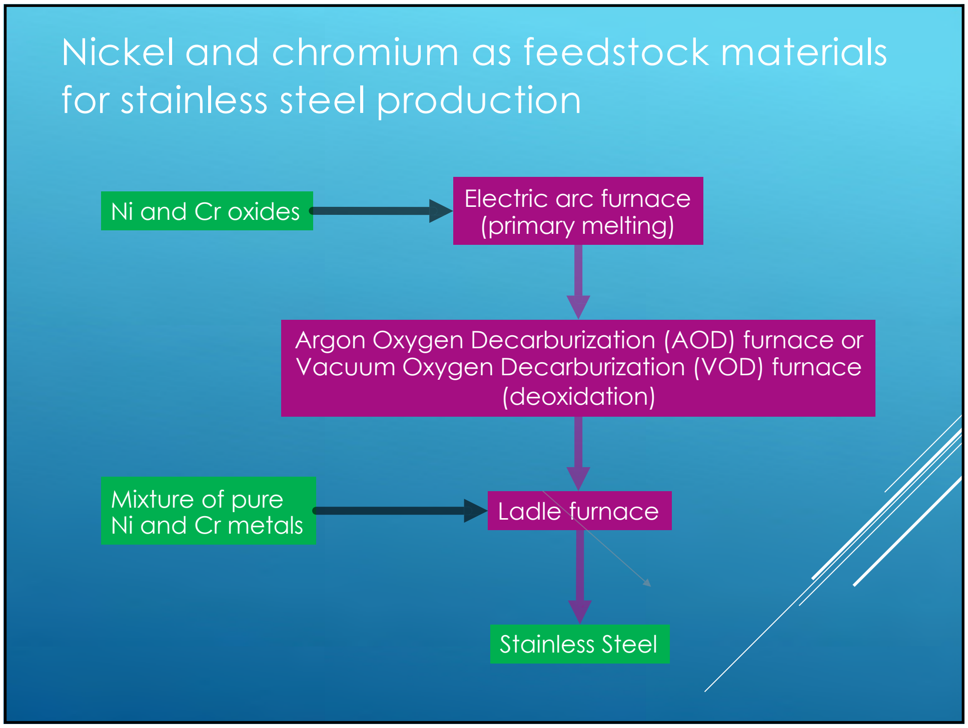
The issue we face is the high level of Ni and Cr contained in the spent etch solution which results in it being classified as **hazardous waste.**

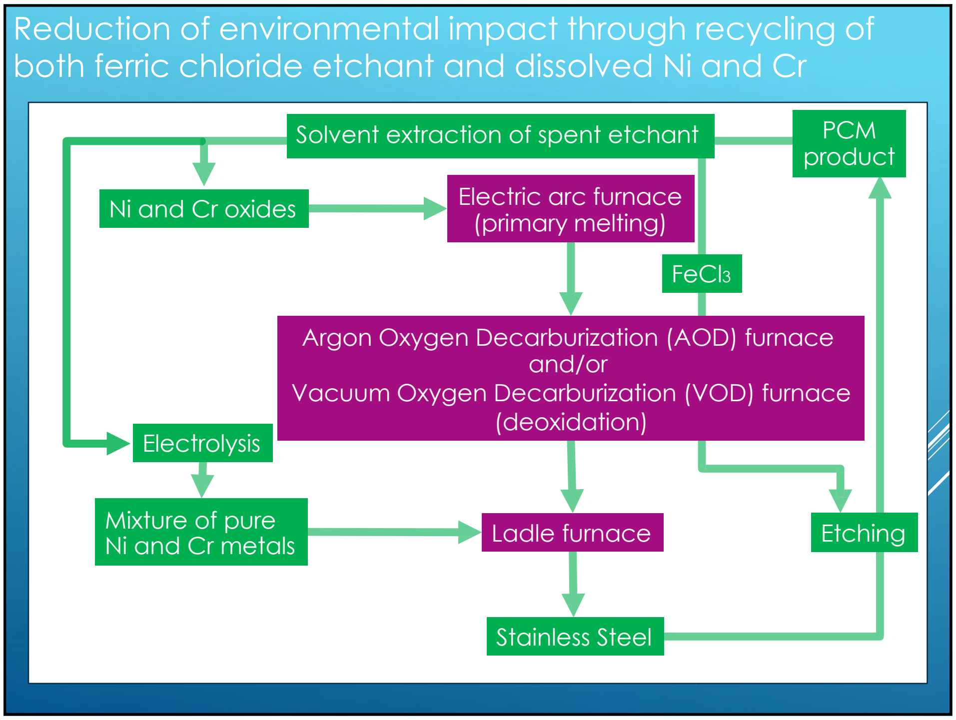
MEGGiTT

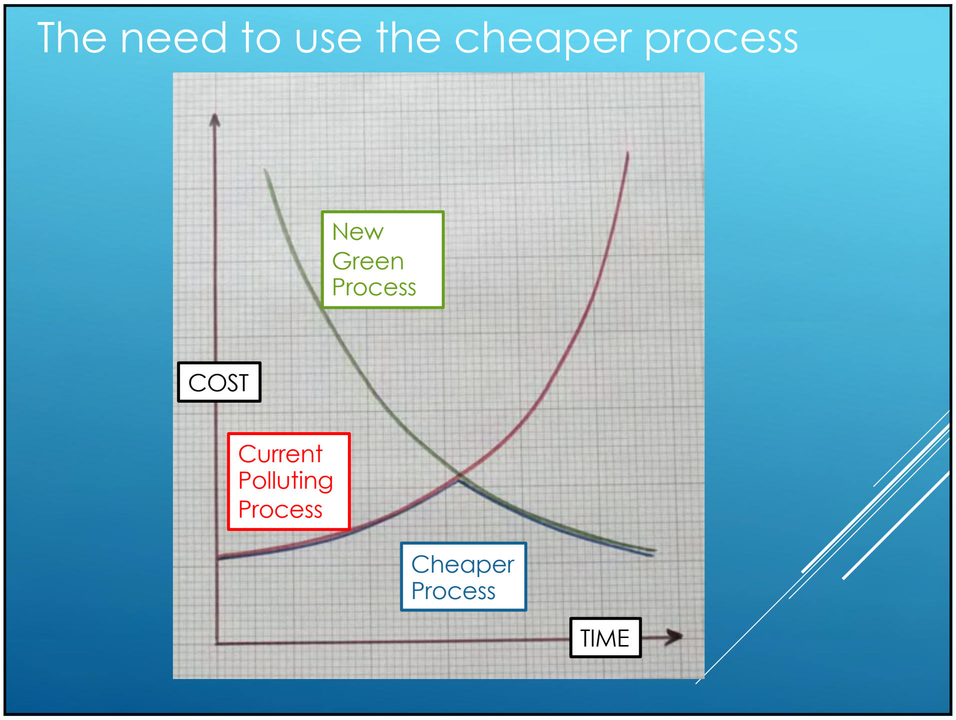

Increasing cost: driven by tighter environmental legislation
Over the last few years we have seen consistent increases in disposal costs.
There is also an ever-decreasing number of treatment companies who can take this type of waste. We now have only 3 in the UK who can take these volumes.
Cost to the business in 2021 was over £500k.
Disposal cost per tonne
Cost (£)
0
100
200
300
400
500
600
700
2018
2019
2020
2021
2022
Year
MEGGiTT

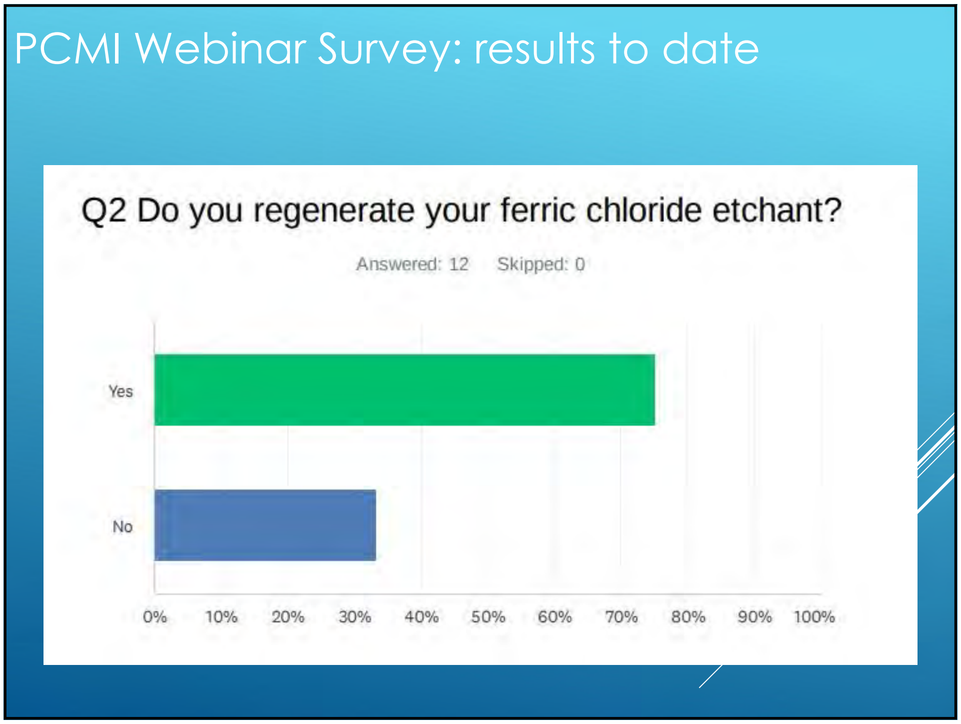

What is the cost of the extraction process and who will carry it out?
Plant costs amortised over 20 years
Solvent and extractant costs
VOC compliance costs
Collection and delivery costs (dependent on location)
Electrodeposition equipment costs to obtain pure Ni electroplate (and what effect does chromium have on the deposit value as it was valued at $65,250 per tonne on 4th March 2022 ?)
Electricity costs for electrodeposition (dependent on location)
Who will make the profits?
Etchers in-house?
A centre financed by a consortium of etchers with % profit based on spent etchant volumes and dissolved %Ni supplied for processing?
External ferric chloride manufacturers? Probably not!

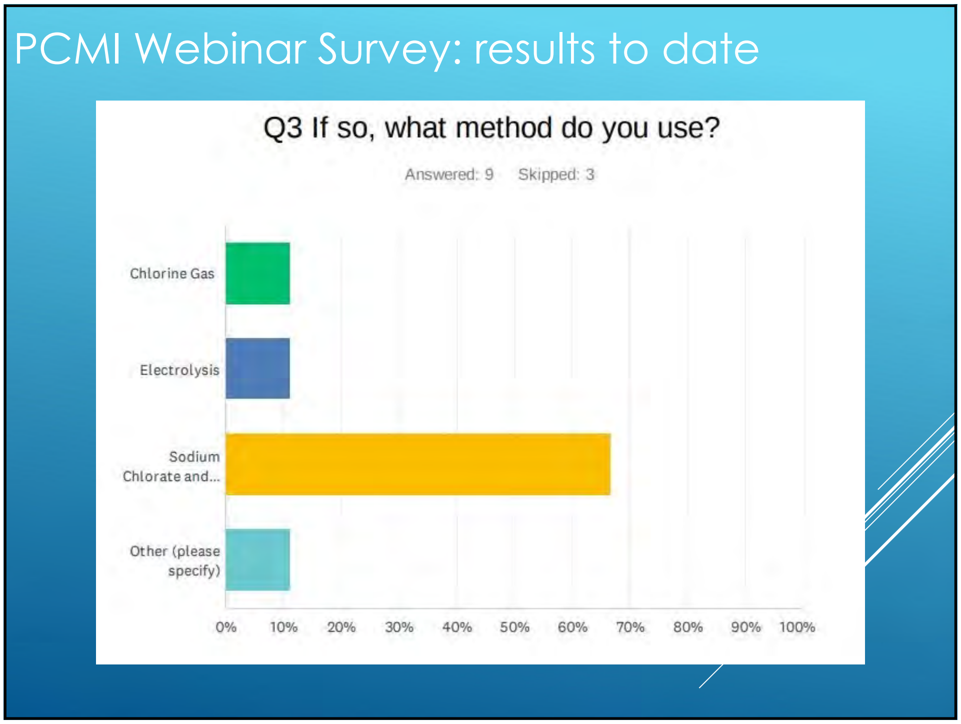

My question is: Can the PCM industry continue to ignore the issue of metal extraction from etchants?
• Currently, to dispose of spent ferric chloride in most areas of the world, individual heavy metal contaminants and their concentrations need not be rigorously specified.
Imagine what will happen when they are!!
• If heavy metals are extracted, they can be useful as valuable feedstock to metal smelters and reduce environmental impact.
• Peter Jefferies (Meggitt) is keen to form a consortium of PCM companies to investigate the technology of solvent extraction and, hopefully, demonstrate its economic viability.


Nickel and chromium as feedstock materials for stainless steel production
Ni and Cr oxides
Electric arc furnace (primary melting)
Argon Oxygen Decarburization (AOD) furnace or Vacuum Oxygen Decarburization (VOD) furnace (deoxidation)
Mixture of pure Ni and Cr metals
Ladle furnace
Stainless Steel

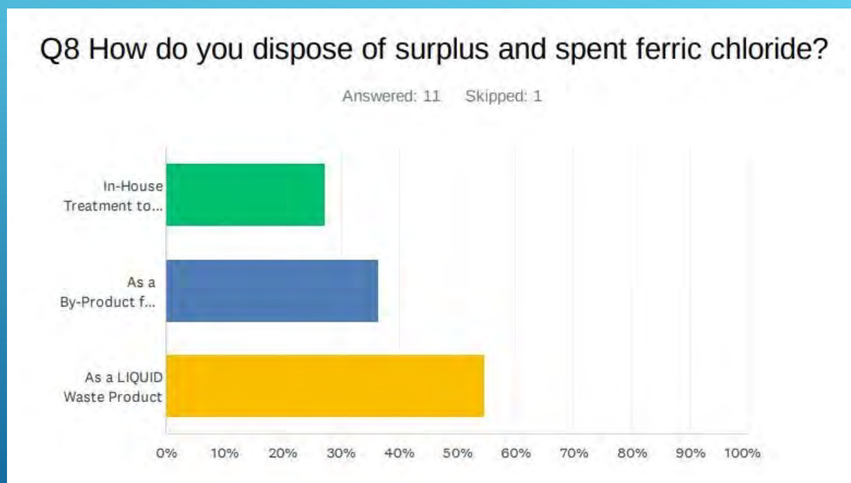

Reduction of environmental impact through recycling of both ferric chloride etchant and dissolved Ni and Cr
Solvent extraction of spent etchant
PCM product
Ni and Cr oxides
Electric arc furnace (primary melting)
FeCl3
Argon Oxygen Decarburization (AOD) furnace and/or Vacuum Oxygen Decarburization (VOD) furnace (deoxidation)
Electrolysis
Mixture of pure Ni and Cr metals
Ladle furnace
Etching
Stainless Steel


The need to use the cheaper process
New Green Process
COST
Current Polluting Process
Cheaper Process
TIME


PCMI Webinar Survey: results to date
Q2 Do you regenerate your ferric chloride etchant?
Answered: 12 Skipped: 0
Yes
No
0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%


PCMI Webinar Survey: results to date
Q3 If so, what method do you use?
Answered: 9 Skipped: 3
Chlorine Gas
Electrolysis
Sodium Chlorate and...
Other (please specify)
0% 10% 20% 30% 40% 50% 60% 70% 80% 90% 100%

PCMI Webinar Survey: results to date



World survey costs of disposal of waste ferric chloride compared to its purchase price on 4th March 2013 (D M Allen, PCM and PEF, 2015)

Country	% of disposal cost compared to purchase price
Italy	104.0
Germany	66.7
Denmark	81.5
Sweden	106.4
Switzerland	53.8
UK	24.9
USA	66.4
USA	**146.8**
USA	**13.4**
Average	73.8

Key:
Lowest value
Highest Value

Can you help to supply us with current costs some 9 years later? We need this data to show the financial benefit of solvent extraction of dissolved Ni and Cr.

David Toson has worked in the PCM industry for 25+ years. He currently serves as the Plant Manager of Chimimetal s.r.l based in Mongrando (BI), Italy.

In his current role, Davide is responsible for the overall management and day-to-day operations of Chimimetal's plant as well as managing their quality systems. Before this, he served as the Production and Process Manager where he oversaw the metal processing sector with chemical photo-blanking, plant revamping, and standardization.

Previous to Chimimetal, Davide worked in Technical Sales at MacDermid. His focus there was on pre- and post-sales service for chemical processes for the production of printed circuits, set up of galvanic lines, and design.

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

CHIMI METAL CHEMICAL MILLING & LASER

Company main detail of the etch department : 5 process lines

2 big machines	volume of chemistry: 2800 liters
2 medium machines	volume of chemistry: 1100 liters
1 small line	volume of chemistry: 600 liters

Regeneration system based on sodium chlorate as oxidizer

MATERIAL HANDLING FOR 2021 AT CHIMIMETAL:
177.409 PANELS OR 165.523 Kg OF METAL HANDLED (MIXTURE OF ALL ALLOYS ETCHED)

AVERAGE SURFACE ETCH 15% OF TOTAL AREA , WE ASSUME 24.500 Kg OF METAL IS DISSOLVED

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

CHIMI METAL CHEMICAL MILLING & LASER

Just to refresh the Chemical reaction

$$2\,Fe^{3+} + Fe \rightarrow 3\,Fe^{2+}$$

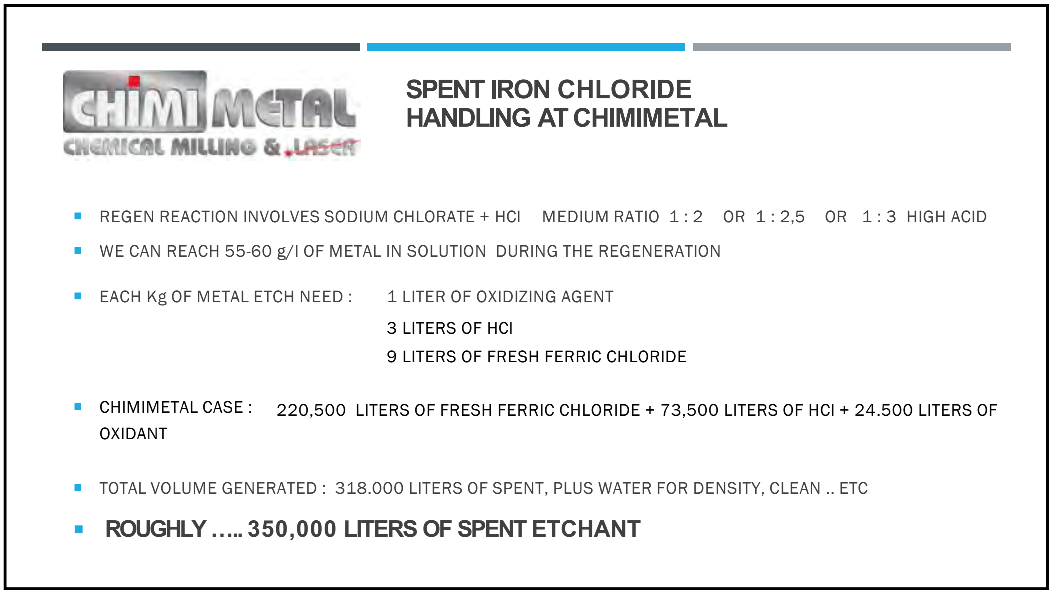
A 40% BY WEIGHT SOLUTION OF FERRIC CHLORIDE CONTAINS 568 g/l of $FeCl_3$, EQUAL TO 195 g/l of Fe^{3+}

- THIS MEANS THAT A SOLUTION CAN ETCH, BASED ON PREVIOUS REACTION APPROX 97.5 g OF PURE IRON (we need two molecules of ferric ion and one atom of iron to balance the reaction), AND ALL THE Fe^{3+} WILL BE REDUCED TO Fe^{2+}

BASED ON OUR EXPERIENCE OF REGENERATION, THE REASONABLE AMOUNT OF METAL IN SOLUTION CAN REACH 45-50 g/l OF METAL TO KEEP THE ETCH SPEED AND THE QUALITY AT A REASONABLE VALUE (say 45 g/l as a guideline)

IF WE RUN THE ETCH PROCESS TO A DEAD LINE , THIS MEANS WE USE AS MUCH ETCH SOLUTION AS A SPENT SOLUTION AND HANDLE, FOR 1 KG OF METAL ETCHED, 22 LITERS OF FRESH FERRIC CHLORIDE SOLUTION (1000 g of Iron /45 g/l)


CHIMI METAL
CHEMICAL MILLING & LASER
SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL
WHAT DOES THIS MEAN TO MY COMPANY CHIMIMETAL ?
WORST CASE USE ETCH CHEMISTRY TO SPENT DEAD LINE:
OVER 2021: 24,500 kg x 22 liter / kg = 540,000 LITERS OF SPENT MADE
REGENERATION CASE: WE ADD MORE BASIC CHEMISTRY BUT WE SAVE FRESH SOLUTION


CHIMI METAL
CHEMICAL MILLING & LASER
SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL
REGEN REACTION INVOLVES SODIUM CHLORATE + HCl MEDIUM RATIO 1 : 2 OR 1 : 2,5 OR 1 : 3 HIGH ACID
WE CAN REACH 55-60 g/l OF METAL IN SOLUTION DURING THE REGENERATION
EACH Kg OF METAL ETCH NEED : 1 LITER OF OXIDIZING AGENT
3 LITERS OF HCl
9 LITERS OF FRESH FERRIC CHLORIDE
CHIMIMETAL CASE : 220,500 LITERS OF FRESH FERRIC CHLORIDE + 73,500 LITERS OF HCl + 24.500 LITERS OF OXIDANT
TOTAL VOLUME GENERATED : 318.000 LITERS OF SPENT, PLUS WATER FOR DENSITY, CLEAN .. ETC
ROUGHLY ….. 350,000 LITERS OF SPENT ETCHANT

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

- SO WE DID A GOOD JOB ..... WE SAVE 190,000 LITERS: BUT WE ARE TALKING OF A RIVER OF SPENT ....

- BUT 350.000 LITERS LEFT AS SPENT ARE: 13 TRUCKLOADS WITH AVERAGE VOLUME OF 28,000 LITERS/TRUCK

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

CLASSIFICATION OF THE SPENT

ON AVERAGE CHEMICAL ANALYSIS OF THE SPENT WE ARE IN THIS SITUATION :

Cromo	CHROME	mg/Kg	EPA 6010D:2018	5025	H400			
Rame	COPPER	mg/Kg	EPA 6010D:2018	2898				
Ferro	IRON	mg/Kg	EPA 6010D:2018	141239				
Mercurio	MERCURY	mg/Kg	EPA 6010D:2018	< 2	H300 H410	H311 H331	H361f H400	H372 H341
Manganese		mg/Kg	EPA 6010D:2018	1371	H373	H411		
Nichel	NICKEL	mg/Kg	EPA 6010D:2018	2230	H400 H372 H360D	H302 H315	H341 H332	H410 H317
Fosforo		mg/Kg	EPA 6010D:2018	766				
Piombo		mg/Kg	EPA 6010D:2018	< 2	H360Df H373	H400	H410	H302
Selenio		mg/Kg	EPA 6010D:2018	4	H413	H331	H373	H301
Vanadio		mg/Kg	EPA 6010D:2018	24	H319 H341	H302 H412	H411 H317	H372 H318

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

FINAL CLASSIFICATION OF THE SPENT :

EUROPEAN LAW AND ADMINISTRATION

2014/955/UE.
1357/2014/UE
2017/997/UE

DANGEROUS REFUSE
with the following hazard characteristics

HP 7, HP 8, HP 10, HP 14

from H7 to Æ HP7 (Carcinogenic) from H8 to Æ HP8 (Corrosive) H10 to Æ HP10 (Toxic for reproduction) [ex teratogen] from H14 to Æ HP14 (Ecotoxic)

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

95 % of the spent due to high content of contamination (nickel) cannot be used as secondary raw material. It can only be managed by companies that purify industrial waste as a flocculant additive.

This is what happens :

We pay truck transport: we pay 850 euro per trip if we are lucky to find return trip. In case not, we need to pay empty trip to our company and full load trip to the disposer (cost then goes up to 1200 euro)

Waste intermediary broker cost: 260 euro/tonne

39.200 kg truck load : 10200 euro + 850 euro = 11.050 euro

x 13 truck loads = 143.650 EURO

Cost of fresh iron chloride = 230 euro /tonne

Buying and waste disposal of the etch solution: 0,23 euro /kg fresh + 0,26 euro /kg spent = 0,49 euro kg

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

Chimimetal year waste : 318.000 liters (density 1,4 gr/cm3) = 445.000 kg

0,49 euro kg x 445,000 = 218,000 euro cost for the NEW ETCHING SOLUTION + DISPOSAL

This drives me crazy …

If we need to produce high qualty parts with high performance alloy: We pay on top of the raw material a surcharge price by kg due to value of the nickel content ……

But when I need to waste the etch chemistry, again the nickel creates a surcharge cost due to extra concentration on the spent

9

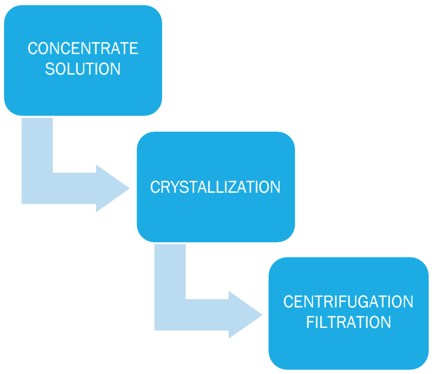
SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL

Is there any possibilty to save money from the spent etchant ???

- *Decrease volume …..*
- Reduce the dangerous classification by decreasing the main contaminant (Nickel)
- Total of partial purification of the etch solution from dissolved salt to re-use as secondary raw material

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL INVESTIGATION IN PROGRESS

Decrease volume .....



SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL INVESTIGATION IN PROGRESS

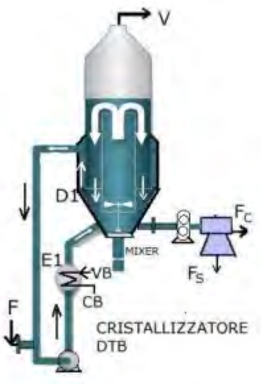
Possible scenarios with Crystallization

Reduce at least 50% volume of the spent

Solvent fraction strips out easily to handle : Water + HCl, neutralisation at facility WWT (Waste Water Treatment)

Reduce cost of the transport to smelter ,

But concentrated salt keeps the HP classification and needs a special service for treatment of the salt ,



CHIMI METAL
CHEMICAL MILLING & LASER

SPENT IRON CLORIDE HANDLING AT CHIMIMETAL INVESTIGATION IN PROGRESS

Reduce the dangerous classification by decreasing the main contaminant (Nickel)

Solvent extraction of nickel: investigation in progress…… by

Prof David Allen
Emeritus Professor of Microengineering, Cranfield University, UK
and
Dr Peter Jefferies
Innovation Technology Leader, Heatric Division of Meggitt, UK

CHIMI METAL
CHEMICAL MILLING & LASER

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL INVESTIGATION IN PROGRESS

Total of partial purification of the etch solution from dissolved salt to re-use as secondary raw material

We are looking into production/ extraction of the total metal including nickel to convert it to a concentrated salt to be recycled 100 %

If we can treat the concentrated salt from crystallization in a batch treatment, we can convert elementary chloride salt into some interesting raw material for the metallurgy industry - like sulfide salt.

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL INVESTIGATION IN PROGRESS

BRIEF HISTORY OF NICKEL METALLURGY

Nickel is a chemical element with the symbol Ni and the atomic number 28.

History

Nickel was first isolated from copper minerals by Axel Frederic Cronstedt in 1751 and takes its name from a mischevous sprite of German miner mythology.

Traditionally, the majority of nickel production comes from sulfide ores.

SPENT IRON CHLORIDE HANDLING AT CHIMIMETAL INVESTIGATION IN PROGRESS

- Most nickel comes from iron ores containing nickel and copper such as magnetic nickel gravel. In order to perform the extraction economically, the nickel must first be enriched by flotation to approximately five percent nickel content. Then the mineral is roasted in a similar way to the production of copper. Here, the mineral is first pre-roasted to convert some of the iron sulfide into iron oxide. Subsequently, silicates and coke are added to slag the iron oxide as iron silicate. At the same time, copper-nickel rough stone is formed from nickel, copper and iron sulfide. Since this is specifically heavier than iron silicate slag, the two phases can be touched on separately.

- Next, the rough stone is filled into a converter and silica is added. Oxygen is injected. As a result, the remaining iron sulfide is roasted in iron oxide and then rubbed. The result is the copper-nickel fine stone

PCMI hosted a live survey session during the 2022 Spring Technical Conference in Köln, Germany. The Session was designed to obtain attendee feedback in-person to foster discussion about the direction in which attendees would like to see PCMI focus its programming and education efforts.

The live survey aspect was hosted on the platform Quizizz. The following is a summary of responses from 41 participants.

Neil Walker, Managing Director from Tecan Ltd (part of Muon) and PCMI Board Member, presented the results to the audience.

Question 1:
Is this your first PCMI Conference?
- Responses:
  - Yes = 46%
  - No = 51%

Question 2:
Where are you/your company from?
- Responses:
  - Europe = 78%
  - United States = 20%

Question 3:
Which option best describes the role you hold at your company?
- Responses:
  - Management = 39%
  - Chemist/Engineer = 41%
  - Operations = 5%
  - Purchaser = 9%
  - Other = 15%

Question 4:
How important is an etching facility tour to your attendance at a PCMI Conference?
- Responses:
  - Very Important/A Deciding Factor = 39%
  - Mildly Important/Not a Deciding Factor = 46%
  - It does not matter to me = 10%

Question 5:
PCMI is considering moving to a digital platform for conferences. Do you prefer a digital booklet or a paper/hard copy booklet?

- Responses:
  - Digital is great = 59%
  - I prefer a paper/hard copy version = 15%
  - No preference = 24%

Question 6:
What is the most important part of a PCMI Conference to you?

- Responses:
  - Technical Education Sessions = 63%
  - Networking = 61%
  - Facility Tours = 27%
  - Social Programming = 17%

Question 7:
Whom would you like to see speak during a future PCMI program?

- Responses to this question were open-ended and included:
  - Altix
  - Automation Equipment Manufacturer
  - Chemcut
  - David Allen
  - Etchant Monitoring
  - Kirk Lauver
  - Metal Specialist
  - Micrometal
  - More Management/Manufacturers Case Studies
  - Proctor & Gamble
  - Universities
  - Various Government Officials

Question 8:
What company would you like to see speak at a future PCMI program?

- Responses to this question were open-ended and included:
  - Aiscent Imaging
  - Altix
  - Automated Processing
  - Chemcut
  - DuPont
  - End-User/Customer of PCM-Processed Parts
  - Etchant Supplier
  - Materion
  - Micrometal
  - Photoresist Company
  - Proctor & Gamble
  - SAT
  - Schmid
  - Tecan Ltd.
  - Top Metal Etchers in the US and Europe
  - Veco, B.V.
  - Waste Treatment Company

Question 9: What benefit do you find most valuable from PCMI?

- Responses:
  - Networking = 71%
  - Technical Conferences = 56%
  - Educational Webinars = 27%
  - Business Referrals = 22%
  - Resources (PCMI Library, Membership Directory, Journals) = 7%

Question 10: What type of future educational topics would you like to see presented from PCMI?

- Responses: (Participants were able to select multiple responses to this question.)
  - Automation = 54%
  - Equipment = 54%
  - Process (Front-End, Wet Processing) = 46%
  - Photoresist = 44%
  - Lamination = 27%

PCMI held a two-part Group Discussion at the 2022 Spring Technical Conference in Köln, Germany. On Monday, May 9th, conference attendees split into groups to discuss: "Which global events have affected your company, its environment, and morale, and how?"

The context provided was that various isolated events often impact industries on a global scale. Some recent events that PCMI identified for the discussions included:

- Global Supply Chain Issues
- COVID-19 Pandemic
- Russian Invasion of Ukraine
- Brexit
- China/US Trade Wars
- Suez Canal Blockage
- Steel Shortages and Long Delivery Times
- Deglobalization
- Shipping Container Costs and LA Port Congestion
- Factory Fires in US Automotive Industry

On Tuesday, May 10th, attendees split back into the same groups to discuss: "What other factors have changed the way your company is doing business?" Some of the factors PCMI identified included:

- Price Increases
- COVID-19 and Variants
- Environmental Issues (wildfires, hurricanes, earthquakes, climate change)
- US Trucker Shortage
- Increase in Threats of Cyberattacks
- Semiconductor Shortages

Overall, the summaries provided by the groups had similar themes and focus. Some things commonly mentioned were:

- COVID-19
  - While COVID-19 disrupted business, it was interesting how governments in different geographical areas handled it.
  - Work environments have shifted in many ways and may never return to a pre-pandemic normal.
  - Many companies are identifying areas in employment contracts that need to be revisited and/or amended.
  - COVID-19 impacted people psychologically and socially.
  - Increased flexibility with working remotely and utilizing video conference software for meetings has proven to be a positive outcome.
  - COVID-19 forced businesses to find alternative ways of doing things and many discovered that some things could not be done virtually/remotely.
  - While there was a reduction in business for aerospace and automobiles, business in the medical field grew.
- Price increases, supply chain issues, material shortages, and labor shortages have affected all industries globally.
- Not only are these large-scale global events affecting the PCM industry, but the consequences of these events are creating a ripple effect of unforeseen issues.
- Adaptation and ability to pivot practices quickly are at an all-time high.
- Cyber threats are more prevalent now, and it is imperative to continue training employees to identify them to avoid company-wide cyberattacks.
- The European Union benefited from the US/China Trade War. However, some feel it is now very challenging to do business in the European Union and the United Kingdom