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High-Performance PVD Targets: A Manufacturer's Look into the Past, a Pause at the Present, and a Peek into the Future

Paul J. Rudnik, Plansee USA LLC, Saline, MI

Physical Vapor Deposition (PVD) coatings have enabled many diverse technologies and thus become omnipresent in our daily lives over the past half-century or so. For example, hard coatings deposited on cutting tools like hobs, mills and inserts have been around for more than 40 years, and their use was a "green" technology due to the improved wear-resistance (leading to a reduction in tool consumption) before the term "green" came into the lexicon. New applications require the continuous improvement of coatings, either through new compositions, new architectures, or both. There is often a need to reduce cycle time, which requires higher power densities. Equipment manufacturers are also constantly evolving their equipment, incorporating new target designs, power supplies and/or other requirements. None of these advances can be achieved without the target manufacturers keeping pace. In fact, sometimes progress does not occur unless the target manufacturer works in tandem with consumers to find a solution. All of this requires a thorough understanding of PVD processes and their implications. To get a glimpse into the possibilities for the future of targets for hard and component coatings, it will be important to see what has been done in the past and what is being accomplished in the present in these and other applications. By illustrating the challenges that have been overcome, a better understanding of the possibilities will exist, which can help us work together to develop the products of the future.

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High-Performance Targets:
A Manufacturer‘s Look into the Past, a Pause at the Present, and a Peek into the Future

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SVC TechCon 2023

Abstract

Physical Vapor Deposition (PVD) coatings have enabled many diverse technologies and thus become omnipresent in our daily lives over the past half-century or so. For example, hard coatings deposited on cutting tools like hobs, mills and inserts have been around for more than 40 years, and their use was a "green" technology due to the improved wear-resistance (leading to a reduction in tool consumption) before the term "green" came into the lexicon. New applications require the continuous improvement of coatings, either through new compositions, new architectures, or both. There is often a need to reduce cycle time, which requires higher power densities. Equipment manufacturers are also constantly evolving their equipment, incorporating new target designs, power supplies and/or other requirements. None of these advances can be achieved without the target manufacturers keeping pace. In fact, sometimes progress does not occur unless the target manufacturer works in tandem with consumers to find a solution. All of this requires a thorough understanding of PVD processes and their implications. To get a glimpse into the possibilities for the future of targets for hard and component coatings, it will be important to see what has been done in the past and what is being accomplished in the present in these and other applications. By illustrating the challenges that have been overcome, a better understanding of the possibilities will exist, which can help us work together to develop the products of the future.

A confession

- **Round**
- **Rectangular**
- **Cylindrical**
- **Lab to Industrial Scale**

Image courtesy of the author

Outline

- A bit of PVD history from a hard coating perspective (Past)
- Plansee and how we get involved
- Manufacturing PVD targets
- Customer Challenges/Opportunities and Innovation (past/present)
  - Hard Coatings
  - Flat Panel Display
  - Energy, microelectronics
- Current projects (present/future)
- Summary

In the beginning…there was TiN

- Harder, higher oxidation temperature than steel
- Coatings maintain sharp cutting edge, consistent chip flow
- Hobs: generate (not cut) gears
  - Milling operation : interrupted cut
- Use it, sharpen, recoat, decoat as needed
- Under same parameters : TiN coated v. Uncoated
  - Half the wear (or less)
  - 2x (or more) parts per sharpening
- Coated can increase rpm by 20-30% to start
- Although gold, it has always been “green”
  - Coated hob could generate 4 - 16x more gears
- Reduced downtime even more important

Image courtesy of the author

Nice start, with some provisions…

- TiN an instant hit with hobs
  - Quality didn't have to be perfect to be better
  - Thickness variation not so critical; decoating not always done
- Broaching and drilling were successful, too
- But some misses and limitations
  - Cast iron, aluminum didn't see similar benefits
  - Run it too hard and even TiN overheated
- Adding carbon was possible with gases
  - Creating gradients and/or layers
  - Solved the cast iron problem
- But what about more elements?

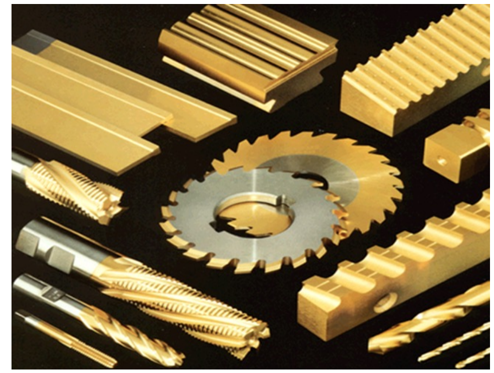
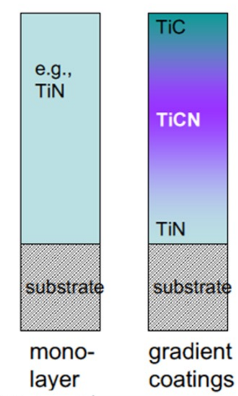
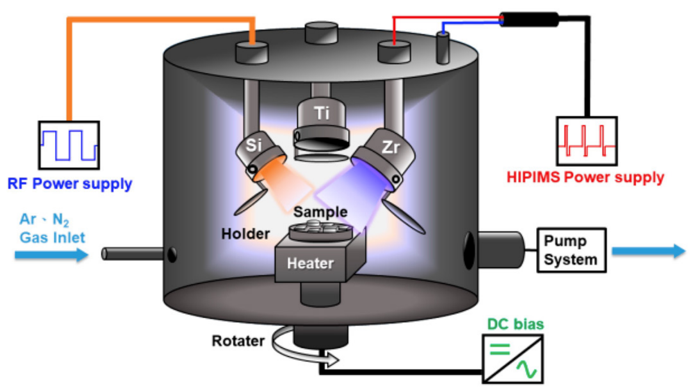


Image courtesy of Star SU

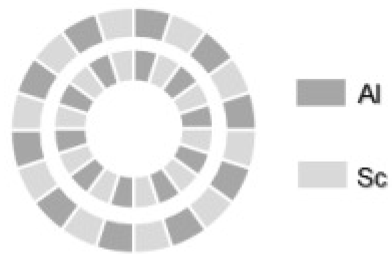


Some ways to deposit multiple elements

- Co-sputtering possible
- Segmented targets manageable
- Even plugs can be successful



Chang, Li-Chun, Yu-Zhe Aheng, and Yung-I Chen. 2018. "Mechanical Properties of Zr-Si-N Films Fabricated through HiPIMS/RFMS Co-sputtering", *Coatings* 8, no 8: 263
https://doi.org/10.3390/coaitngs8080263



Caemona-Cejas, J.M., etal, "Homogeneity and Thermal Stability of Sputtered Al0.7Sc0.3N Thin Films", *Materials* **2023**, *16* 2169,
https://doi.org/10.3390/ma16062169

Cemecon patented design for TiAlCN coatings

But this doesn‘t always work to scale...

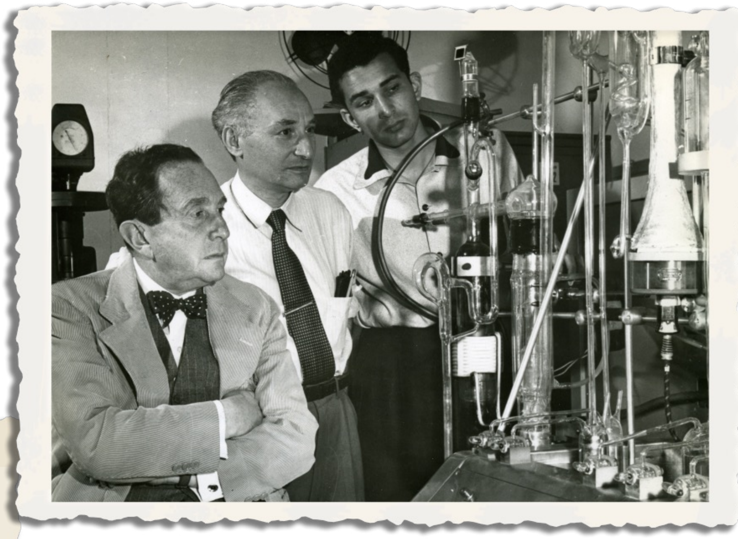
Hauzer HTC-2000, courtesy of Ton Hurkmans, IHI Group

View glass coater, YouTube

Thus, you need to think about other ways to make the targets

Plansee

Plansee has been producing refractory metals since **1921**.



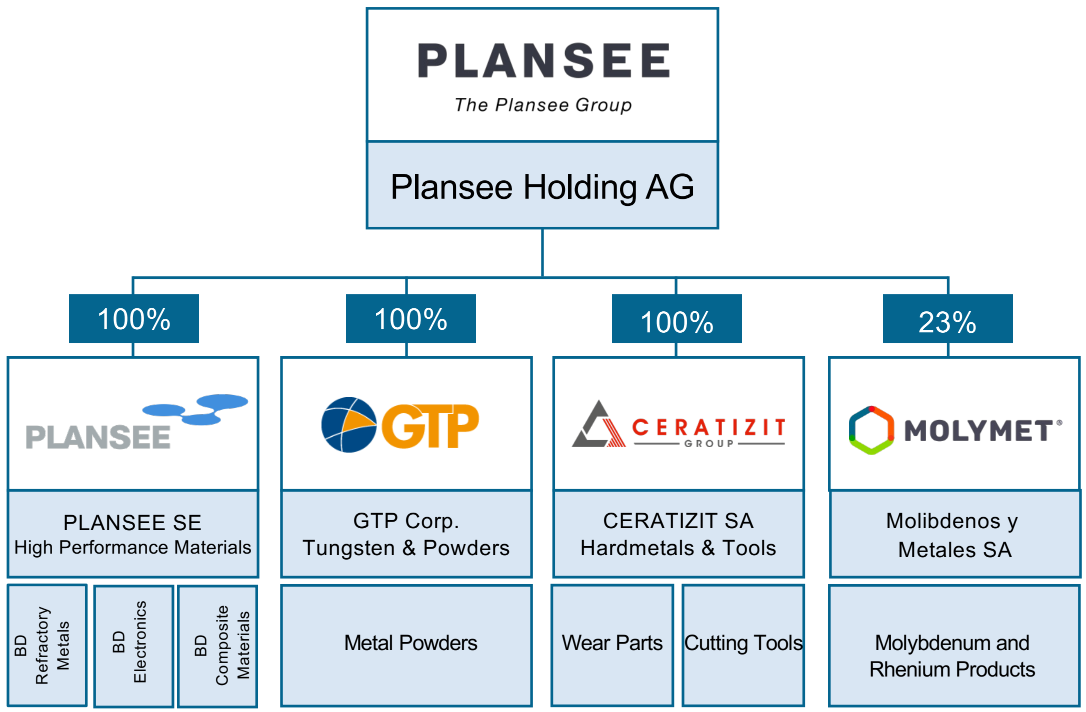
Company founder **Dr. Paul Schwarzkopf** started manufacturing **tungsten wires** for incandescent lamps with just 15 employees in **Reutte, Austria**.

In addition to filaments, we now produce thousands of products from refractory metals and composite materials using powder metallurgy.

Dr. Paul Schwarzkopf named Plansee after the **lake of the same name**. Even back then, the water from the Plansee was an important source of energy for the company, one of the key factors in choosing the site.

The Plansee company headquarters is located in Reutte, Austria. A large proportion of the production activities as well as all central services are located here

Plansee High Performance Materials

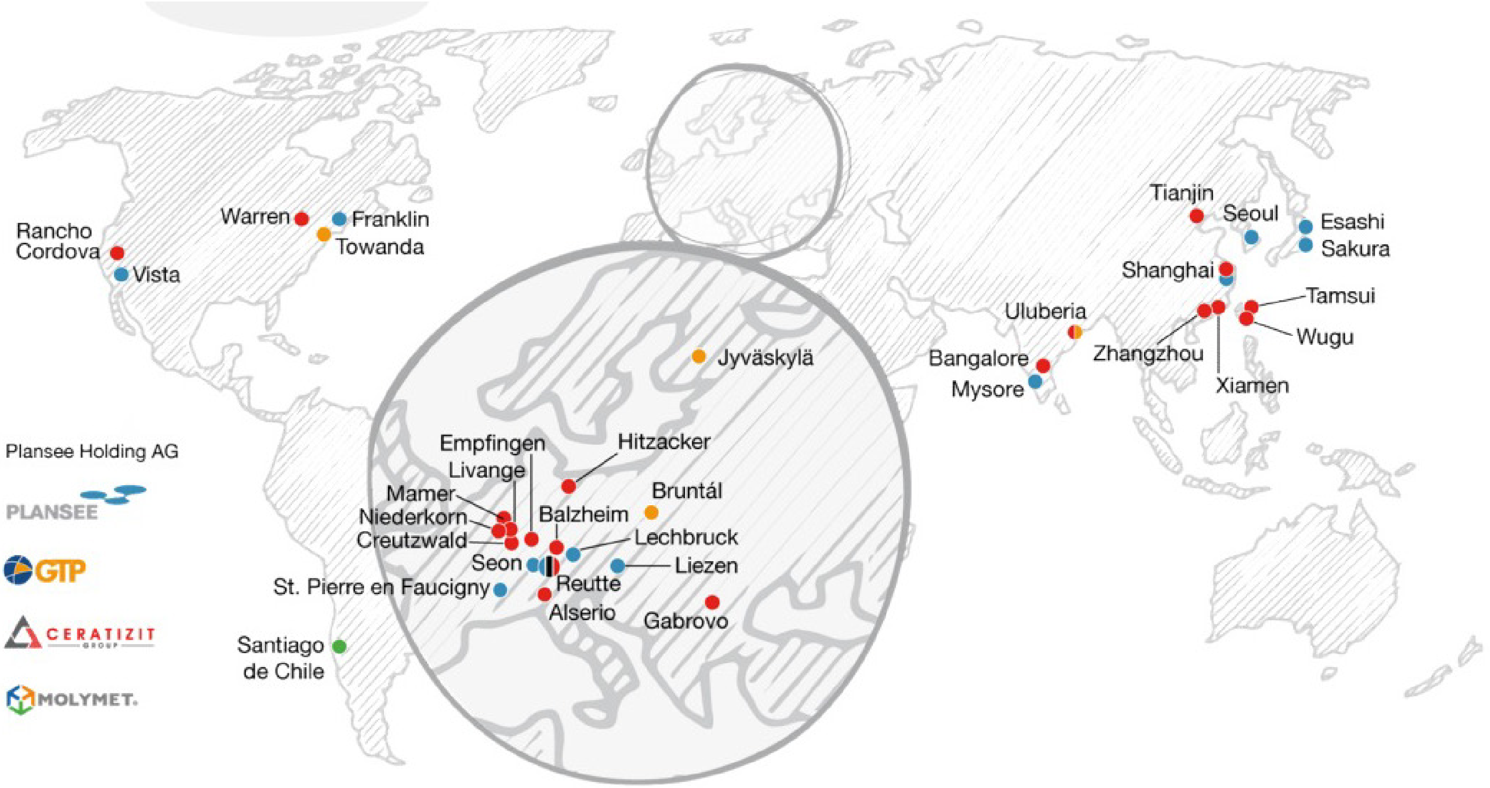


Plansee Group worldwide

We are represented in **28 countries** with **3,500 employees**, including **12 manufacturing sites** in Europe, Asia and in the US

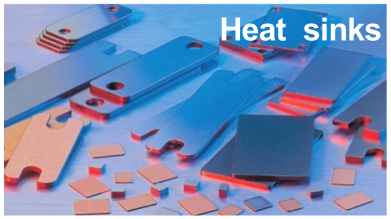
Our international supply chain and production network ensure **supply security** for our customers

- Plansee Holding AG
- PLANSEE
- GTP
- CERATIZIT GROUP
- MOLYMET.



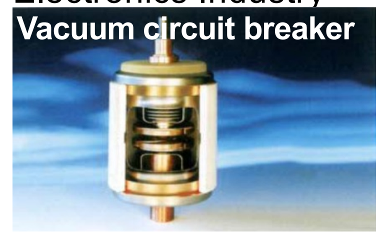
Focus on refractory metals: Mo, W, Cr, Ta, Nb & their alloys

Semiconductors

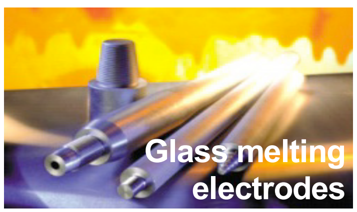


Lighting Industry

Electronics Industry



Glass Industry

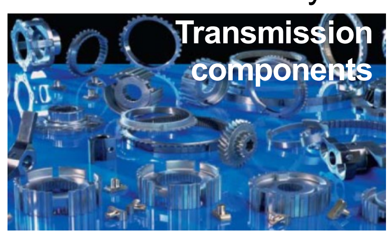


Metal Forming

Medical

Thin Film Technology

Automotive Industry



Industrial Furnaces

Thin film materials

Displays TFT-LCD, OLED, mini/µ-LED	**Energy** Thin film photovoltaics & electrochromic devices	**Semiconductors & Microelectronics**	**Hardcoating & Tribology**
Mo 3N7	Mo 3N7	Mo 3N7	Ti-based (TiAl, TiAlX)
MoTa, MoNb, MoTi, MoW	Mo-Na	W 3N7	Al-based (AlCr, AlCrX)
W 3N7	Cr 3N5	Cr 3N5	Cr-based (CrTi)
MoO_x	W 3N7	Nb 3N5, Ta 3N5	Borides (TiB, CrB, WB)
	W, W-Ni, W-Ni-X	MoO_x 3N	Silicides (CrSi, TiSi, MoSi)
	MoO_x, LiPO	TiW 3N5	Carbides (SiC, WC, B_4C)
			Nitrides (TiN, AlN)
			Metals (Ti, Zr, Si, Ge)

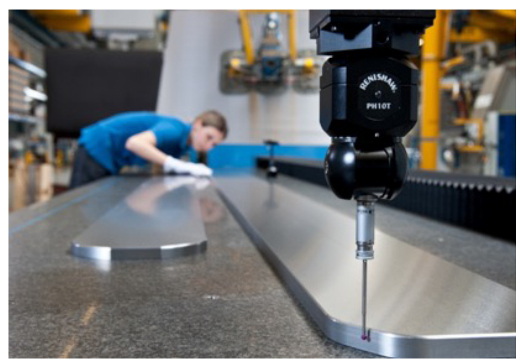



Manufacturing of PVD targets

Production process – Mo, W

Oxide → Reduction → Metal powder → Mixing Alloying → Pressing → Sintering → Forming → Heat treatment → Machining Joining Coating → Quality assurance → Recycling

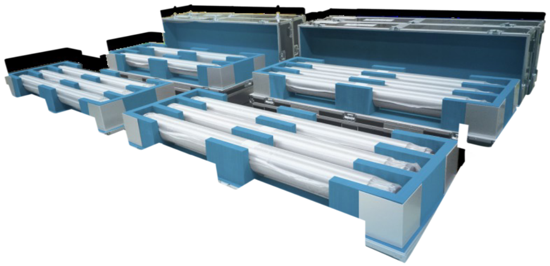
- **Oxide**
- Reduction
- **Metal powder**
- Mixing Alloying
- Pressing
- Sintering
- Forming
- Heat treatment
- Machining Joining Coating
- Quality assurance
- Recycling



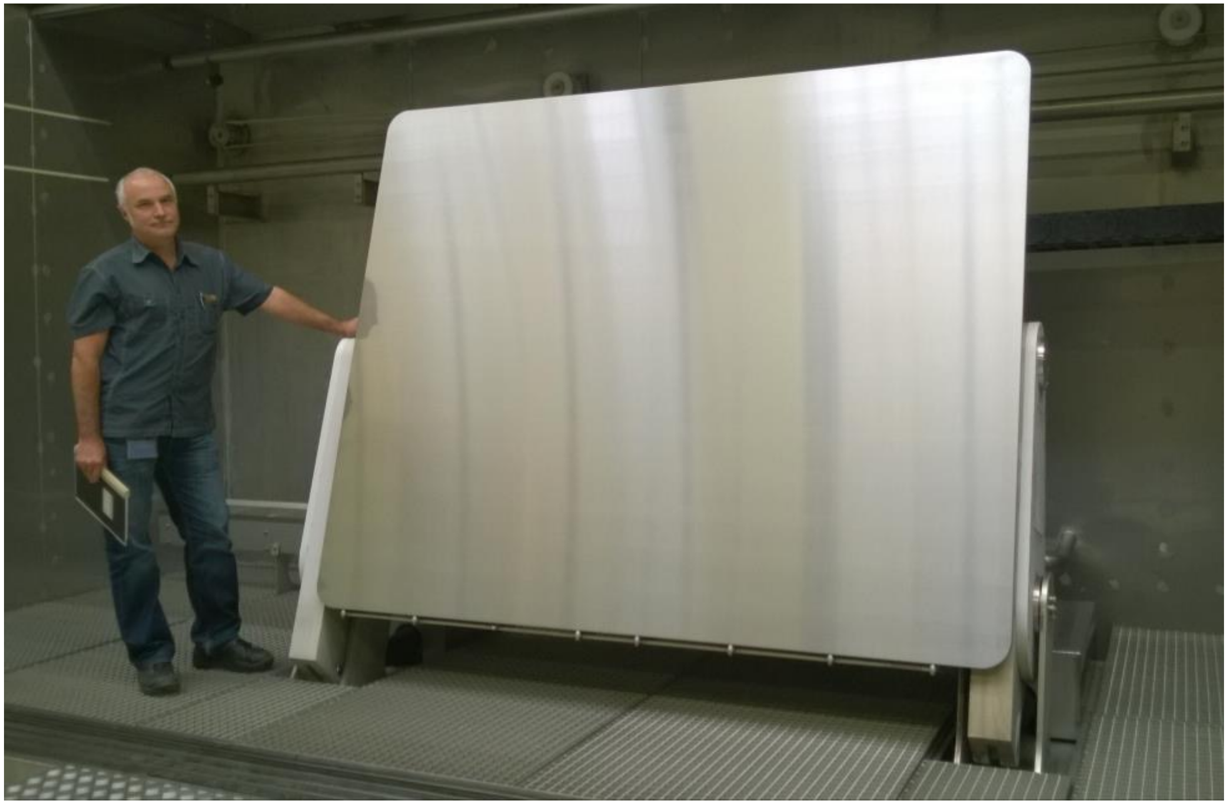
Manufacturing Solar & Micro-Electronics

- Large-scale manufacturing of refractory materials (Mo-, W-)
  - Cold Press → Sinter → Deformation
- Production time: weeks
- Ingot size: 200 – 900 kg
- Targets: 4000 mm cylindrical, 1800 x 2300 mm planar

Construction of the
Hot Rolling Mill
Reutte Austria



The Largest Single-Piece Mo Target



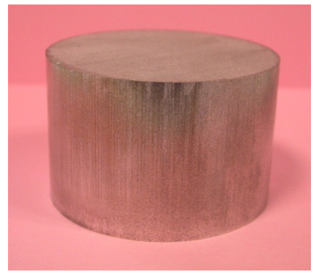
Hard coatings has a special portfolio

Al-based Materials:		
TiAl-Type	standard compositions in at%: (on stock)	TiAl-75/25, TiAl-67/33, TiAl-50/50 TiAl-33/67, TiAl-25/75
TiAl-Type	further compositions :	TiAl (25 at% ≤ Al ≤ 99 at%)
TiAlX-Type	with X = B, Y, Cr, Nb, Ta, Si, Mo, …	e.g. TiAlY, TiAlB, TiAlSi, TiAlMo, TiAlTa
AlCr & AlCrX-Type	With X = Zr, Nb, Ta, Si, Mo, …	e.g. AlCr, AlCrSi, AlCrW, AlCrB
Pure Metals:		
Cr-HP	monolithic or bonded	99.8%
Cr-UHP	monolithic or bonded	99.95%
Si	bonded on Cu BP	99.99%
Ti, Zr		99.2%
Ta, Nb, Ru		99.95%
Composites & Ceramic Materials:		
TiSi	available compositions	TiSi (5 at% ≤ Si ≤ 25 at%)
WC	binderfree, Ni/Co binder	WC
Cr- and Ti- alloys		Cr-B, Ti-B, Cr-Ti, Cr-Si, …
Borides, Silicides, Carbides, Graphite		SiC, TiB2, B4C, WB, MeC/C, …

Manufacturing Options Hard Coating

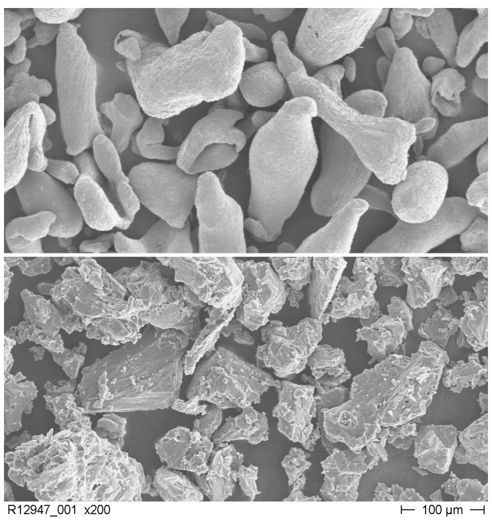
- Different production route for Hard Coating targets
  - TiAl, AlCr, TiSi, TiB_2, WC, etc..
- Main manufacturing methods:
  - Cold forging of TiAl, AlCr
  - Hot pressing (HP)
  - Spark Plasma Sintering (SPS)

Manufacturing of Al based targets

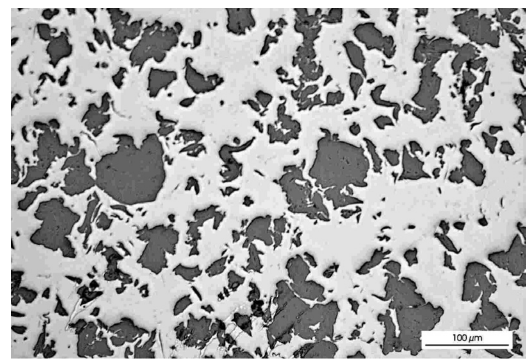


Al

Ti



TiAl



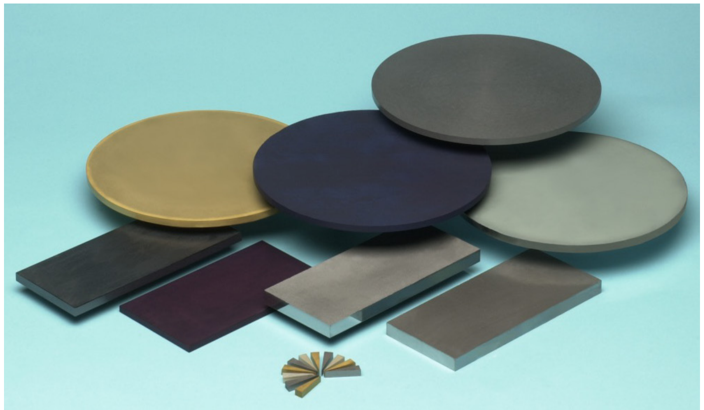
Requirements for densification of Al based materials:
- sufficiently high-volume fraction of ductile Al powder
- sufficiently high press and forging forces

Hot Pressing and Spark Plasma Sintering for Ceramics

- Production of binder-free WC and TiB_2 targets
- Process development and prototyping for new materials:
  - Carbides: SiC, WC/C, TiC/C
  - Borides: TiB_2/C, TiB, NbB_2, ZrB_2, CrB_2, W_2B, WB
  - Nitrides: TiN, TiN/AlN, ZrN
  - Silicides: CrSi

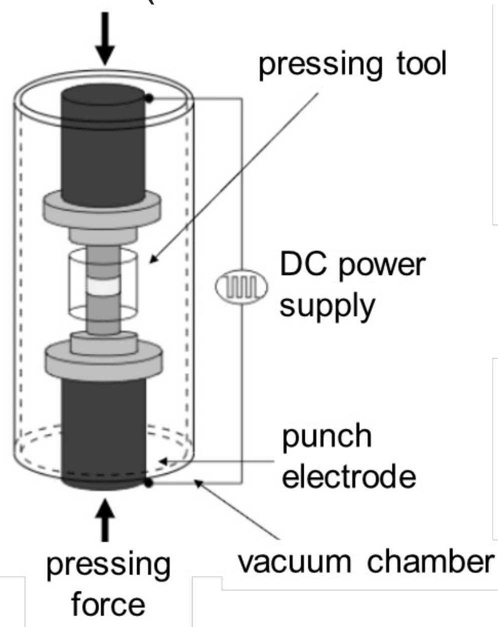
Vacuum Hot Press at Plansee:

- Max force: 4.000 kN
- Chamber size: dia 470 x 800 mm
- Max plate size: dia 400 mm or 300 x 300 mm
- Max temperature 2200°C (2500°C)



Spark Plasma Sintering – complement to Hot Pressing

- Rapid densification technology with homogeneous heating in direct electrical current continuity and compression by mechanical pressure
- Production at Plansee since 2012; rapid prototyping and flexibility of complex conductive materials
- FAST (Field Assisted Sintering), Direct Sintering Process



	SPS	Hot Pressing	HIP
Cycle time	Short (10-60 min)	8-16 h	8-16 h
Heating rate	Up to 2000 K in 5 min	10 K/min	5 K/min
Materials	Only for electric conductive materials. Fine grain structure.	For all materials. Limitation for high vapour pressure materials (contamination).	Metals, alloys. Critical for exothermal reactions.
Dimensions	Optimal for discs and plates up to 300 mm	Optimal for plates up to 260 x 310mm, discs with 300-400 mm	Optimal for large sized blocks and rods

Customer Challenges

Historical development of PVD hard coatings

Binary compounds (Ti-N, Ti-C, Cr-N), early 1980's

Metastable solid solutions (Ti-Al-N, Ti-Zr-N, Ti-Hf-N, Ti-Nb-N), from 1986

Multilayer / Superlattice structures (TiC/TiB_2) from 1984

Nanocomposite structures ($nc\text{-}TiN/a\text{-}Si_3N_4$) 1990's

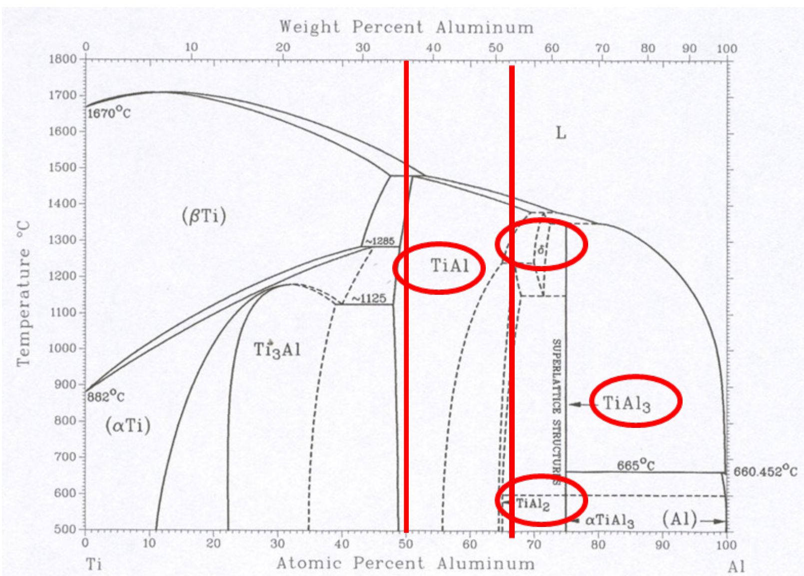
HIPIMS

Things our customers worry about

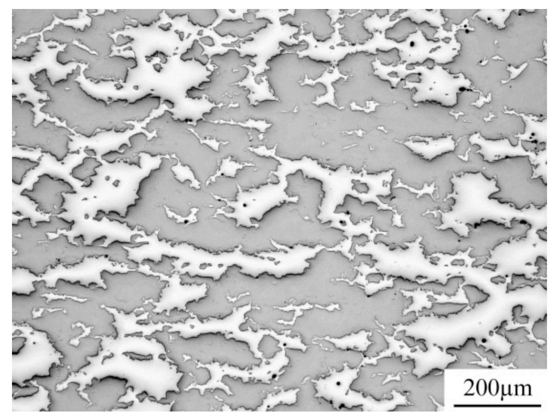
- Composition
  - multiple elements, brittle/ceramic materials
- Heat: most of power into target is excess
- Deposition rate: high throughput needed
  - Bonding, thermal evaporators
- Magnetic coating materials
- Improvements on ceramics
- Cylindrical innovations
  - Target utilization

Powder metallurgical targets

- Brittle intermetallic phases in molten TiAl 50/50 at% targets
  - Increased hardness
  - Prone to breakage
- Molten TiAl 50/50 at% has lower thermoconductivity than powder met
- Systems with 3 or more elements easily viable by PM => ideal for advanced developments



Ductile microstructure of powder metallurgical TiAl 50/50 at%



Coating Development

Historical development of Al based PVD hard coatings and comments on targets

Binary compounds
Ti-N, Cr-N early 1980's

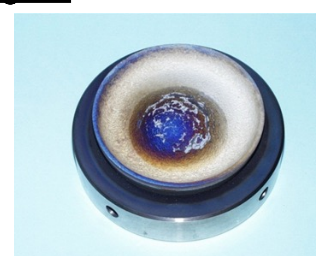
<u>Ti targets</u>
T_m = 1668°C, α = 8,6 x 10^{-6} K^{-1}
<u>Cr targets</u>
T_m = 1857°C, α = 4,9 x 10^{-6} K^{-1}

Metastable solid solutions
Ti-Al-N from 1986

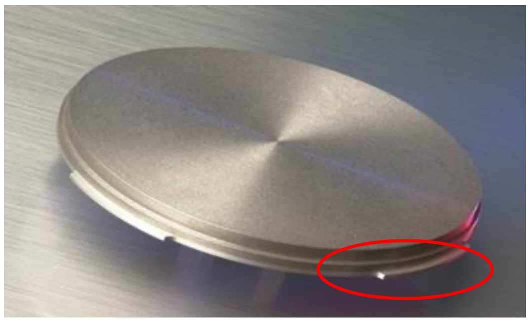
<u>Molten TiAl 50/50 at% targets</u>
T_m = 1480°C, α = 9 x 10^{-6} K^{-1}

Metastable solid solutions
Al-Ti-N

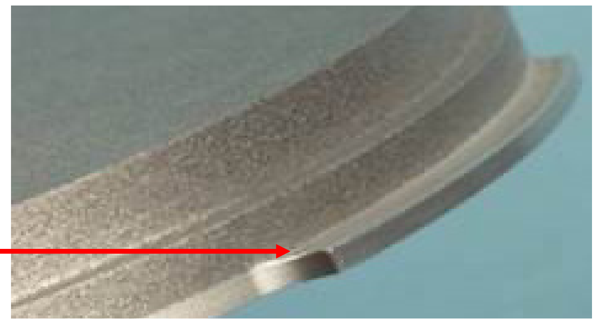
<u>Powder metallurgical TiAl 33/67 at% targets</u>
T_m = 660°C, α = 18 x 10^{-6} K^{-1}
$T_{exotherm}$ = 500°C



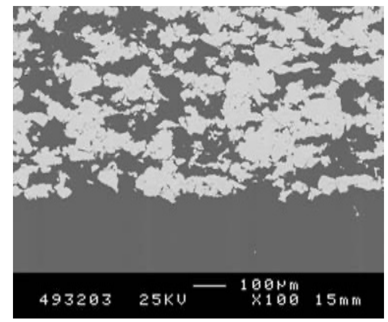
Al-based Targets with Heatsink



Need: In applications with higher heat transfer requirements, targets with integrated pure Al bottom (heatsink) are available



Design: Direct connection of TiAl with Al bottom plate (<u>without bonding interface</u>) due to powder metallurgical two-step pressing operation



Advantages: smoother film surface with less droplets due to higher thermal conductivity, as well as higher mechanical strength from the heatsink

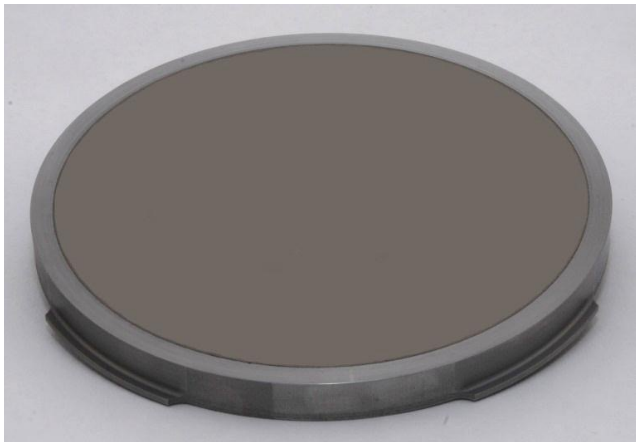
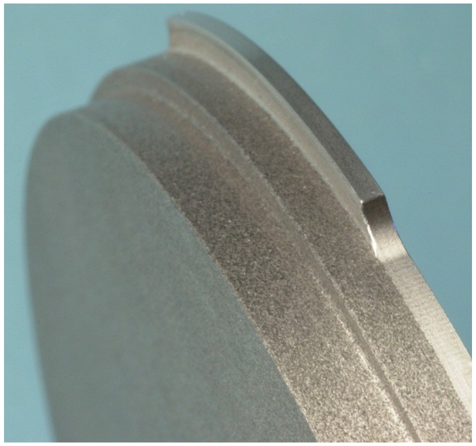
Holder for brittle ceramic Arc Cathodes

- Binder-free WC cathodes via HP or SPS
- Machining a brittle ceramic target with threads and arc-confining lip is difficult and expensive
- Thermal, electrical and mechanical connection via back-cast copper
- Redesign has : WC disk, copper body, and Mo or ZrO_2 ring to maintain arc
- Cheaper, more durable: more likely to be used

Standard design

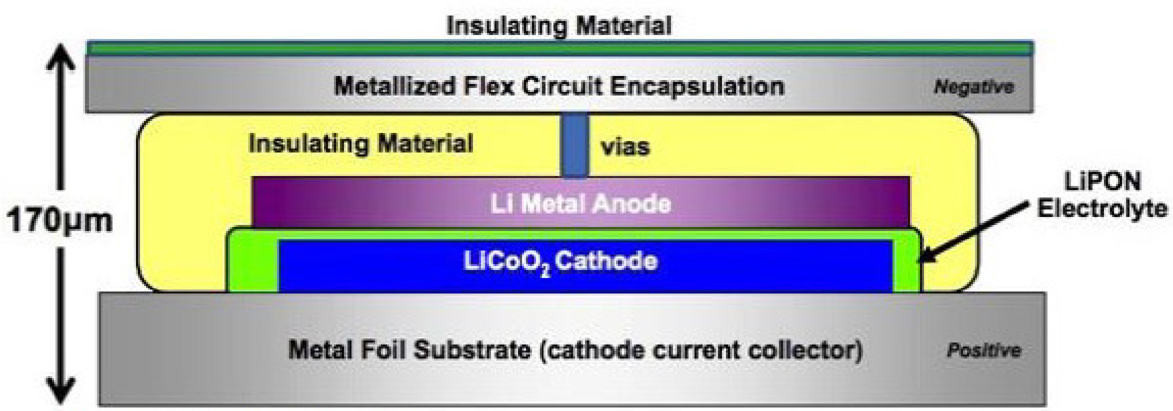
Solutions for brittle Cr-based and ceramic materials

Cr alloy

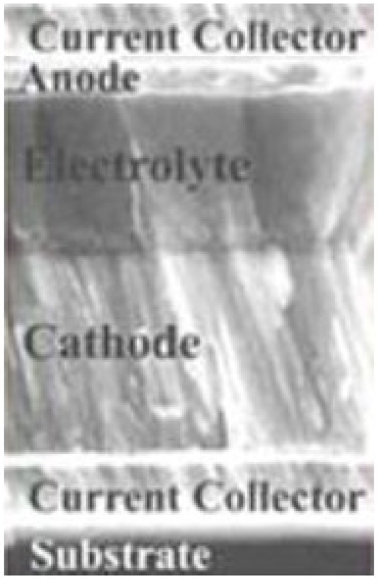
Deposition rate examples

Thin-Film Battery Structure



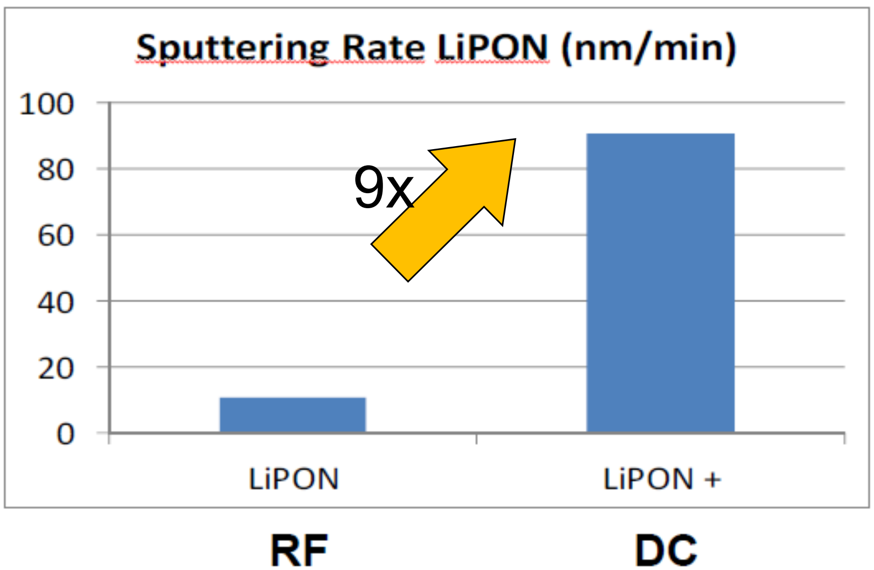
Source: Infinite Power Solutions

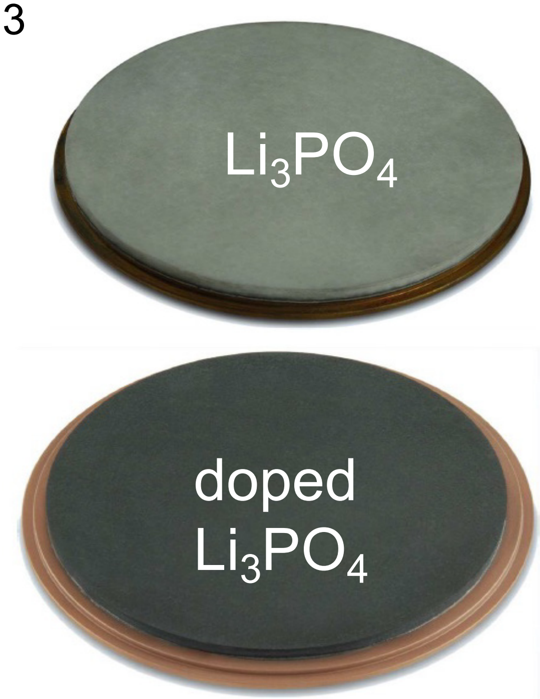
- **Li**: Li target / Li evaporation
- **LiPON**: Li_3PO_4 target, RF sputtering in N_2
- **$LiCoO_2$**: $LiCoO_2$ target



High-Rate DC Sputtering of LIPON

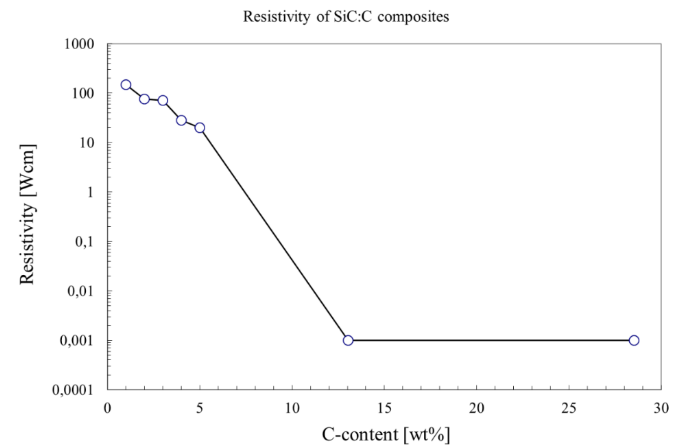
- Thin-film battery application
- LIPO RF-sputtered in N2, deposition rate is bottleneck
- Conductive LIPO target can be DC-sputtered, patented in 2013

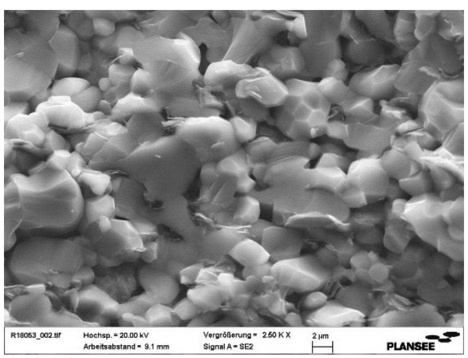


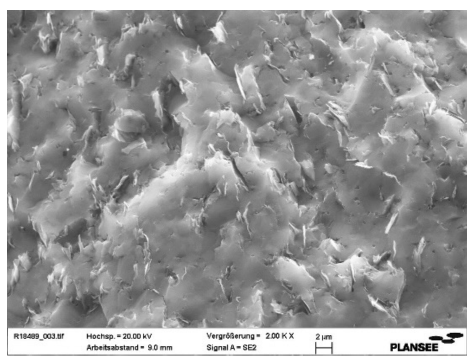


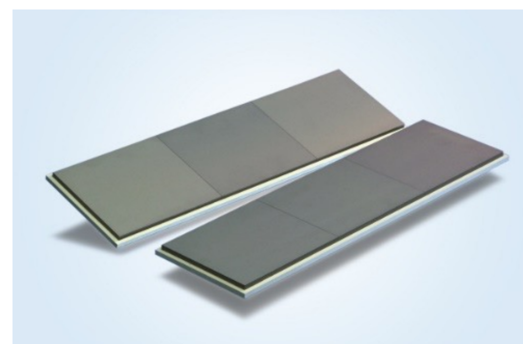
Microstructure design

- Additions of carbon increase deposition rate and material toughness
- Examples:
  - TiC/C, SiC/C, B_4C/C …

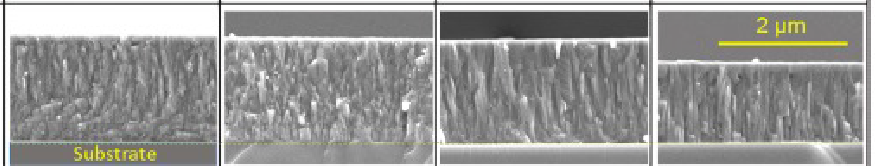
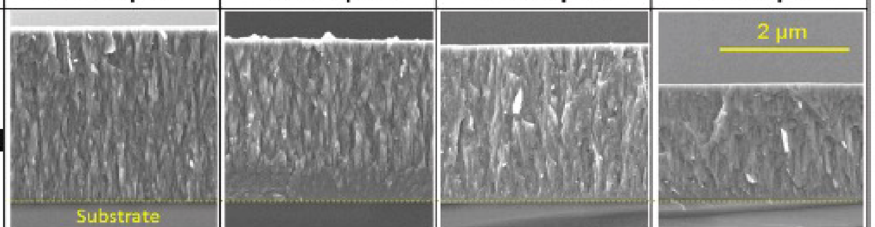


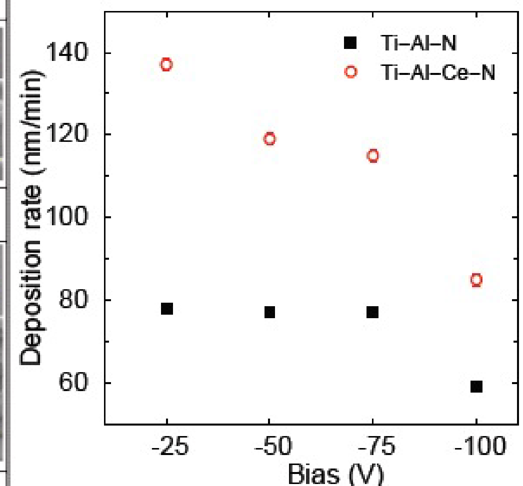

SiC+C


B_4C+C


TiC+30mol%C

Doping of TiAl to increase deposition rate

SEM	-25 V	-50 V	-75 V	-100 V
$Ti_{0.42}Al_{0.58}N$				
	2.05 µm	1.99 µm	1.99 µm	1.54 µm
$Ti_{0.43}Al_{0.55}Ce_{0.02}N$				
	3.36 µm	3.09 µm	3.00 µm	2.22 µm



Deposition time:26 min

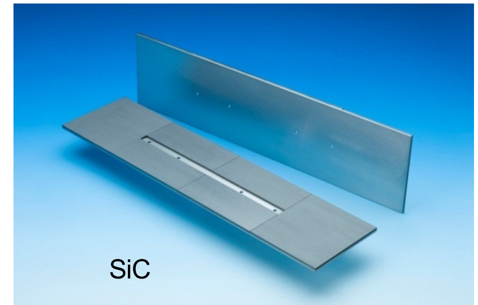
» Morphology is denser and more compact with increasing bias voltage.

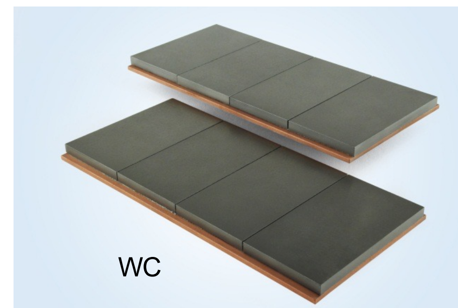
» Deposition rate of $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ is 1.75 times higher than that of $Ti_{0.42}Al_{0.58}N$.

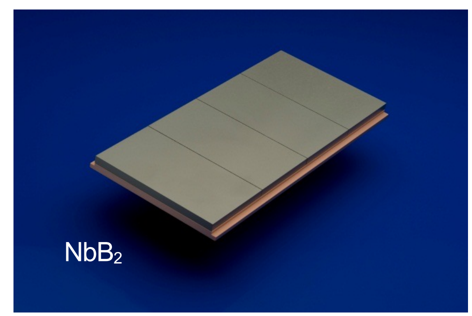
- Asanuma, Polcik, Kolozsvari, Klimashin, Riedl, Mayrhofer, ICMCTF 2017 Poster

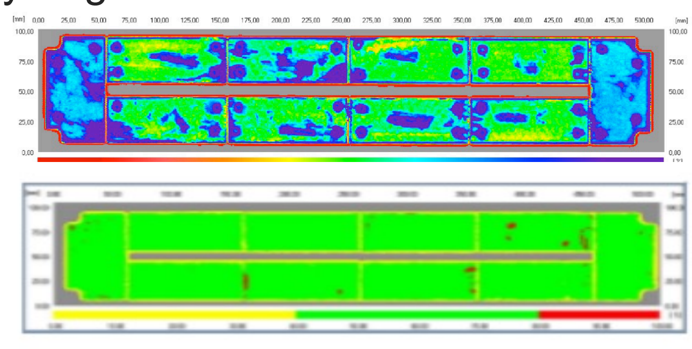
Bonding of targets for Hard Coatings

- Ceramic targets usually have to be bonded
- Bonding quality has a high impact on the maximum power applied to the targets due to the low melting point of Indium
- Bonding quality is defined by:
  - Fraction of bonded area (wetting quality, oxidation of Indium, Cu diffusion and embrittlement of Indium
  - Has to be confirmed by ultrasonic test
- Plansee operates local bonding shops in Korea, Taiwan, Japan & China for flat panel display targets









Upper: poor quality bond   Lower: desired bond quality

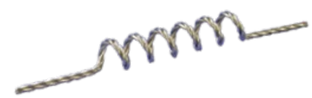
Thermal evaporation / Applications and solutions

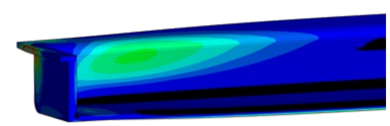
Evaporators, heaters, shieldings, customized components & assemblies used in high-tech applications:

- OLED metal layer deposition
- mini / µ-LED packaging layer / metallization
- Battery / energy (e.g. TE of Li-based materials)
- Optical coatings & CVD processes in various industries
- …

Plansee has experience for **various types of evaporator design**

- Point source (e.g. crucibles, heaters, coils, boats)
- Linear source (e.g. vertical / horizontal TE systems >2m)
- Customized / box-shaped design (e.g. Roll to roll coating)
- Refractory metals have low solubility to molten Lithium



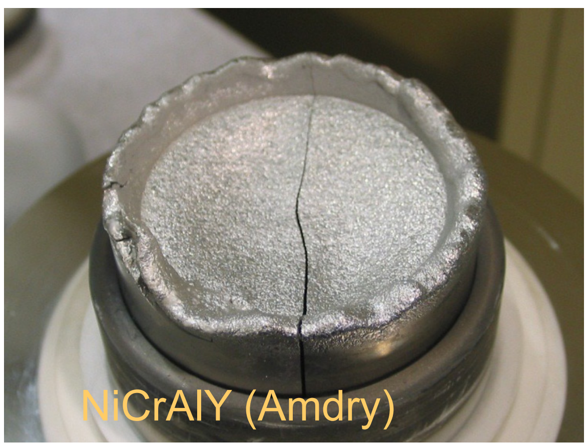


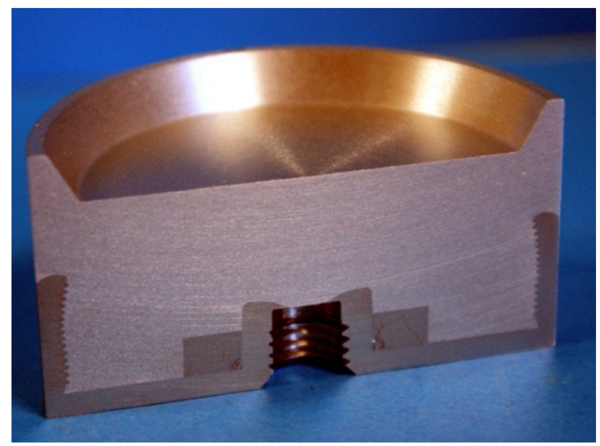
Evaluation of stress distribution in crucibles used in high-temperature evaporation

Magnetic materials

(M)CrAlY Cathode for turbine blade coating

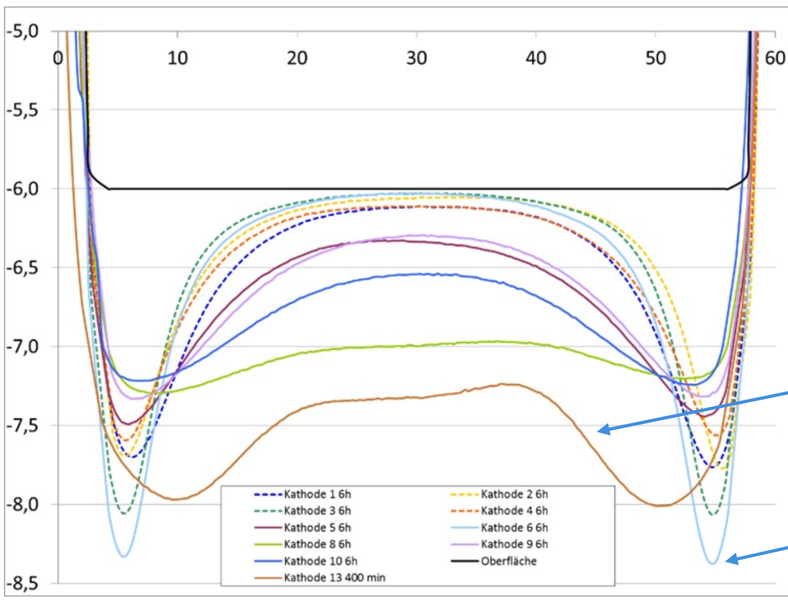
- Deposition by arc evaporation as an alternative to thermal spray
- New "Smart Cathode" design for accelerated arc movement to avoid cracking
- Improved erosion profile uniformity





Innovative Target Design for magnetic materials

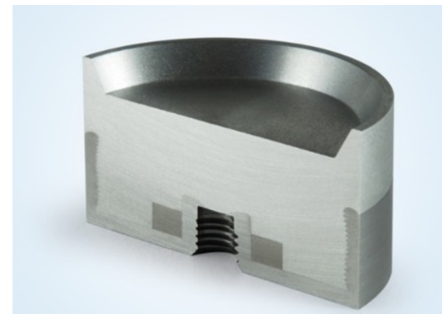
- Integrated magnets which control the arc
- Used numerical modeling to assist design

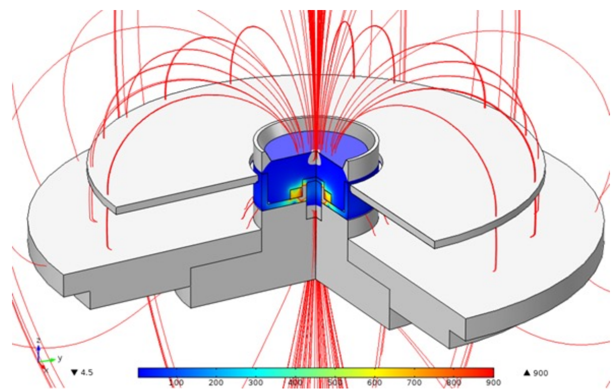


Improved erosion profile

Original erosion profile

Erosion profile for Titanium SMART Arc Cathodes as a function of design of the magnetic insert

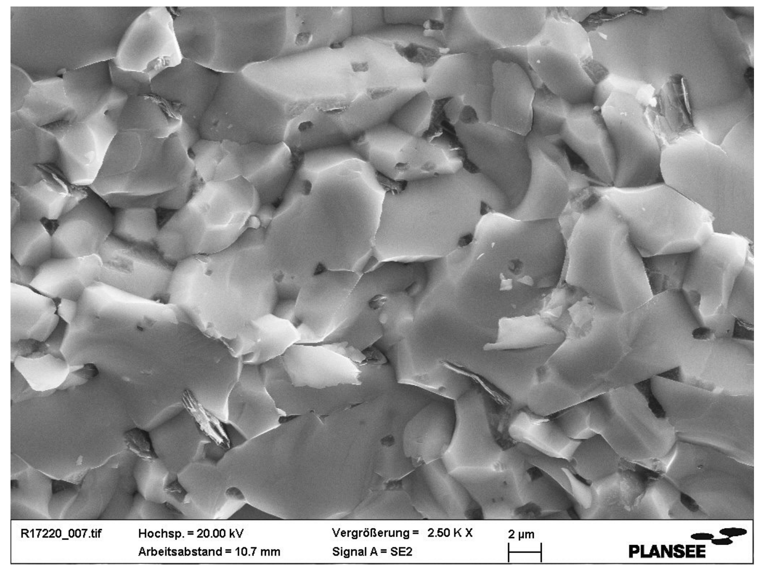




Improved ceramics

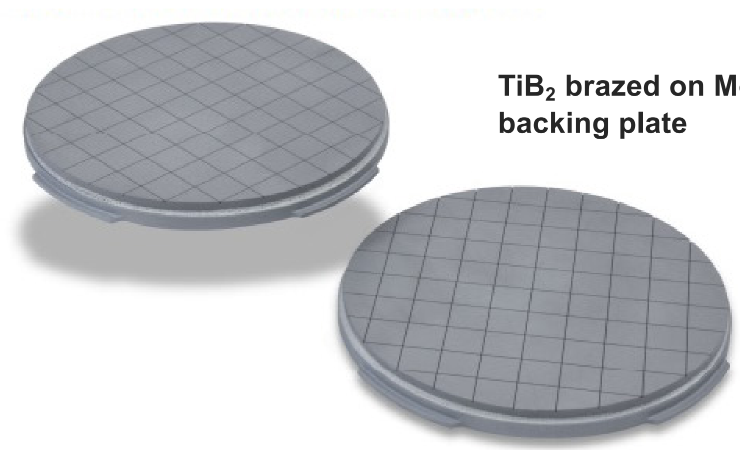
Microstructure design for higher thermo shock resistance

- Ceramics historically only sputtered due to limited thermoshock resistance
- Increase thermoshock resistance by introducing carbon on grain boundaries
  - Helps minimize crack propagation
- Patented by Plansee for TiB_2/C cathodes for arc evaporation



TiB_2/C microstructure

Targets with increased strength

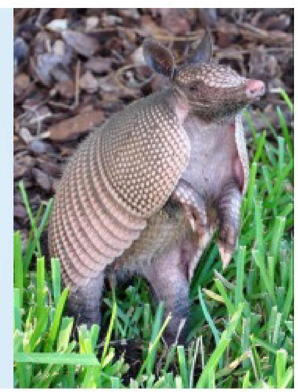


TiB_2 brazed on Mo backing plate

CrB_2 brazed on Mo backing plate

Armadillo structure

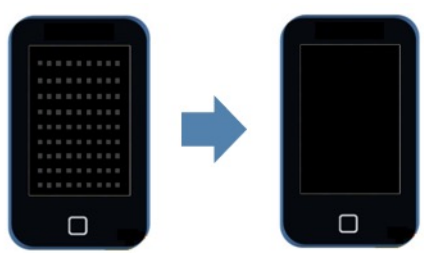
Used TiB_2 brazed on Mo backing plate



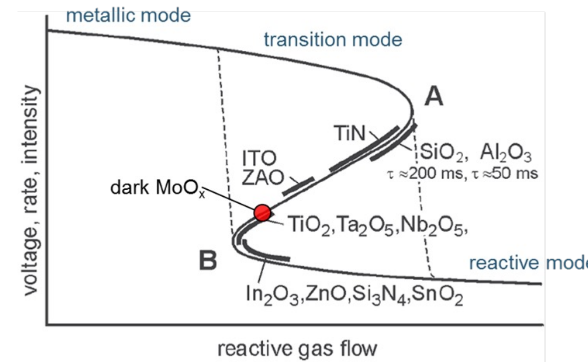
https://de.Wikipedia.org/

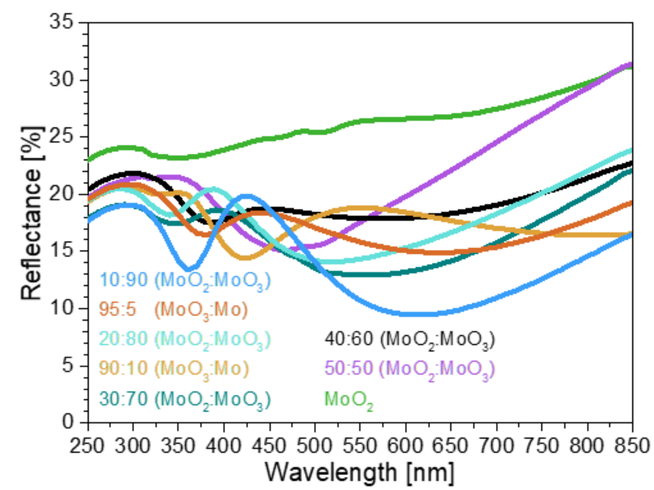
Non-reactive deposition from Mo-oxide target

- Great interest in developing black matrix layer for flat panel displays
- Dark Moly oxides can be deposited to cover sensor lines in capacitive sensors
- Full reactive deposition can be tricky (need O_2 30-50%by vol)
  - Feedback control necessary with multiple sensors
- Range of Moly oxide targets MoO_2 … MoO_3 tested
  - Deposition pure Ar, no O_2 added; film thickness not optimized



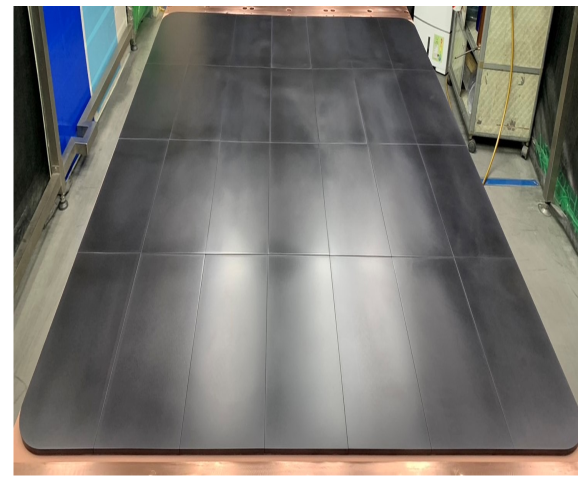
x sensor line
y sensor line
dark oxide

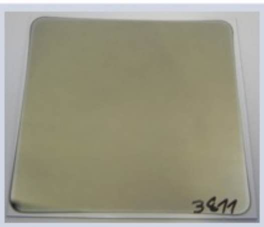
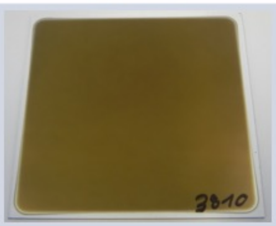
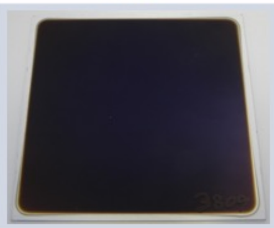




Non-reactive deposition from Mo-oxide target

- Choose the right composition and optimize the thickness
- Introduced 2015 at SVC
- Other elements have since been added; used in production
- Not limited to moly oxide, other materials being explored
- Major advantages of “sub-oxide” targets
  - Less oxygen needed => easier to control
  - DC, not RF, sputtering => higher deposition rates



MoO_x 15nm	MoO_x 35nm	MoO_x 55nm	MoO_x 75nm
			
R = 59,7%	R = 16,9%	R = 4,2%	R = 12,9%

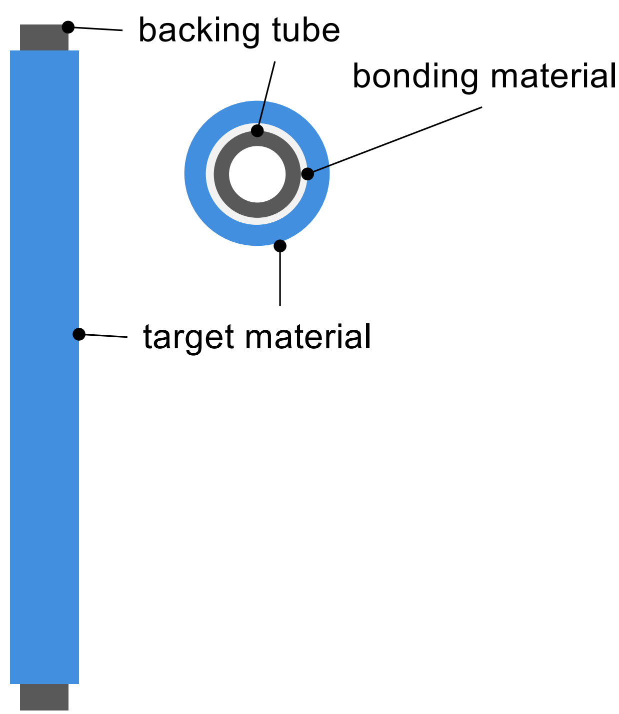
Optimized film thickness

PLANSEE

Cylindrical targets

Cylindrical target types - Mo

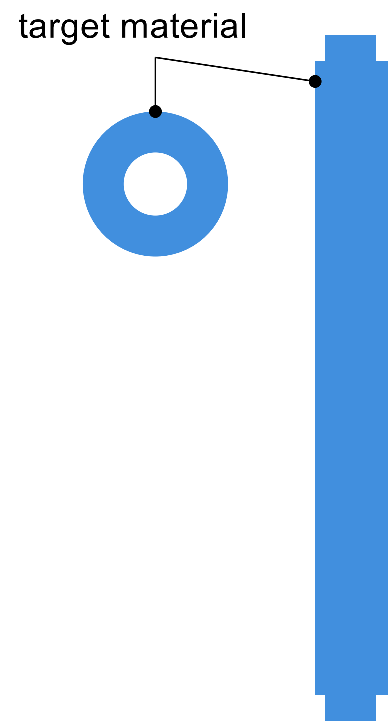
Bonded



Backing tube: stainless steel, Ti

Bonding Material: In, In alloy

Monolithic



No additional bonding step necessary

Higher power density utilization possible

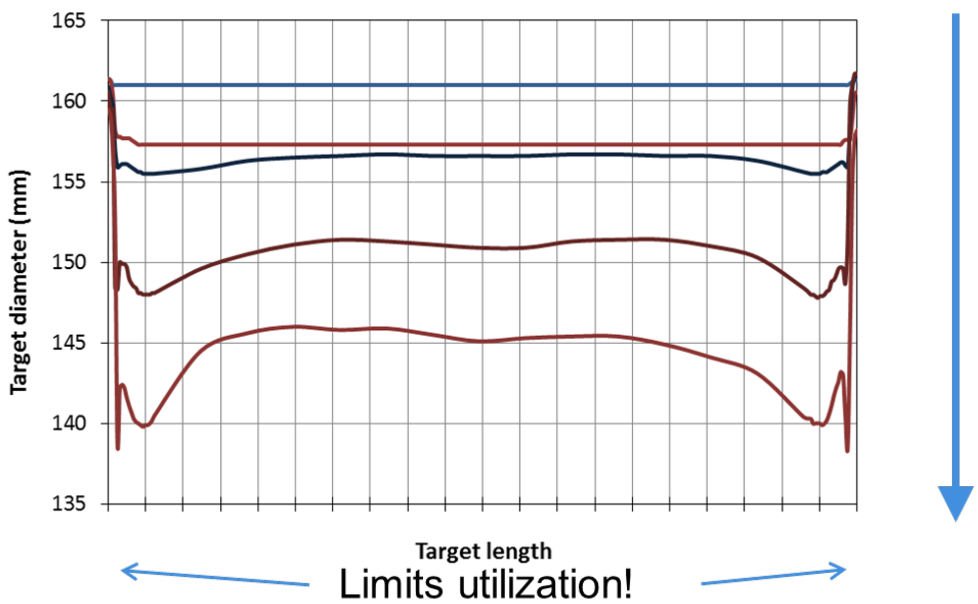
Improvements in monolithic design

- In some cases, instrument chilled water cooling caused corrosion of monolithic Mo targets
- Starting pH of 9 => pH of 4
- Increase of electrical conductivity
- Additional inhibitors needed to offset, this was expensive and not a perfect solution

- Introduce ID coating on monolithic target
- Prevents direct contact with cooling water
- Stable pH, no additional inhibitors required
- Direct-cooled multi-element targets experience similar issues

Increased target utilization

- In cylindrical targets, extensive erosion often occurs at ends due to magnetic trapping
  - Decrease overall utilization
- "Dogbone“ cylindrical target can overcome this problem
  - Increased material at the ends compensates for added erosion

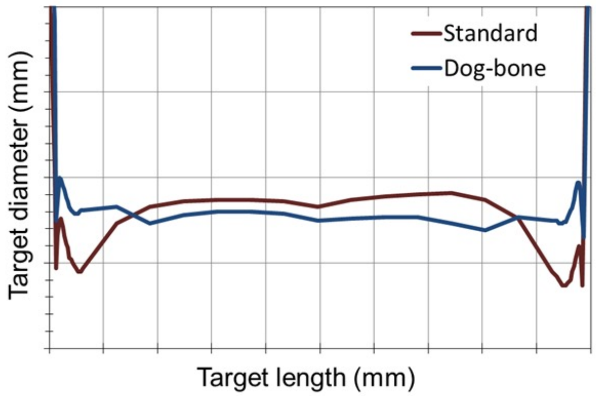


Increasing kWhr
(target lifetime)

Improved utilization with dogbone design

Standard
(~ 75% utilization)

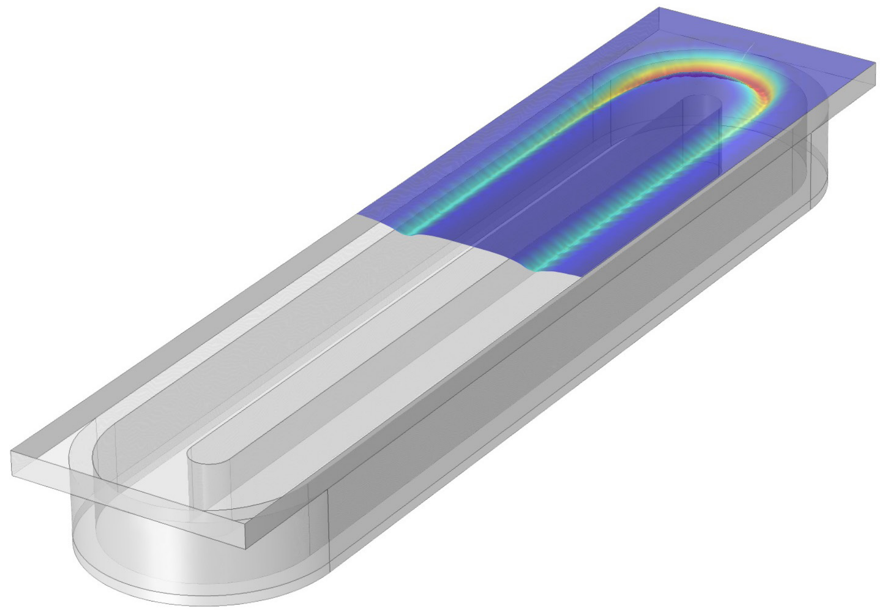
Dog-bone
(> 85% utilization)



Numerical modeling

Increasing sputtering yield

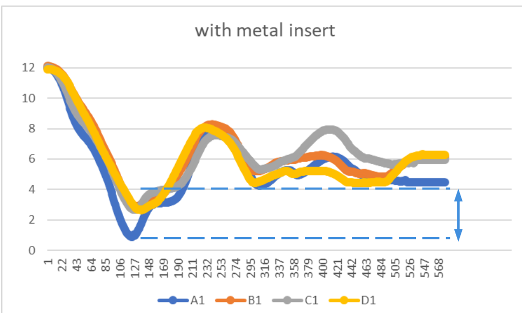
- Numeric modeling of plasma simulates erosion of the target during DC magnetron sputtering
- Optimum magnetic design avoids localized excessive erosion area
- More uniform erosion yields higher overall utilization and less scrap

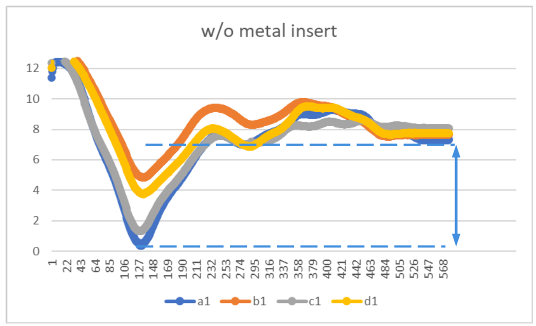


Magnetic field adaptation to improve utilization

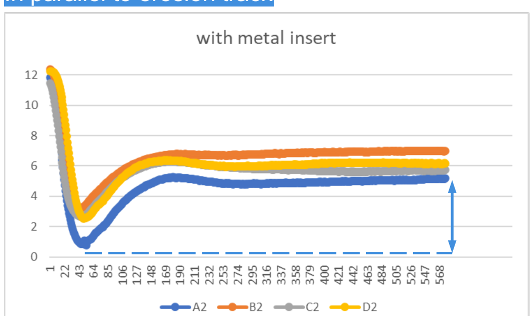
- Planar target design, 2nd generation improvement (1st gen 2011)
- Plansee adaptation increases lifetime by additional 10%

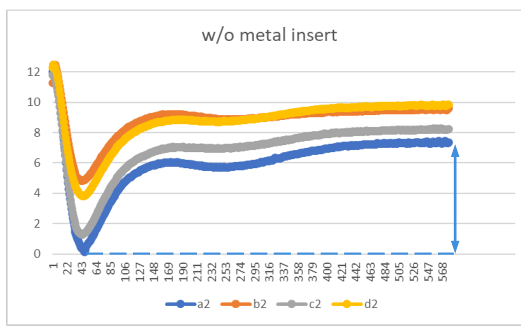
Perpendicular to erosion track

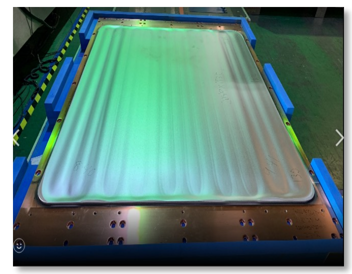


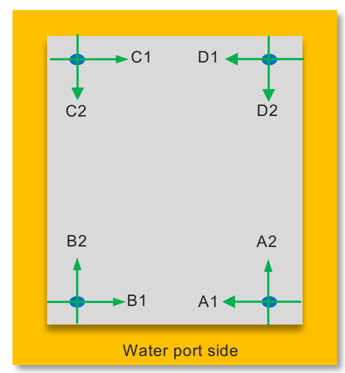


In parallel to erosion track









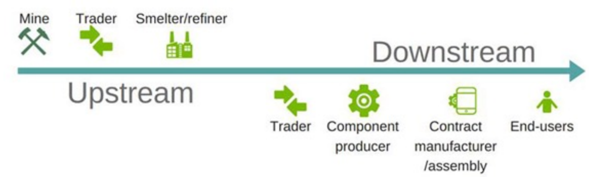
Future Challenges

Megachallenges and megatrends

- Manpower, Equipment
- Supply chain
  - Energy, Materials
  - War in Ukraine, increasing geopolitical tensions
- Electrification, Internet of things
  - Tooling & Power demands changing, increasing computer chips need
- Conflict Minerals
- Sustainability
  - Plansee initiatives
  - Electroplated vs PVD Chromium

Conflict Minerals

- By 2009, US acknowledged that gold was the principal source of funding for the world‘s deadliest conflict, then raging in the Dem. Rep of the Congo (DRC).
- Dodd-Frank Wall Street Reform and Consumer Protection Act (2010)
  - auditing of supply chains
  - Reports to SEC; Plansee not required, but our customers were
- Gold as well as tin, tantalum, and tungsten of concern => so-called "3TG“
  - Key products of cellphones
- Plansee was among first companies audited as smelter (2013) and then again as downstream producer (2016)
- Regulation (EU) 2017/821: implemented 1 January 2021
- CMRT: Conflict Minerals Reporting Template
  - List of smelters / producers that are independently verified as "conflict-free“
- Enhanced consumer awareness of where and how materials are produced



Sustainability

Mission statement

It is my conviction that those entrepreneurs who know how to align their business goals with the goals of society will integrate into our society and will be accepted by society in the long run. We must strive to create conditions so that everyone can be a human being in the industrial working world.

Walter M. Schwarzkopf, 1965

Sustainability has been in our DNA for 100 years. We have always been a sustainable company and want to become even more sustainable in the future. For our employees, our neighborhood and as a strong partner for our customers.

Andreas Feichtinger and Ulrich Lausecker

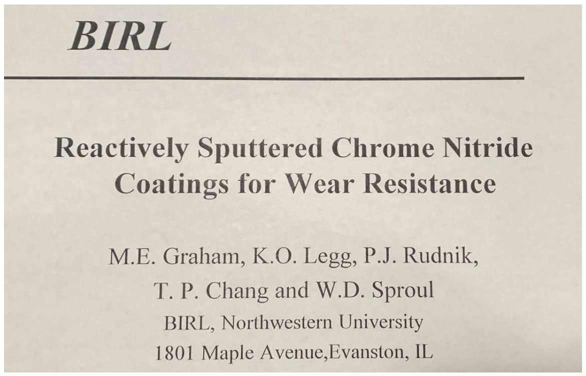
Sustainability initiatives at Plansee

- Mo scrap/byproducts conditioned, sold to steel mills => ~100% efficient
- Multiple other recycling/reuse projects undertaken in past 15 years
- Tungsten recycling through GTP >70%; WC recycled >20 years
- Goals: Carbon neutral by 2030, carbon net-zero by 2050
  - Scope 1 (direct emissions), Scope 2 (indir. emissions - purchased energy)
  - Scope 3 (indirect emissions along entire value chain, incl mining)
- On 27 March 2023, signed agreement to switch over to electrolysis from natural gas for the production of hydrogen

Selected projects with customers

- **Apple Clean Energy Program**
  100% recycled raw materials and renewable energy for the manufacture of components for Apple devices
- **ASML**
  Reuse, Refurbish, Rework, Recycle
  ASML Sustainability Excellence Award 2022
- **MediX-Tec**
  Life-Cycle-Management for rotating X-ray anodes

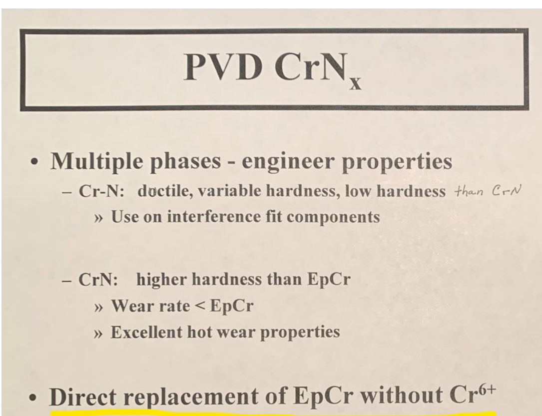
Electroplated vs. PVD Cr – not really new



BIRL

Reactively Sputtered Chrome Nitride Coatings for Wear Resistance

M.E. Graham, K.O. Legg, P.J. Rudnik,
T. P. Chang and W.D. Sproul
BIRL, Northwestern University
1801 Maple Avenue,Evanston, IL



PVD CrN_x

- Multiple phases - engineer properties
  - Cr-N: ductile, variable hardness, low hardness than CrN
    - » Use on interference fit components
  - CrN: higher hardness than EpCr
    - » Wear rate < EpCr
    - » Excellent hot wear properties
- Direct replacement of EpCr without Cr^{6+}

- Paper presented at ICMCTF 95;
- project begun fall 1993: EPA, DARPA, DoD sponsors
- Electroplated Cr produces Cr^{6+}, a known carcinogen (1500X worse than benzene)
- PVD Cr doesn‘t produce Cr^{6+}
- But is it really eco-friendly? Nobody worried about supply chains back then

PVD coated piston rings

Sustainable Chromium PVD targets

- Customer approached Plansee in 2020
- Interested in PVD Cr, knew electroplated chromium problematic due to Cr^{6+}
- Investigate entire supply chain : compliance with ISO & other stds, recycling used targets reqd
  - 80% of CO_2 is produced in manufacturing the raw material => recycling critical to closed loop
- Two grades of pure chromium produced today
  - Electrolytic chromium requires liquid chromic acid (H_2CrO_4) which is pure hexavalent chromium
  - Aluminothermic chromium requires Cr oxides mixed with Al powder to create a thermite reaction
    - Cr oxides also produced from chromic acid, but in closed loop with less risk for contamination
- Recycling of used targets
  - 30% utilization => 70% available for new
  - Mechanical methods (crushing and sieving), no Cr^{6+} produced
- Not 100% Cr^{6+} free, but Aluminothermic and recycling is a significantly better solution

Summary

Historical development of PVD hard coatings

Binary compounds (Ti-N, Ti-C, Cr-N), early 1980's

Metastable solid solutions (Ti-Al-N, Ti-Zr-N, Ti-Hf-N, Ti-Nb-N), from 1986

Multilayer / Superlattice structures (TiC/TiB_2) from 1984

Nanocomposite structures (nc-TiN/a-Si_3N_4) 1990's

Borides, High-entropy "alloys", more diverse and purer materials

HIPIMS

Final comments

- PVD is a flexible technology to deposit thin films of all types
- PVD coatings appear everywhere
  - We look through them (eyeglasses, windows..)
  - We‘re entertained by them (TVs, phones, tablets..)
  - We process information better because of them (computers)
  - We are empowered by them (solar cells, auto engine parts)..
- PVD coatings will continue to evolve and improve and find more places in our lives

- The source of PVD coatings is not "just a piece of metal“ : there is tremendous technology built into them
- Understanding the application allows us to bring innovations and solutions to our customers
- Together we can make science look like magic

Acknowledgements


Anytime you see a turtle
up on top of a fence post,
you know he had some
help.
- Alex Haley

Just some of the folks who‘ve helped me along the way

- Bill Sproul and entire BIRL team
  - Mike Graham, Keith Legg, Ming-Show Wong, Tony Lefkow, Zeno Szychlinski, Mike Wieczorek
  - W.-D.Münz, B. Windows, I.Petrov, J. Greene, L.Hultman, T.Hurkmans, J.Schneider, A.Matthews, A.Inspektor
- Bill Langendorfer and GoldStar/ StarSU
  - J.Lawton, M.Tennutti, J.O‘neil, K.Switzer, K.Puska, G.Erkens, G.Lake
- Folks at Guardian Glass
- Plansee: Uli Miller, Peter Polcik, Joerg Winkler, Christoph Adelhelm, Christian Linke, Szilard Koloszvari, Tsutomu Kuniya, Conrad Polzer
- My customers for giving me the chance to support their efforts and contribute in a small way to their successes.
- A host of others, too numerous to list here

Thanks for your attention

Any questions??

Strong Metals. Strong Products.

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