Plansee SE Reutte - Business Unit: Industries, Market Unit: Thermal Processes
Rudolf Holzknecht - Manager Application Group Glass & Quartz Glass Manufacturers

STRONG METALS

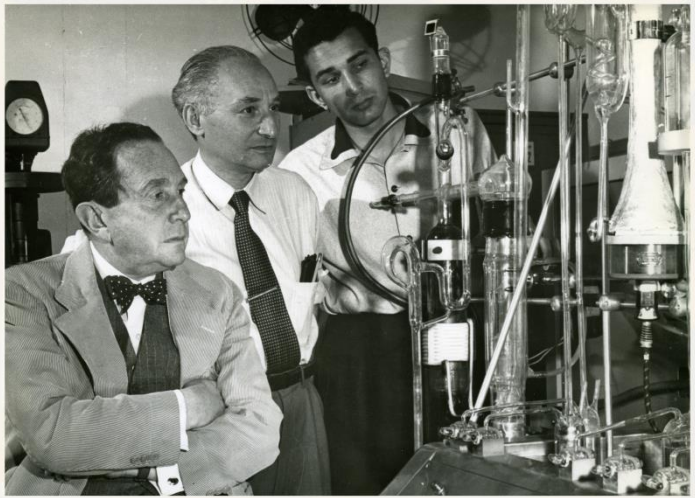
Johns Manville

Reutte, March,09th, 2016

- History, facts and management, Sites, Market Units and products
- Research and development, Sustainability and additional benefits
- Materials, Production process
- Glass melting equipment & technology
- Glass melting electrodes
- “GTR” Glass Tank reinforcement
- Stirrer
- Quartz glass and Glass wool production

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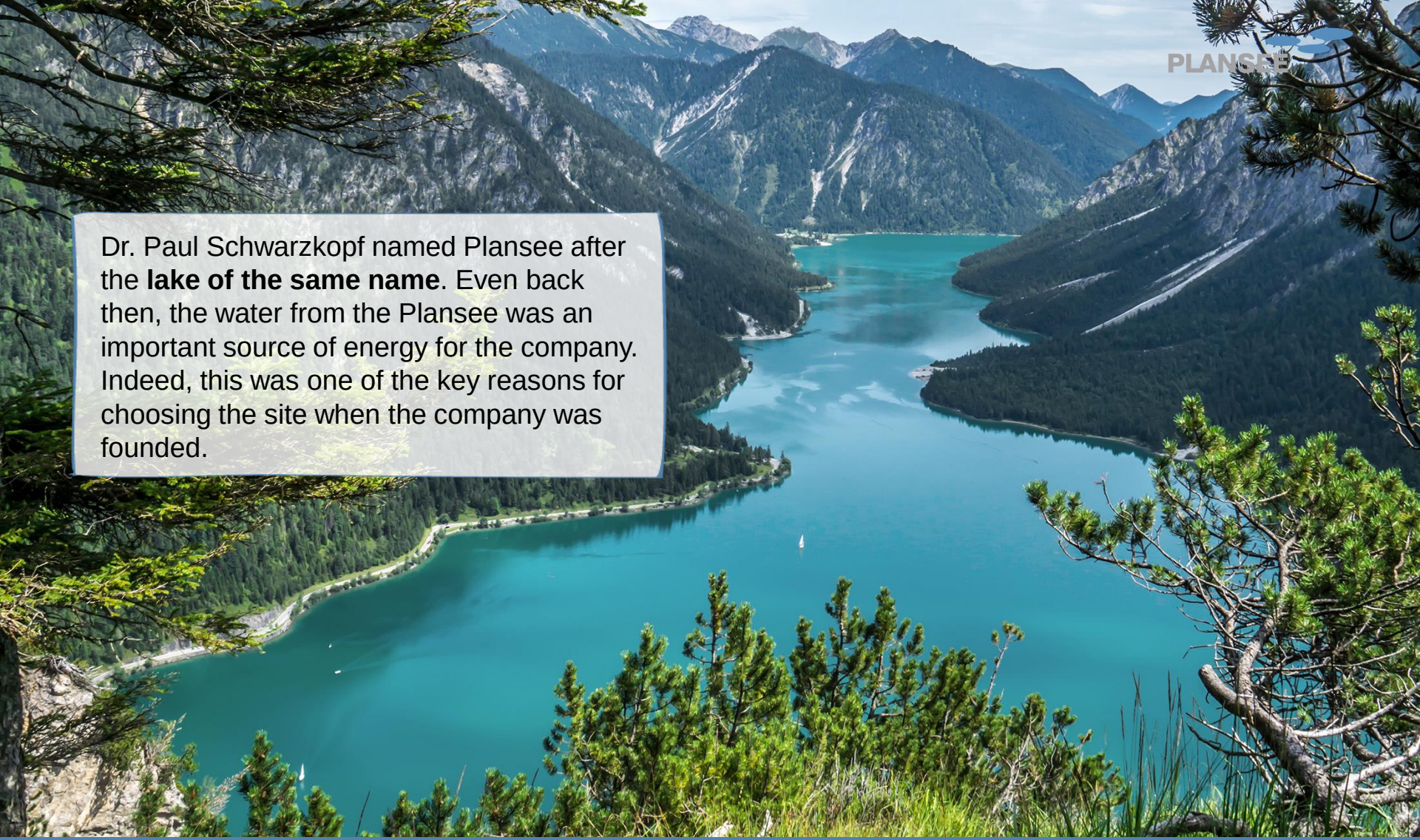
Plansee has been producing refractory metals since **1921**.





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

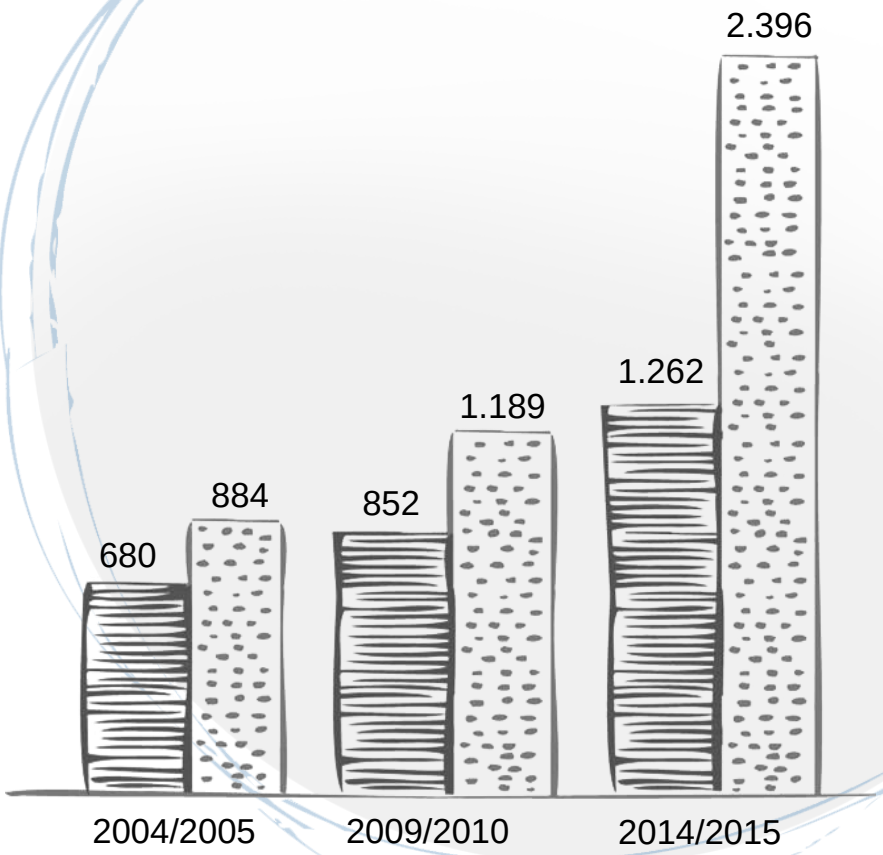
In addition to filaments, we now produce thousands of products from refractory metals and composite materials.



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. Indeed, this was one of the key reasons for choosing the site when the company was founded.



Plansee is now a group of companies with a global presence and over 6,000 employees. With its **divisions and holdings**, the Plansee Group covers every stage of tungsten and molybdenum processing.



Sales of the Plansee group in million euros. The fiscal year ends on the last day of February.

Consolidated figures of Plansee Group.

All associated companies, where the Plansee Group holds more than 20 percent of the shares.



From powder manufacture to the finished component:

the Plansee Group is an **independent and private company** that you can rely on.

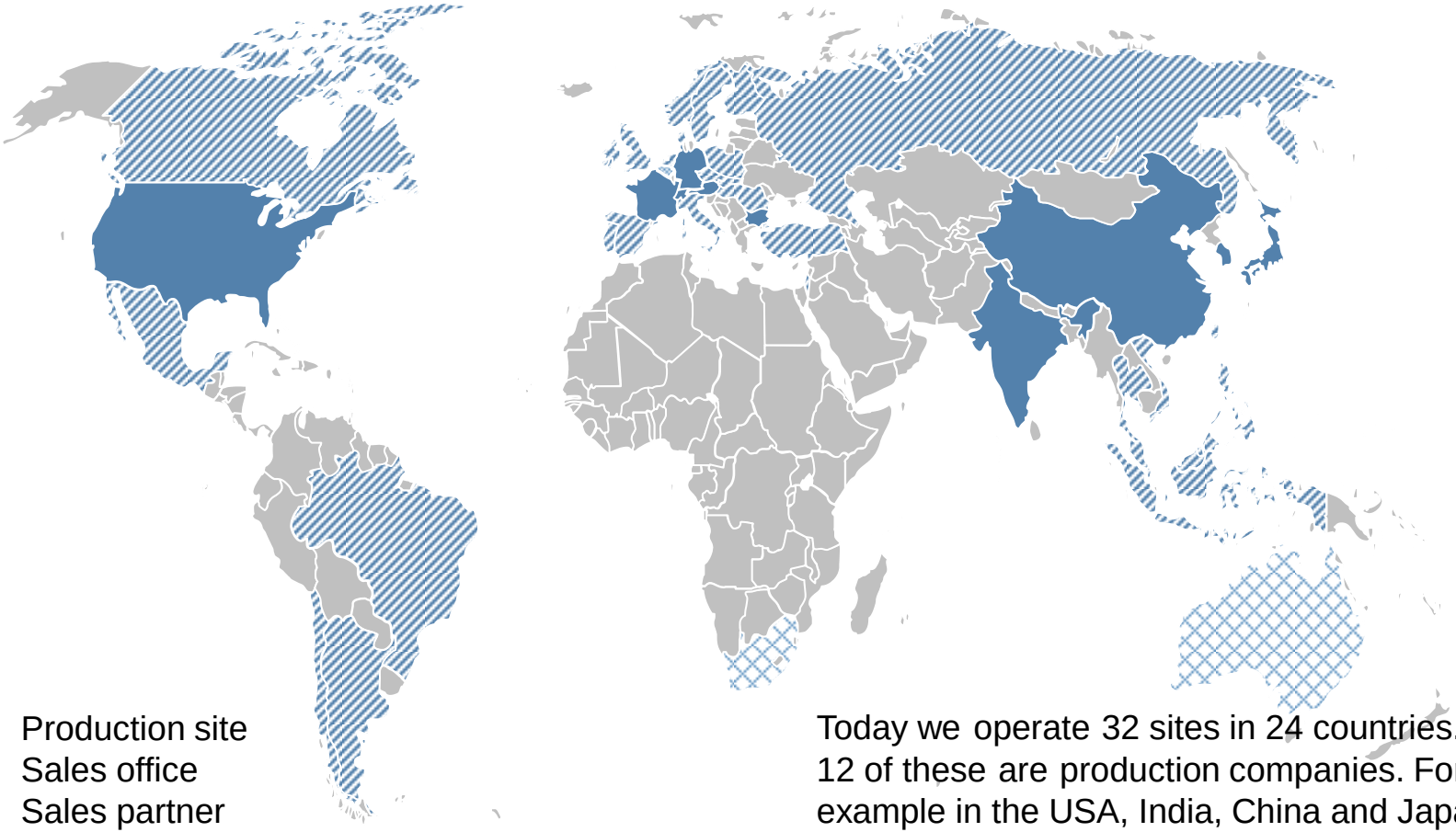
The Plansee High Performance Materials division stands for **expertise** and **continuity**. This can also be seen in the length of service of our current Executive Board.



Bernhard Schretter
President
With Plansee since 1986

Hermann Walser
Executive Vice President
With Plansee since 1984

Dr. Wolfgang Köck
Executive Vice President
With Plansee since 1988



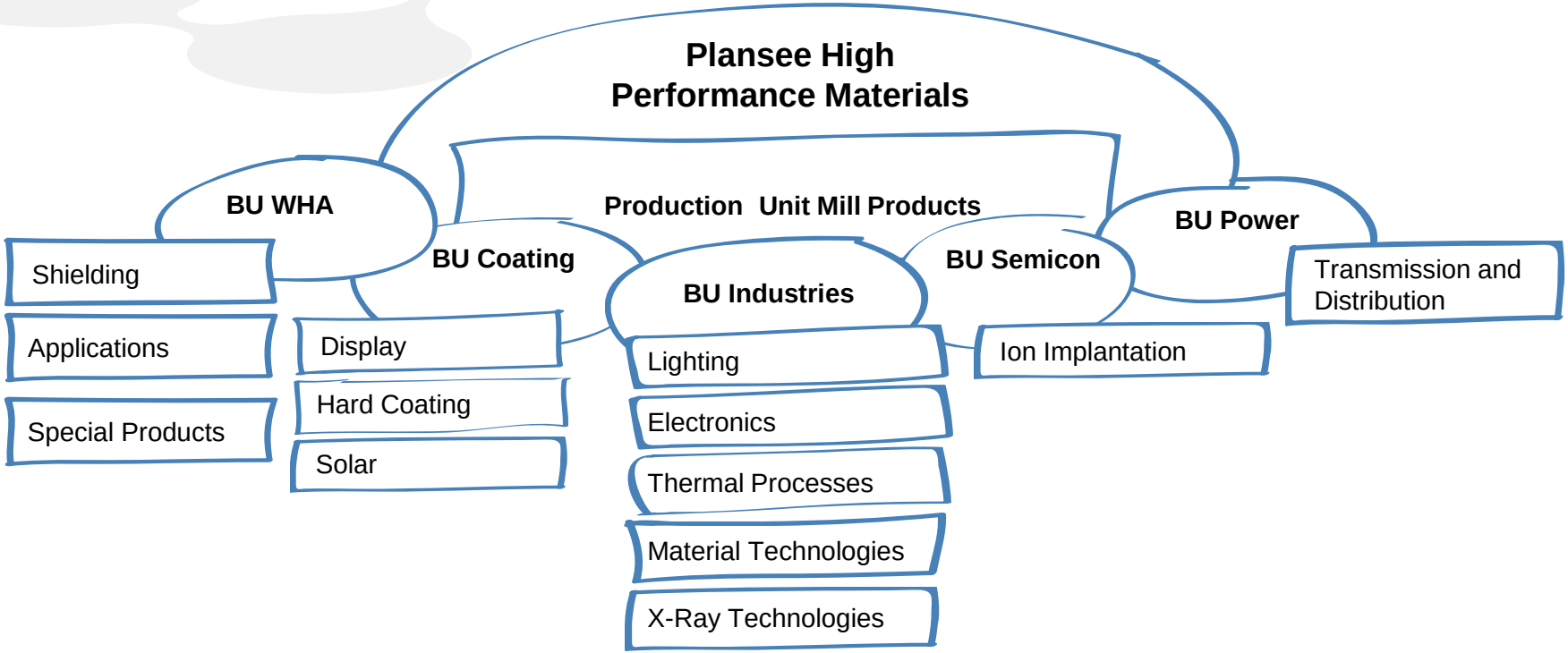
Production site
Sales office
Sales partner

Today we operate 32 sites in 24 countries. 12 of these are production companies. For example in the USA, India, China and Japan.

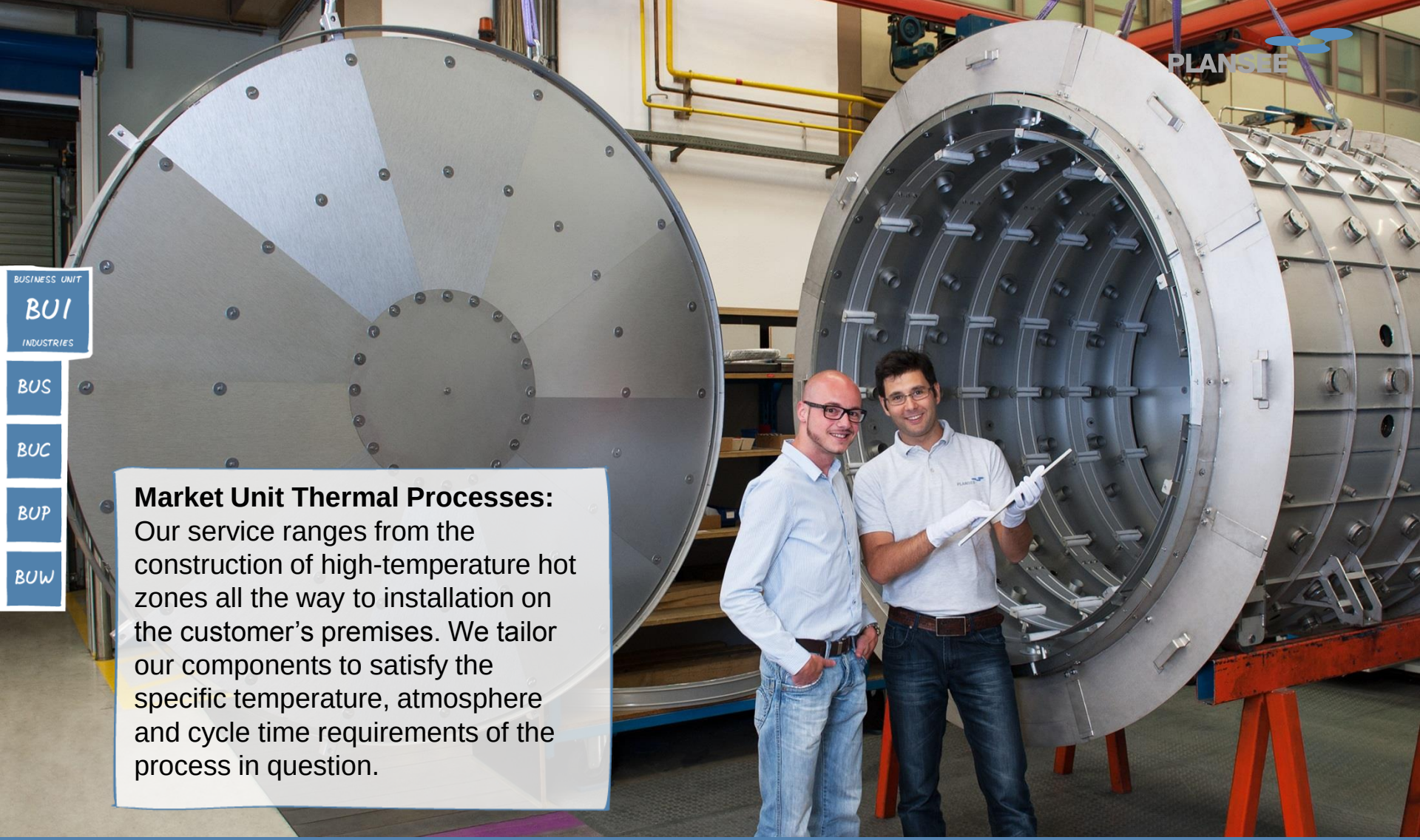


PLANSEE

The Reutte site in Austria is **Plansee's head office**. A large proportion of the production as well as all the central services are located here.



Plansee is divided into **market-oriented business units**. As a result, Plansee is not just the **leader in terms of shipped volumes**, but also an **application specialist** providing custom products for your industry. Here are some examples of our Market Units:



Market Unit Thermal Processes:
Our service ranges from the construction of high-temperature hot zones all the way to installation on the customer's premises. We tailor our components to satisfy the specific temperature, atmosphere and cycle time requirements of the process in question.

BUSINESS UNIT
BUI
INDUSTRIES

BUS

BUC

BUP

BUW



Hot zones for
high-temperature furnaces



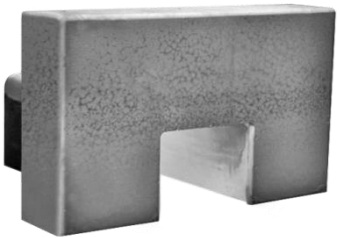
Crucibles for
sapphire crystal production



Heaters for
high-temperature furnaces



Stirrers for the
glass industry



Glass tank
reinforcement



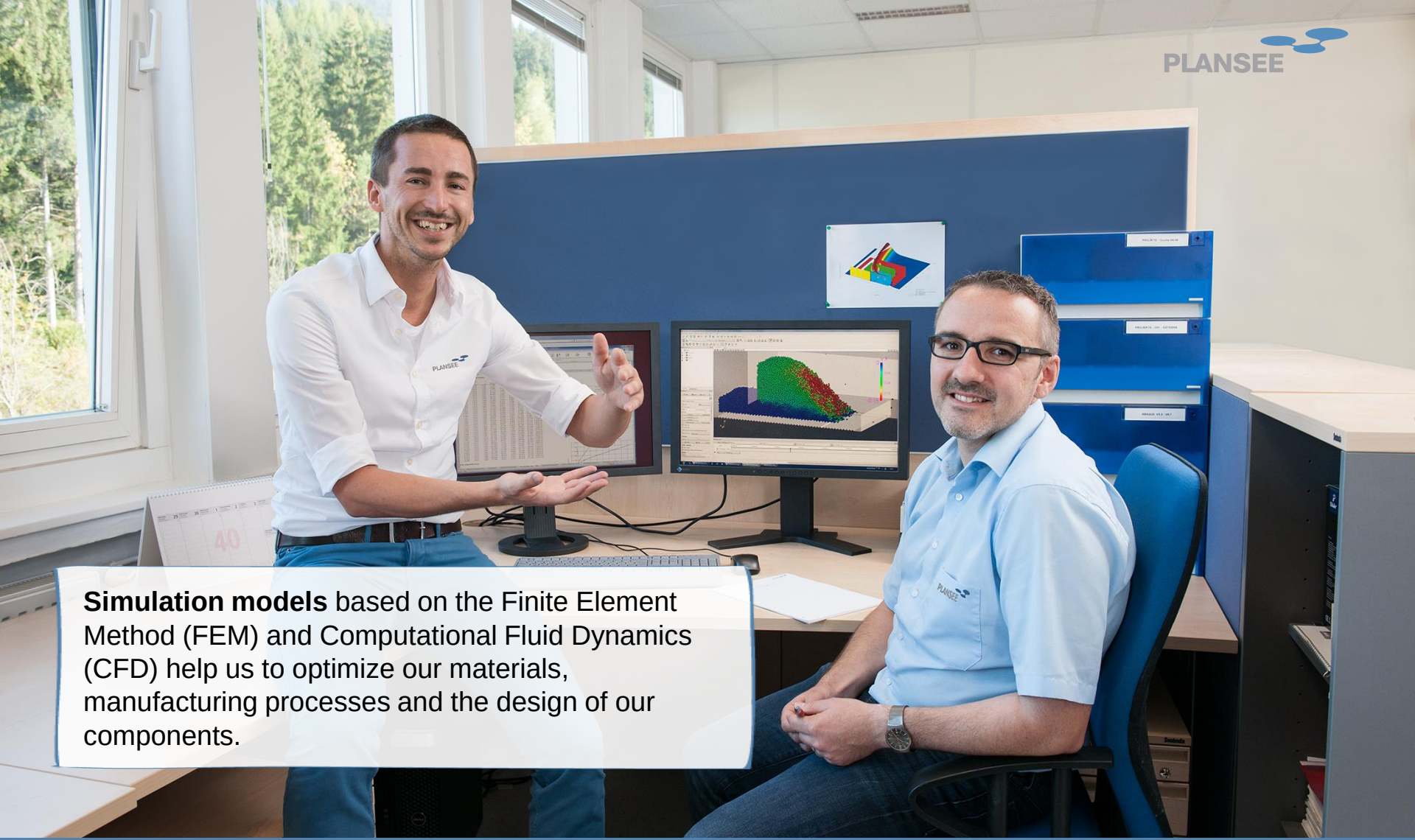
Glass melting
electrodes



At Plansee, we place particular emphasis on research and development. Our scientists are constantly working on new products and materials in collaboration with customers and leading research institutes.



Our innovation teams are responsible for developing new production processes, among other things. One example: based on the concept of the 3D plastic printing process, we have further developed a selective laser melting process for refractory metals. This means that complex and particularly intricate parts can now simply be “printed”.



Simulation models based on the Finite Element Method (FEM) and Computational Fluid Dynamics (CFD) help us to optimize our materials, manufacturing processes and the design of our components.

In our **test laboratories**, we use mechanical tests and conduct chemical and metallurgical analyses to check the impeccable quality of our materials. At Plansee, we also cover many non-destructive test methods such as ultrasonic tests, eddy current testing and thermographic inspections. Our test laboratories are accredited by the responsible ministry.





Research is one of our traditions.
We have been extending invitations to the international Plansee Seminar every four years since 1952. Here, renowned experts from the field of powder metallurgy present their latest findings relating to the development, production and use of refractory metals.

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Sustainability and additional benefits



Tungsten and tantalum are partially sourced from regions of conflict and are classified as “conflict materials”.
As a company aware of its responsibilities, we are extremely particular about our raw materials procurement.

The Electronic Industry Citizenship Coalition (EICC) and the Global e-Sustainability Initiative (GeSI) are among the organizations to certify that our tantalum and tungsten are procured exclusively from **ethically sound sources**.

If you have any questions about our sustainable raw materials procurement, Andreas Feichtinger is happy to help:
andreas.feichtinger@plansee.com

Sustainability and additional benefits

Dr. Heinz-Otto Berten
Head of Quality Management

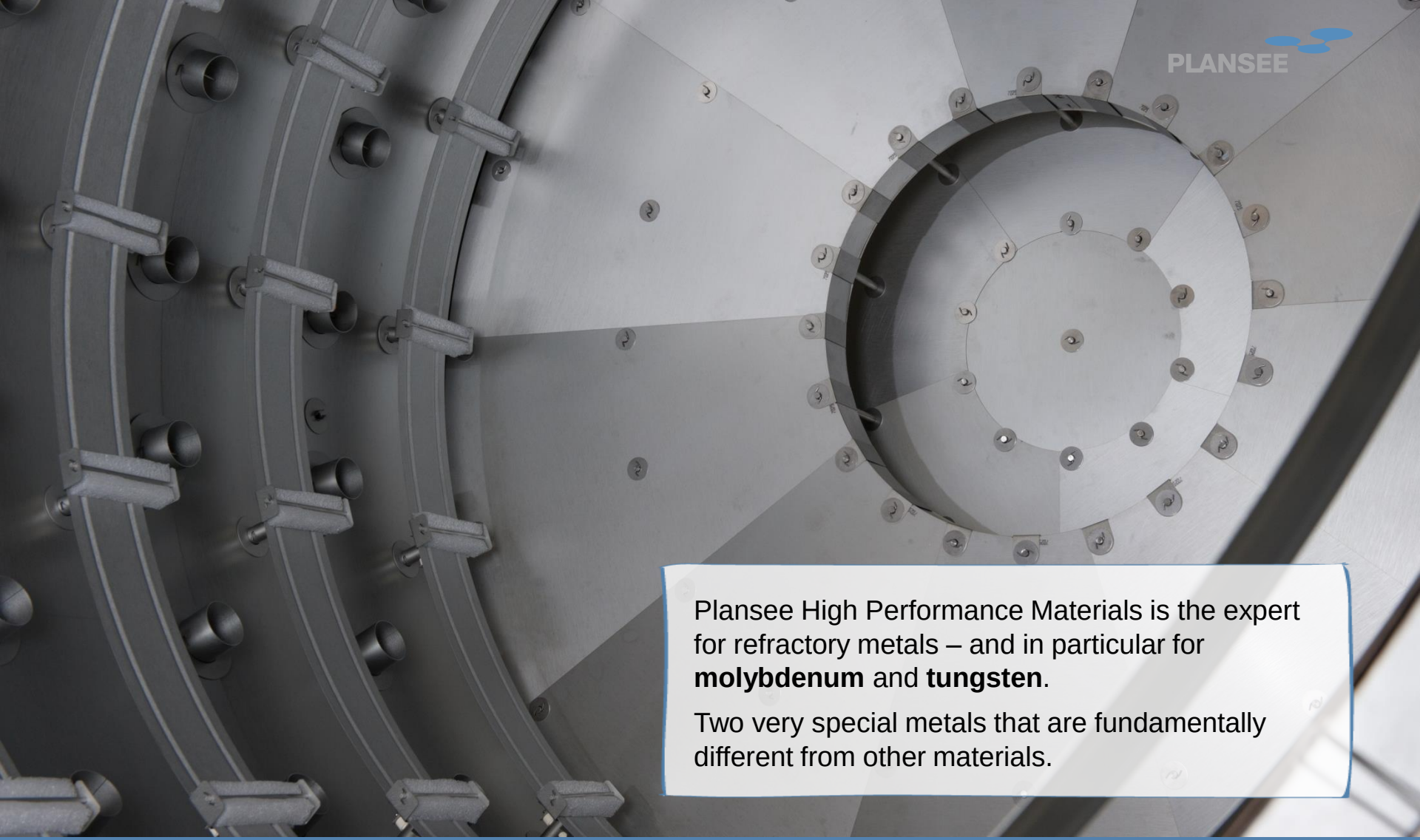


Our quality management system is certified to **ISO 9001:2008** . We have an **ISO 50001**-compliant energy management system, meet all the **OHSAS 18001:2007** Occupational Health and Safety criteria and are certified in accordance with the **ISO 14001:2004** environmental management standard.

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Plansee SE Reutte - Business Unit: Industries, Market Unit: Thermal Processes
Rudolf Holzknecht - Manager Application Group Glass & Quartz Glass Manufacturers
5th June 2012

Material & Production process



Plansee High Performance Materials is the expert for refractory metals – and in particular for **molybdenum** and **tungsten**.

Two very special metals that are fundamentally different from other materials.



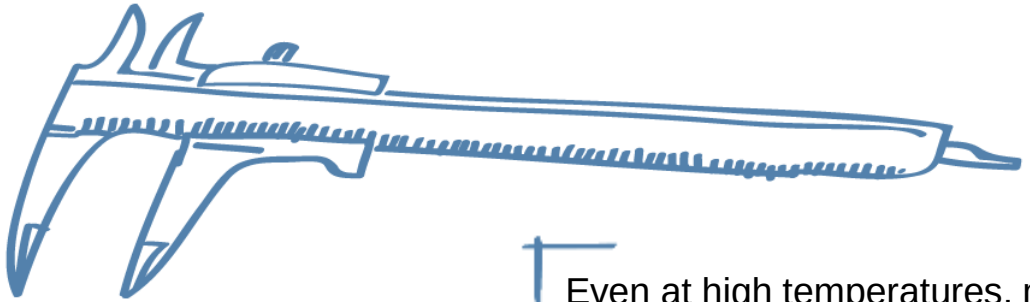
Molybdenum and tungsten are particularly **heat-resistant** and remain **dimensionally stable** and **extremely strong** even at high temperatures.

Molybdenum has a melting point of 2 620 °C. And at 3 420 °C, tungsten has the highest melting point of all metals.

Both metals have **a very low vapor pressure** and are particularly suitable for high-temperature applications in a vacuum or a protective gas atmosphere.

Our metals combine excellent heat resistance with **good electrical and thermal conductivity**. While some other metals such as copper are outstanding conductors, they cannot withstand high temperatures.

By contrast, ceramic materials have good heat resistance but do not conduct electricity.



Even at high temperatures, molybdenum and tungsten only expand very little.

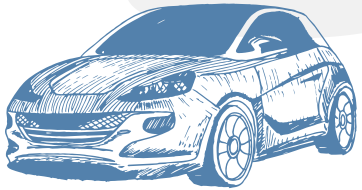
Their **coefficient of thermal expansion** is similar to that of semiconductor materials or sapphire. As a result, our customers often use molybdenum and tungsten in combination with these materials.



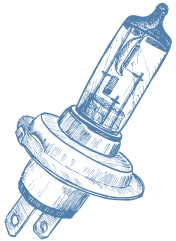
Tungsten is a heavy metal. **It reliably shields against X-ray and gamma radiation**. The density of tungsten is 60 percent higher than that of lead.



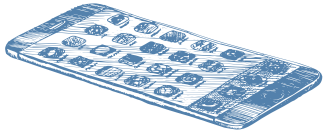
Our materials are **corrosion-resistant** in contact with many substances – even at high temperatures. For example, when exposed to metal or glass melts. We further optimize their corrosion resistance with special coatings and alloy additions.



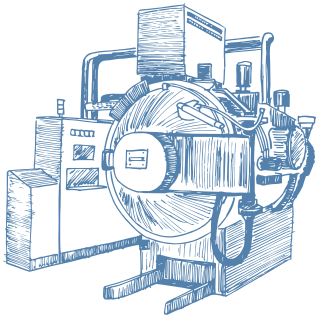
Automotive industry



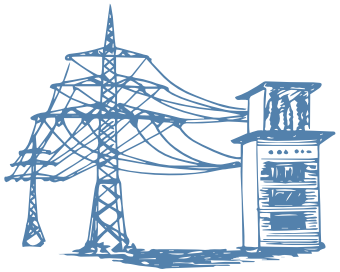
Lighting industry



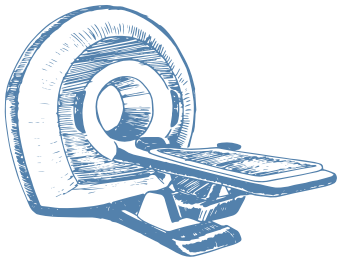
Electronics



Machine and plant equipment



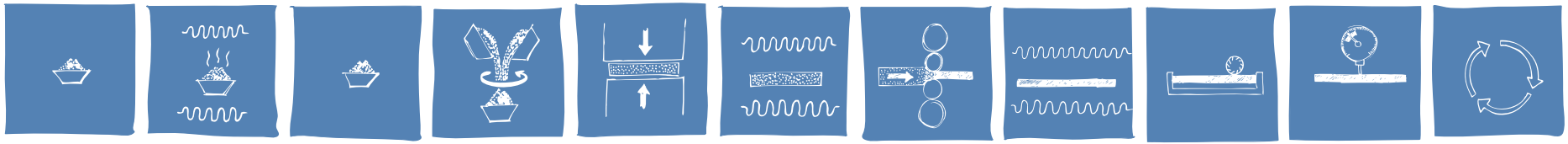
Power engineering



Medical technology

The special properties of our materials make them indispensable for many industries.

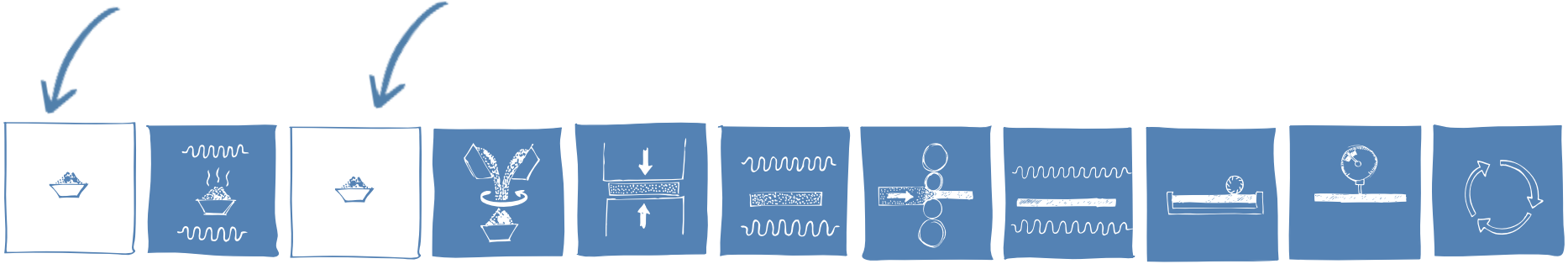
Production process



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

We use powder metallurgical methods to manufacture our refractory metals and composite materials. The Plansee Group covers the entire production process, from ore concentrates right to the customer-specific component.

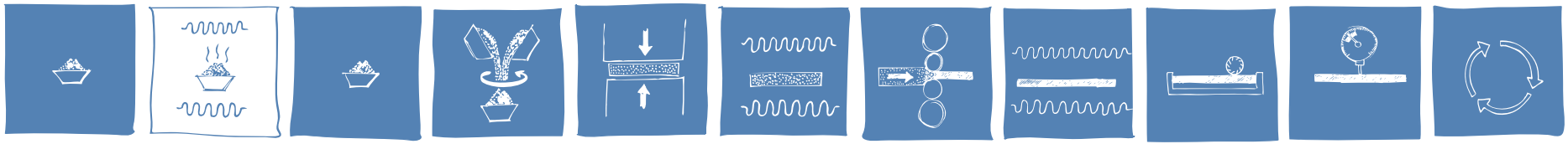
Production process



Molymet (Chile) is the world's largest processor of molybdenum ore concentrates and our main supplier of molybdenum trioxide. The Plansee Group has a 20% share in Molymet.

Global Tungsten & Powders (USA) is a division of the Plansee Group and our main supplier of **tungsten metal powder.**

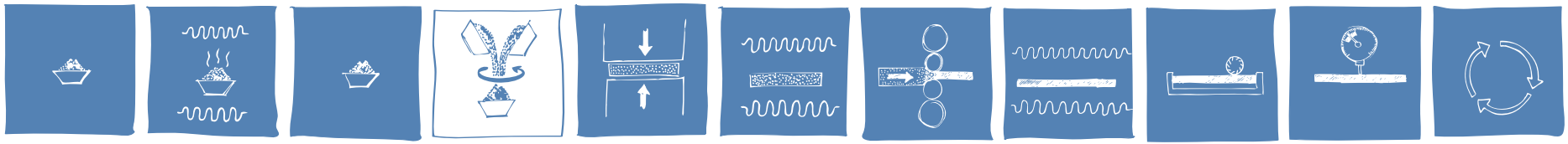
Production process



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

Reduction based on the example of molybdenum: We subject molybdenum trioxide to a two-stage reduction process in a hydrogen atmosphere in order to obtain metallic molybdenum powder. The first stage sees molybdenum trioxide (MoO_3) reduced to molybdenum dioxide (MoO_2). Highly pure molybdenum powder (Mo) is obtained in a second reduction stage.

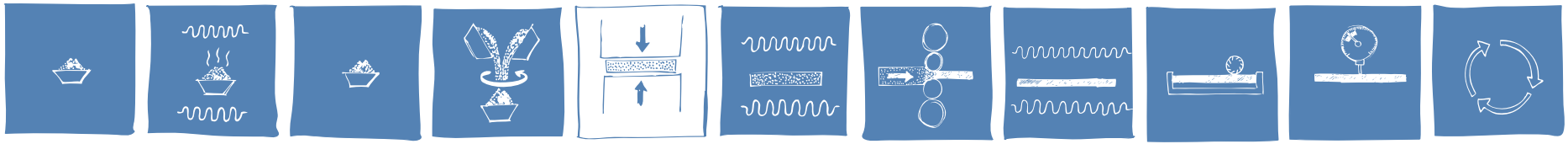
Production process



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

One of Plansee's core areas of expertise is the **production of especially high-performance alloys**. Their high quality results in part from the homogeneous distribution of the individual alloying components.

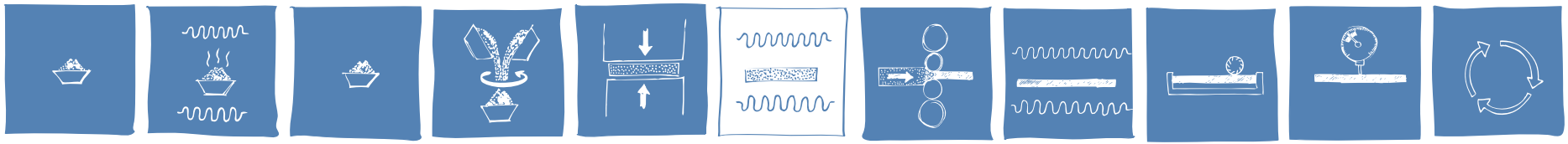
Production process



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

We **compact our metal powders** and metal powder mixtures to form so-called “green compacts”. In the case of end products with particularly complex geometries, we press these green compacts to a corresponding near-net shape.

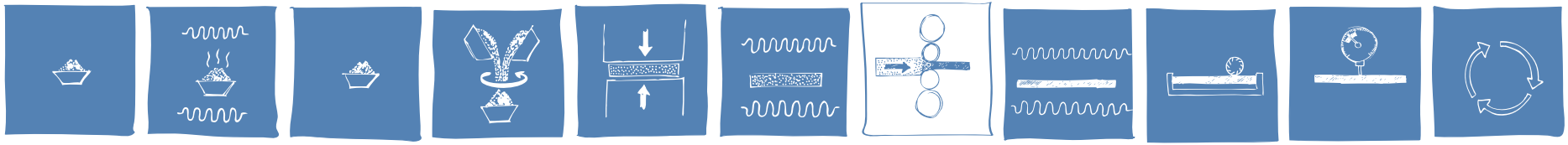
Production process



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

The core technology in powder metallurgy is sintering. The green compact is heated in a sintering furnace in a protective gas atmosphere. The powder grains coalesce to form a low-porosity sinter block.

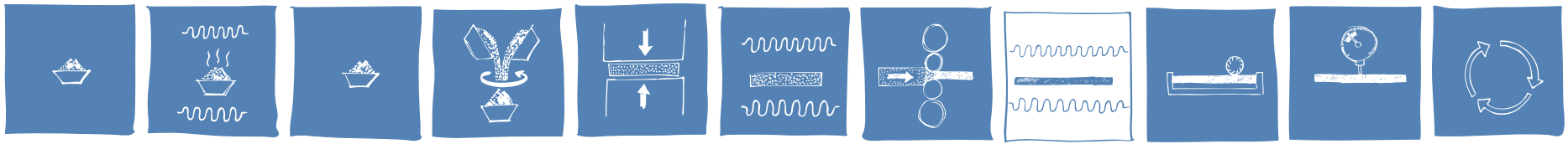
Production process



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

We **deform the sinter blocks** on the world's largest deformation equipment for refractory metals to produce highly resilient semi-finished products. The more our materials are worked the more their density and mechanical strength increase.

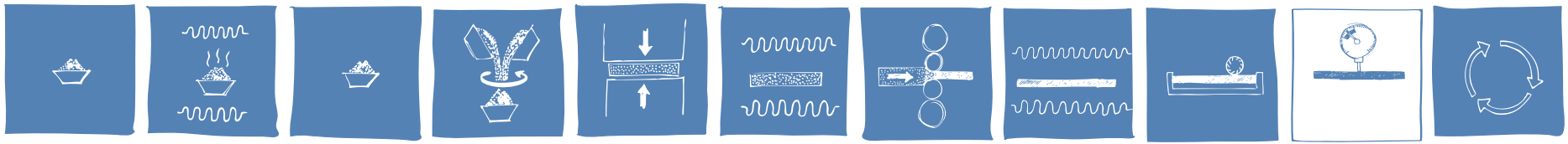
Production process



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

Heat treatment allows us to compensate for mechanical stresses, influence material properties and ensure that our metals can be machined successfully.

Production process

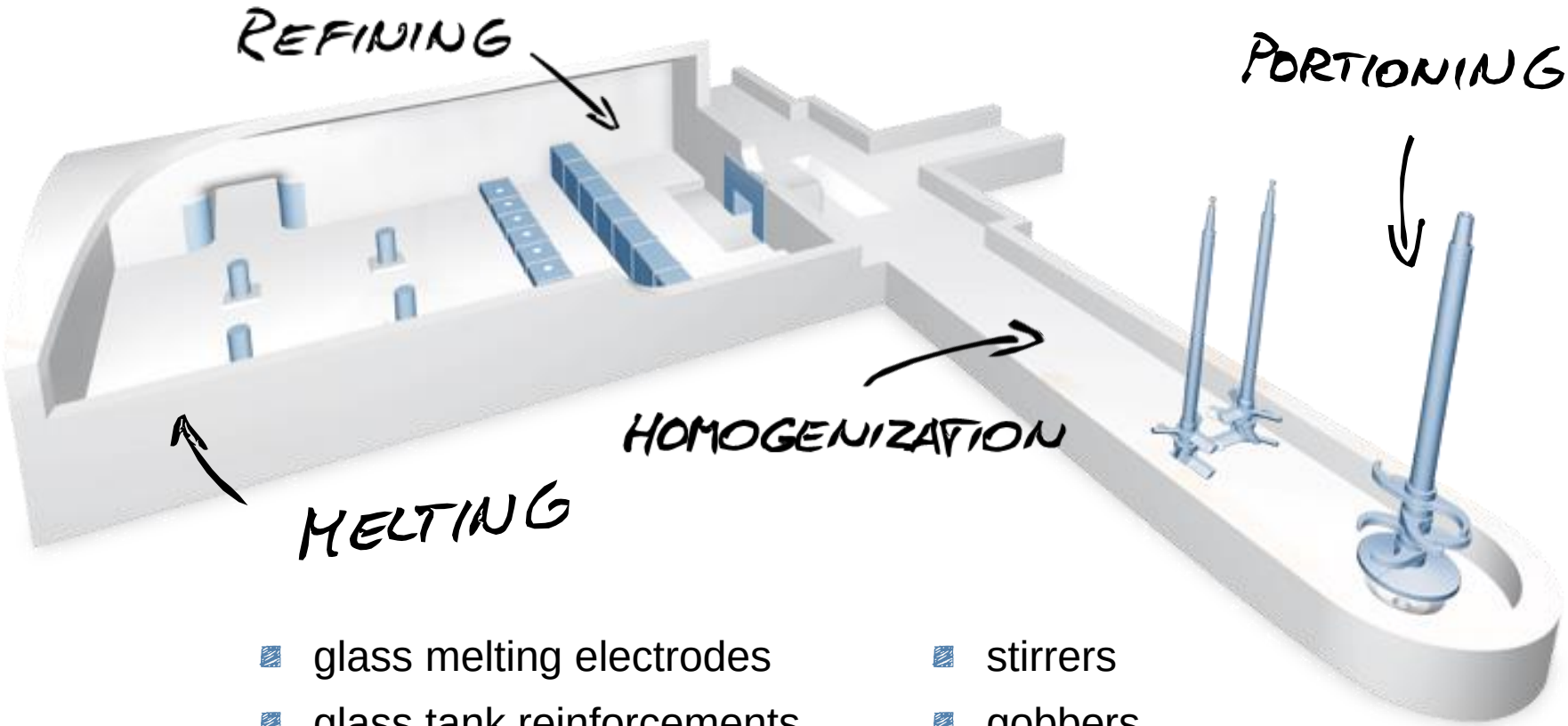


Oxide | Reduction | Metal powder | Mixing Alloying | Pressing | Sintering | Deforming | Heat treatment | Machining Joining Coating | Quality assurance | Recycling

Very early in its history, Plansee already set up a **Quality, Safety and Environment Management System.**

- History, facts and management, Sites, Market Units and products
- Research and development, Sustainability and additional benefits
- Materials, Production process
- **Glass melting equipment & technology**
- Glass melting electrodes
- “GTR” Glass Tank reinforcement
- Stirrer
- Quartz glass and Glass wool production

Plansee product portfolio.
Our gladiators in your arena.



- glass melting electrodes
- glass tank reinforcements
- stirrers
- gobbers

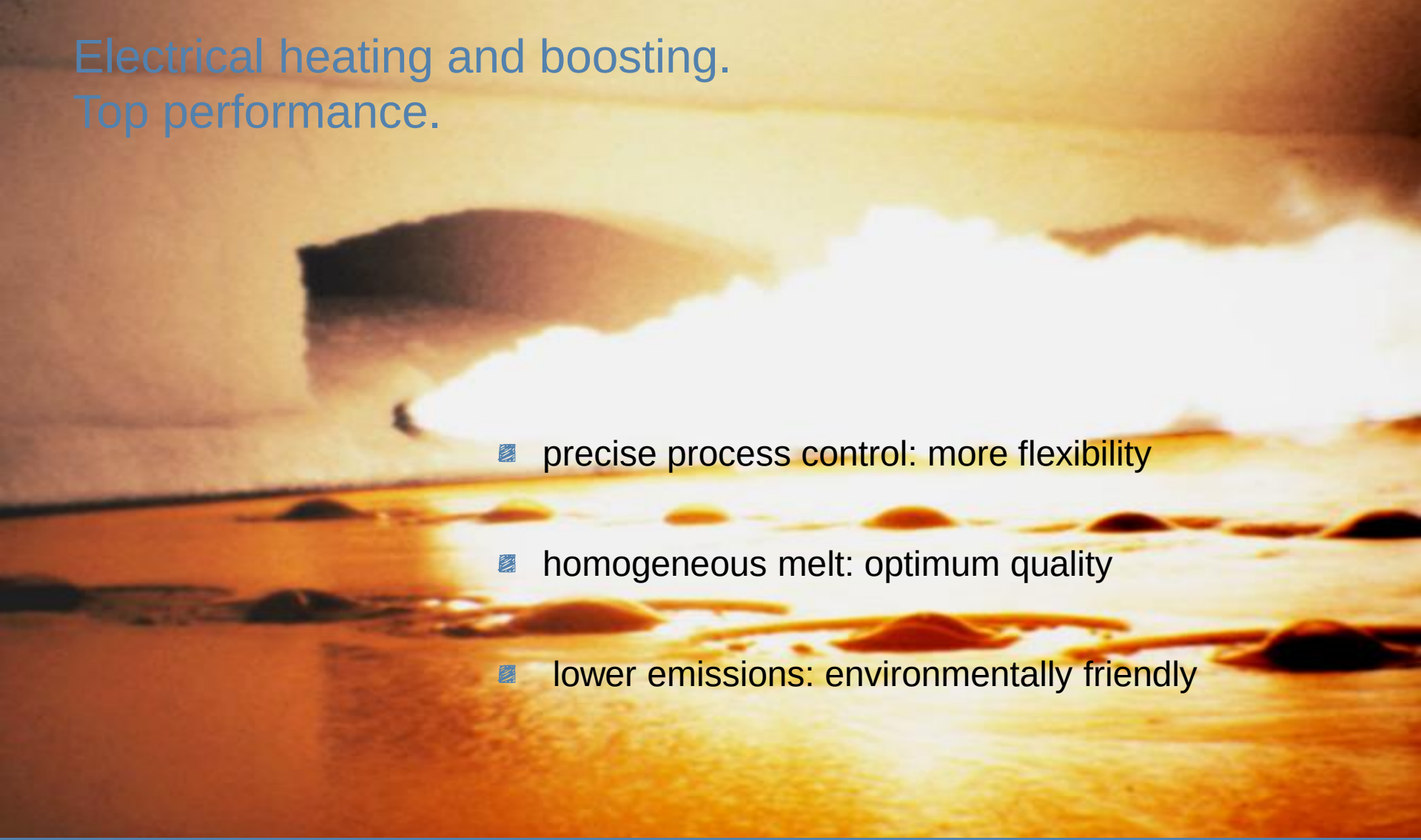
Plansee glass melting electrodes.

PLANSEE

STRONG METALS

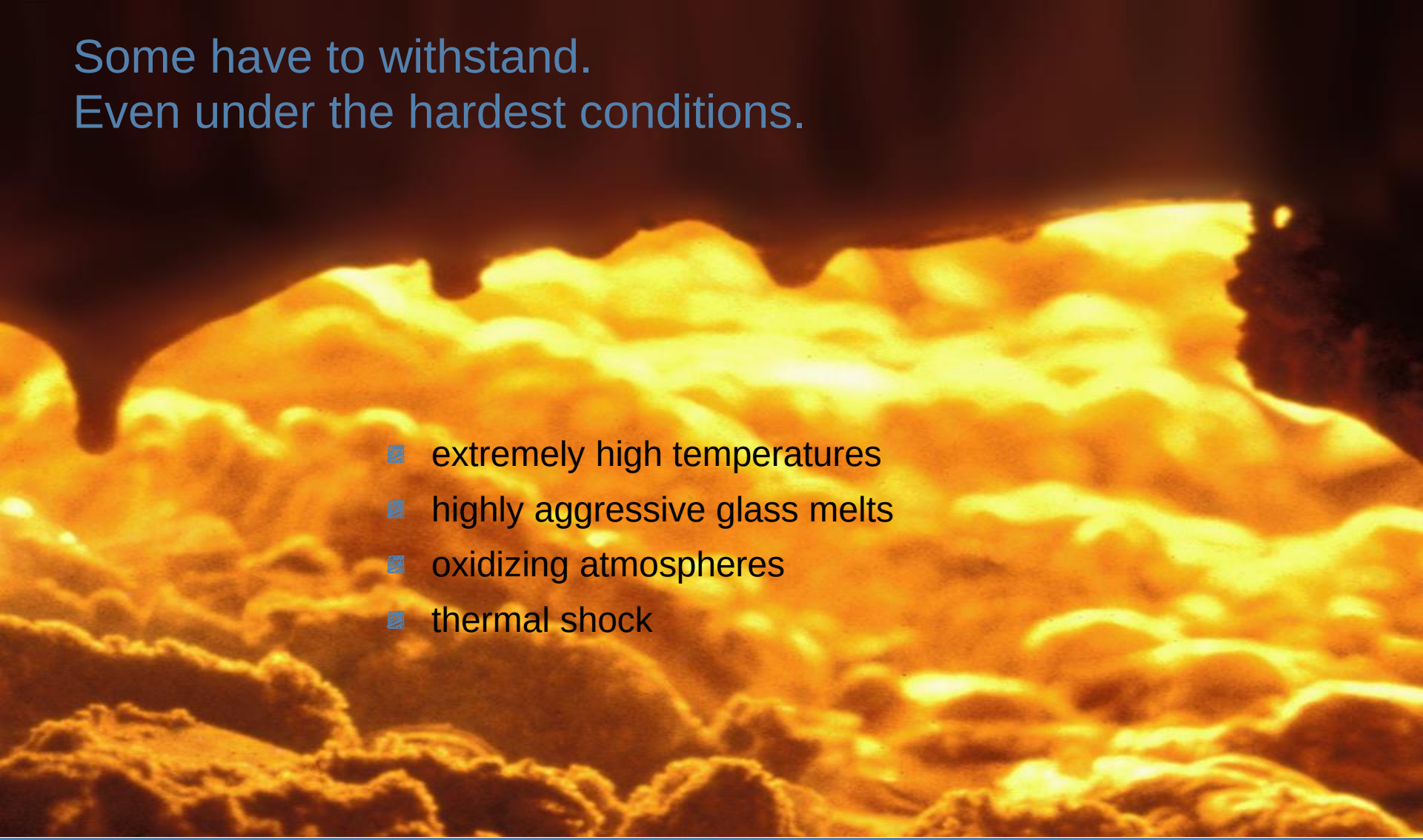


Electrical heating and boosting.
Top performance.



- precise process control: more flexibility
- homogeneous melt: optimum quality
- lower emissions: environmentally friendly

Some have to withstand.
Even under the hardest conditions.



- extremely high temperatures
- highly aggressive glass melts
- oxidizing atmospheres
- thermal shock

Molybdenum & $MoZrO_2$.
Your special force in the glass tank.



- melting point 2620˚C / 4748˚F
- high temperature strength
- optimized creep behavior
- excellent corrosion resistance against glass melts

Molybdenum & $MoZrO_2$.
Your special force in the glass tank.



- melting point 2620˚C / 4748˚F
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Highest corrosion resistance.
Extra hard and dense surface.

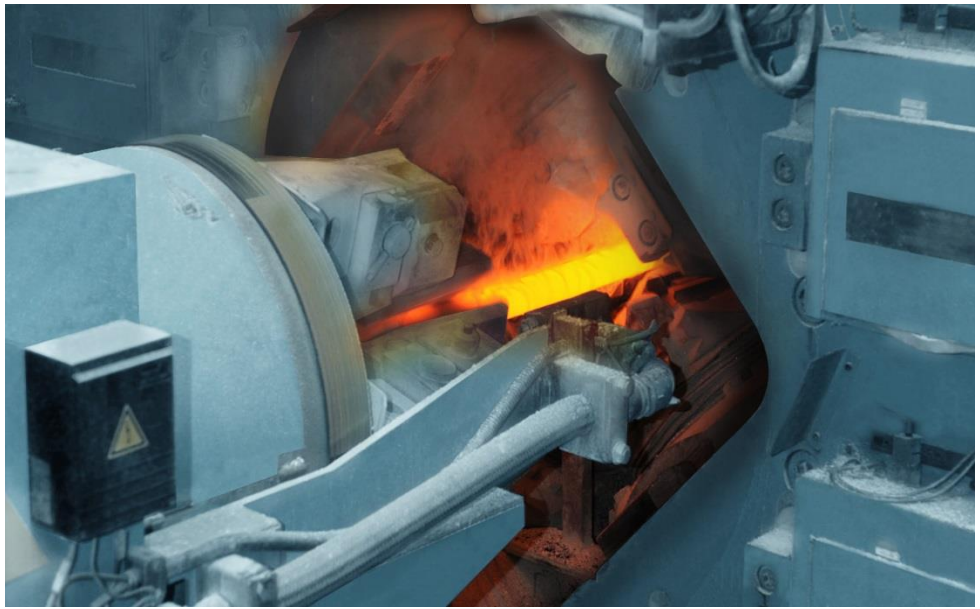
Advanced radial forging and hot rolling processes guarantee:



- tight tolerances on thickness and diameter
- optimum straightness and flatness
- excellent surface wear resistance
- longer service-life

Highest corrosion resistance.
Extra hard and dense surface.

Advanced radial forging and hot rolling processes guarantee:



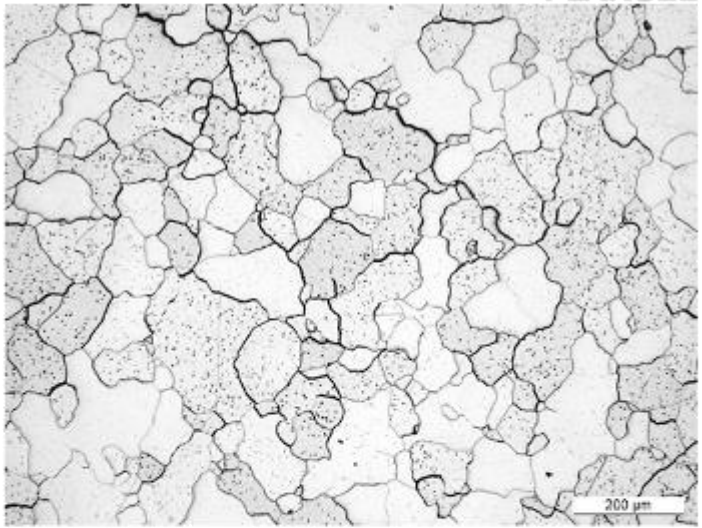
- tight tolerances on thickness and diameter
- optimum straightness and flatness
- excellent surface wear resistance
- longer service-life

Optimized creep strength.
Unaffected operation.

Coarse grain-structure of PLANSEE molybdenum minimizes bending during operation:

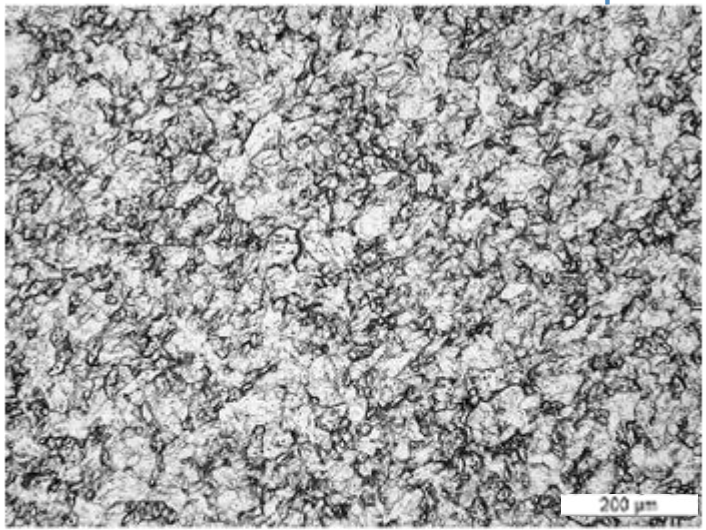
- smooth operation
- high efficiency
- minimum wear

PLANSEE



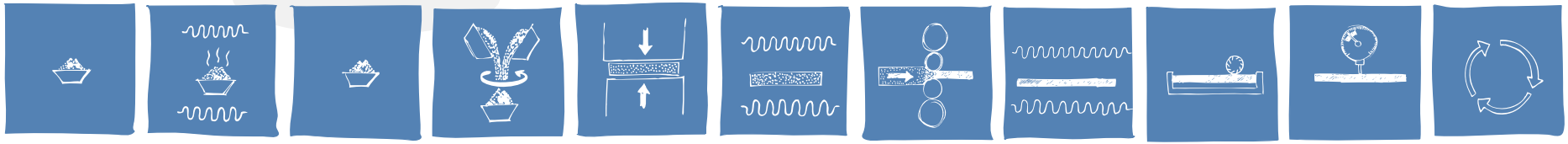
Coarse grain-structure for best creep-resistance

Competitor



Fine grain-structure with low creep-resistance

Production process



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

100 % TRACEABILITY

We use powder metallurgical methods to manufacture our refractory metals and composite materials. The Plansee Group covers the entire production process, from ore concentrates right to the customer-specific component.

Using pure molybdenum oxide, we guarantee the highest material quality.

For bubble free glass without any discoloration.

Availability.
Ex-stock delivery - Worldwide.



- standard dimensions via PLANSEE Express
- quick delivery of electrodes with metric threading or tapered design

Your wish is our command.
Customized finishing.



- dimensions, diameters, tolerances
- designs and threads
- surface condition
- cooling hole
- coatings

Certified quality.
No compromise.

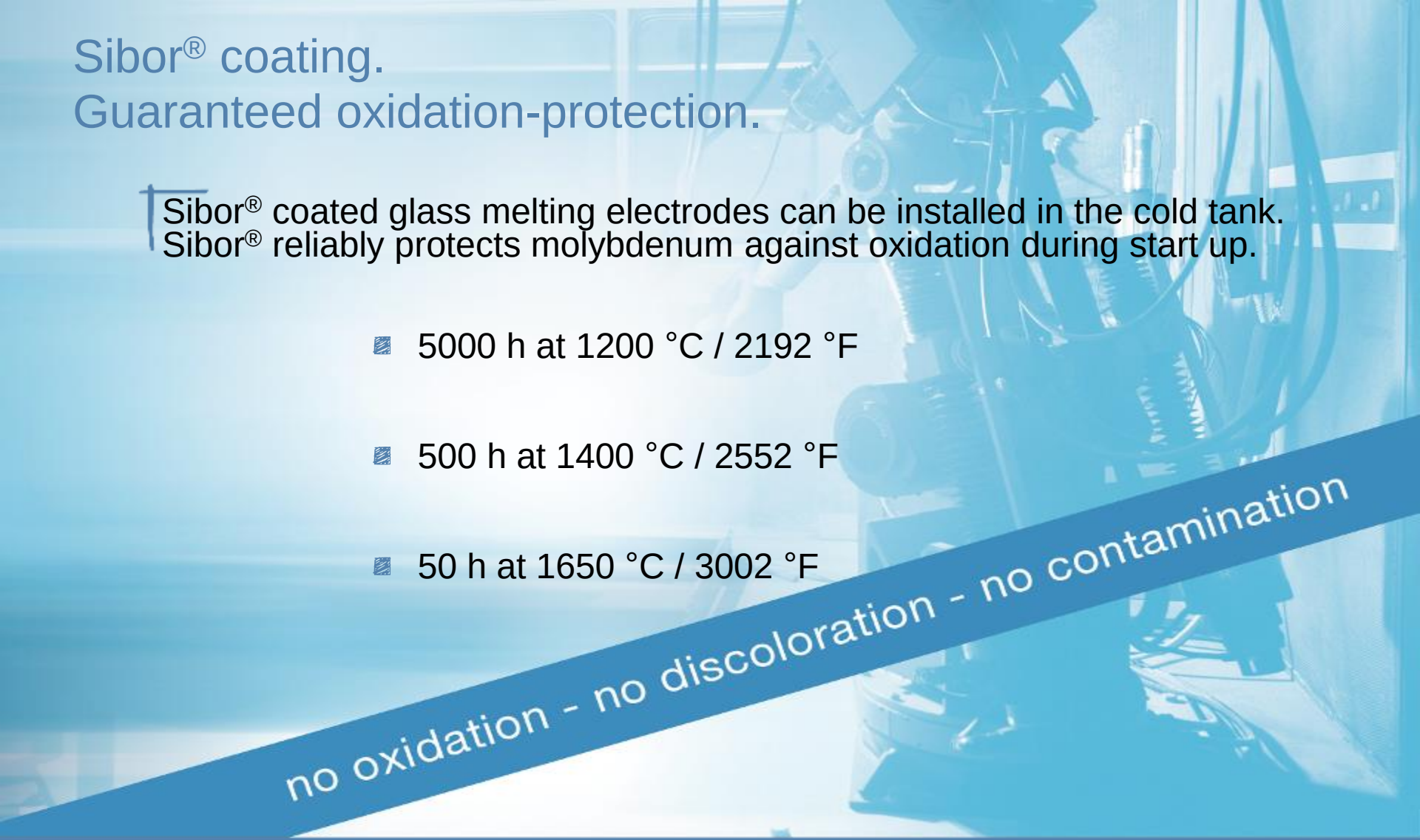
- 100% ultrasonic-tested
- batch analysis for purity and grain structure
- straightness, diameter and threading inspection



Sibor® coating.
Guaranteed oxidation-protection.

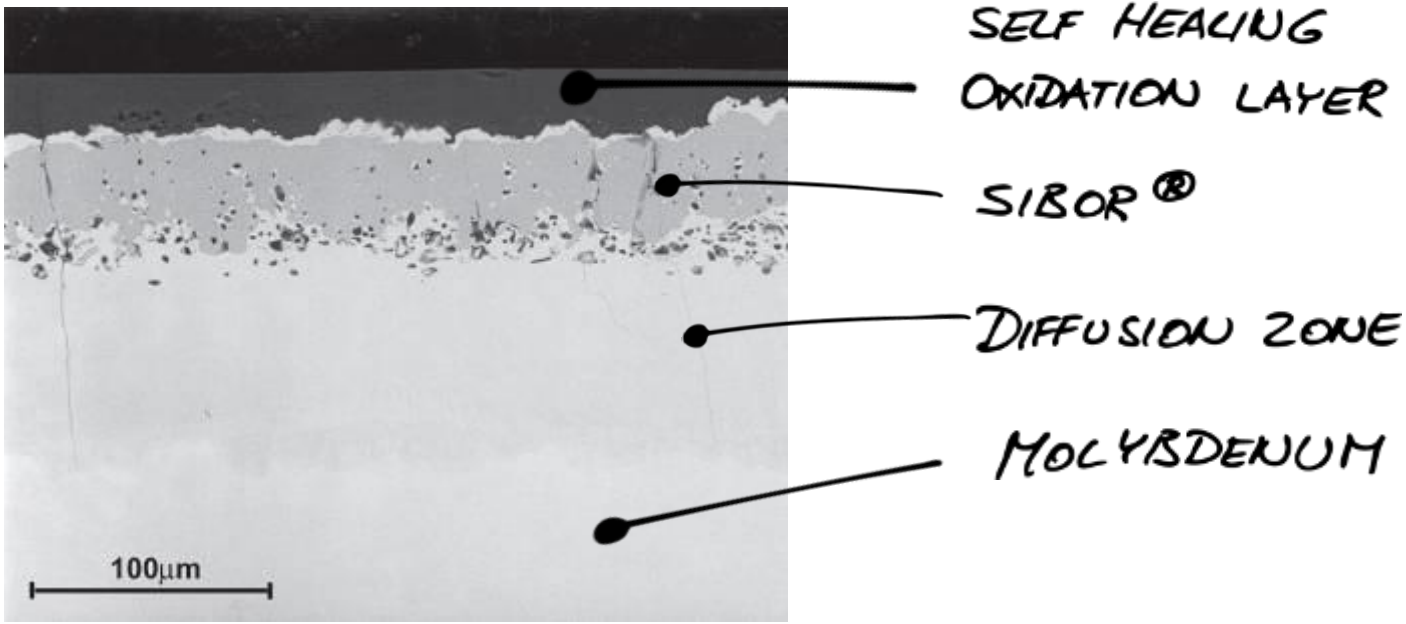
Sibor® coated glass melting electrodes can be installed in the cold tank.
Sibor® reliably protects molybdenum against oxidation during start up.

- 5000 h at 1200 °C / 2192 °F
- 500 h at 1400 °C / 2552 °F
- 50 h at 1650 °C / 3002 °F



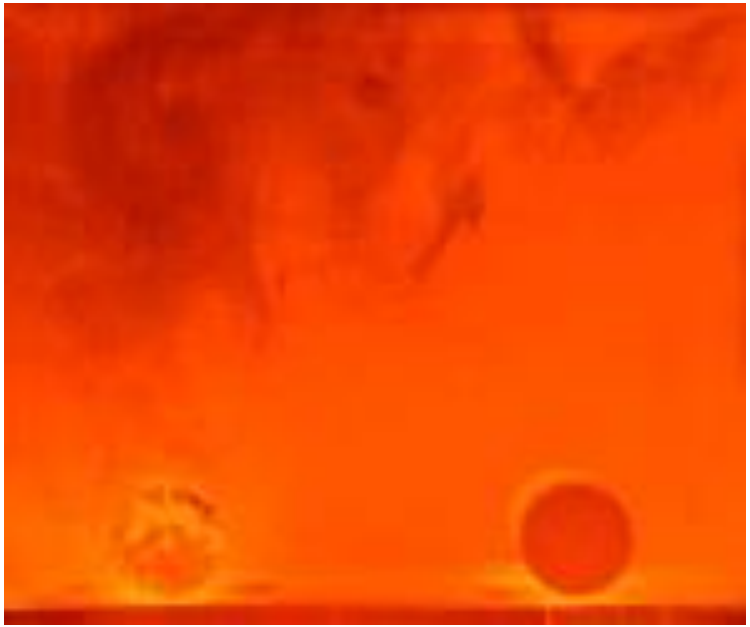
Sibor® coating.
Guaranteed oxidation-protection.

- The silicon (Si) and boron (B) based coating reacts with molybdenum and forms a dense and stable SiO_2 layer.



Sibor® on molybdenum electrodes. Safe and cost-effective.

SIBOR® coating reliably protects molybdenum from oxidation.



- Coated glass melting electrodes can be installed in the cold glass tank.

SIBOR® PASSES THE TEST

Plansee SE Reutte - Business Unit: Industries, Market Unit: Thermal Processes
Rudolf Holzknecht - Manager Application Group Glass & Quartz Glass Manufacturers
5th June 2012

MoZrO2 “a new material for GME”

$MoZrO_2$ – a new material for GME

PLANSEE

Demands on a perfect GME:

- High electrical conductivity
- High creep resistance up to 1500°C
- Good corrosion resistance against the glass melt
- No negative influence on the glass quality
- Good machinability
- Good handling

$MoZrO_2$ – a new material for GME

Demands on a perfect GME:

Shortly said:

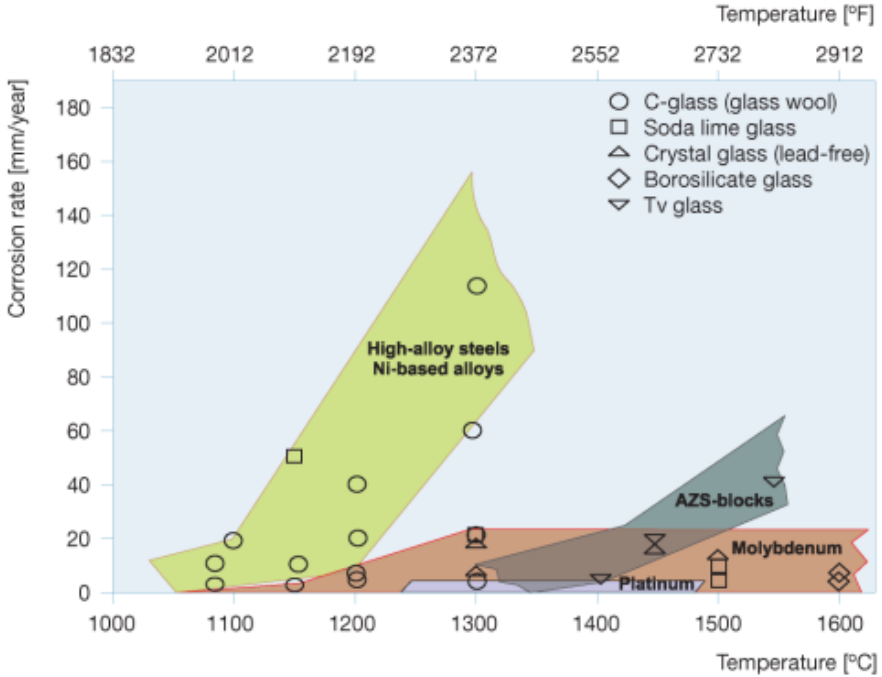
- Inexpensive
- Excellent performance
- Long lasting
- Easily available

$MoZrO_2$ – a new material for GME

Which materials can be used in a glass tank?

Refractory metals

- Molybdenum
- Tungsten
- Platinum



$MoZrO_2$ – a new material for GME

Which materials can be used in a glass tank?

Refractory metals

- Molybdenum is the first choice

or even better

PLANSEE improved Molybdenum

$MoZrO_2$

$MoZrO_2$ – a new material for GME

What are the properties of $MoZrO_2$?

- Same electrical conductivity as Molybdenum
- Higher creep resistance
- No negative influence on glass quality
- Good machinability
- **Higher corrosion resistance in many types of glass than pure Molybdenum**

$MoZrO_2$ – a new material for GME

PLANSEE

What are the properties of $MoZrO_2$?

Mechanical-Technological Properties of Mo, W and Mo 5 Vol.-% ZrO_2

	Creep Test 1600 °C; 15MPa Vacuum *	Notch Tensile Test 800 °C; Vacuum *		
Material Ø approx. 43 mm	Creep Rate [s^{-1}]	Tensile Strength [N/mm^2]	0.2-Proof Stress [N/mm^2]	Elongation [%]
Mo	4.4×10^{-6}	226	97	16.9
Mo 5% ZrO2	9.5×10^{-7}	335	246	6.3
W	1.2×10^{-7}	358	174	12.6

** Mean values of samples taken from the middle section and the edge of the rod.*

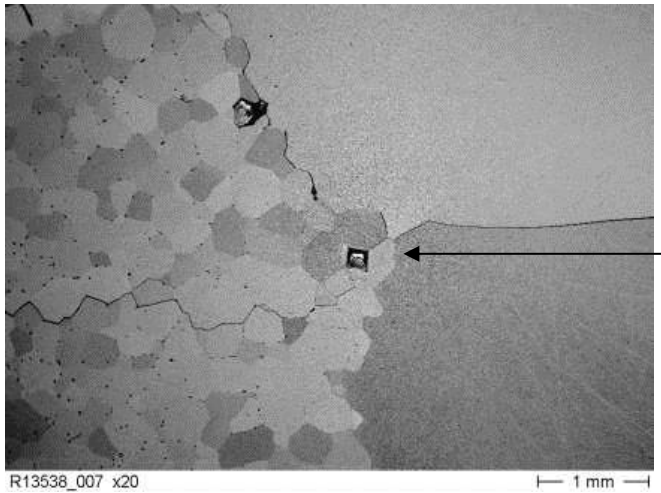
1 Martinz/Matej/Leichtfried, 2001, 15th Plansee Seminar Reutte, A
2 Matej et al, 2007, Glass Conference Teplice, CZ
3 Gohlke et al, 1997, 14th Plansee Seminar Reutte, A

$MoZrO_2$ – a new material for GME

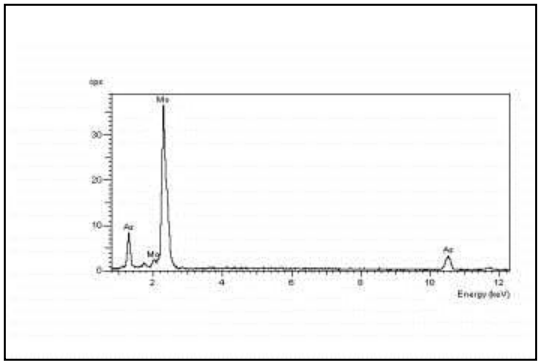
What are the properties of $MoZrO_2$?

Pure molybdenum and MoZrO2 rods were immersed in molten Antimony (Sb2O3) and cyclically heated to

- 12h isotherm at 1200° C
- 14h cycles of 880 to 1000°C /24 min each



Mo – Sb_2O_3 refined glass

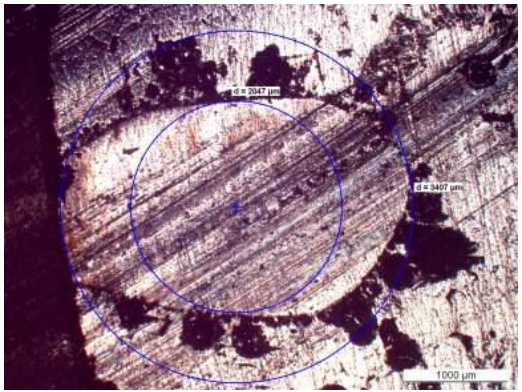


1 Martinz/Matej/Leichtfried, 2001, 15th Plansee Seminar Reutte, A
2 Matej et al, 2007, Glass Conference Teplice, CZ

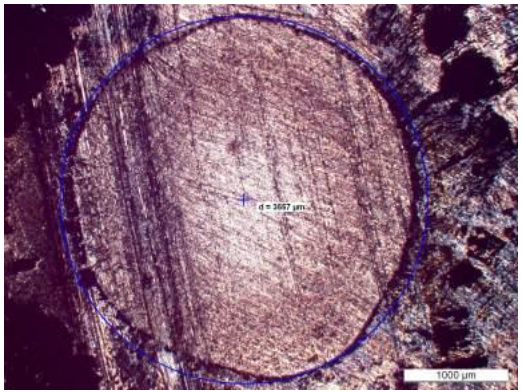
$MoZrO_2$ – a new material for GME

PLANSEE

Result: Increased corrosion resistance of $MoZrO_2$



Mo - Sb



Mo-ZrO_2 - Sb

Material	decrease of radius Radius in µm	relative corrosion ratio
Ø43mm		
	average decrease	
Mo	1440	1.6
$MoZrO_2$	882	1.0

Matej et al, 2007, Glass Conference Teplice, CZ
Average decrease out of 2 samples

$MoZrO_2$ – a new material for GME

PLANSEE

Result: Increased corrosion resistance of $MoZrO_2$

Test: corrosion behaviour in GREEN and white container glass

- under a load on 1 A/cm²
- at 1400°C
- for 12h

Result: weight loss in GREEN container glass melt

- pure molybdenum	14.75 mg/ electrode [1]
- $MoZrO_2$	10.15 mg/ electrode [1]

-30%

$MoZrO_2$ – a new material for GME

PLANSEE

Result: Increased corrosion resistance of $MoZrO_2$

Test: corrosion behaviour in green and WHITE container glass

- under a load on 1 A/cm²
- at 1400°C
- for 12h

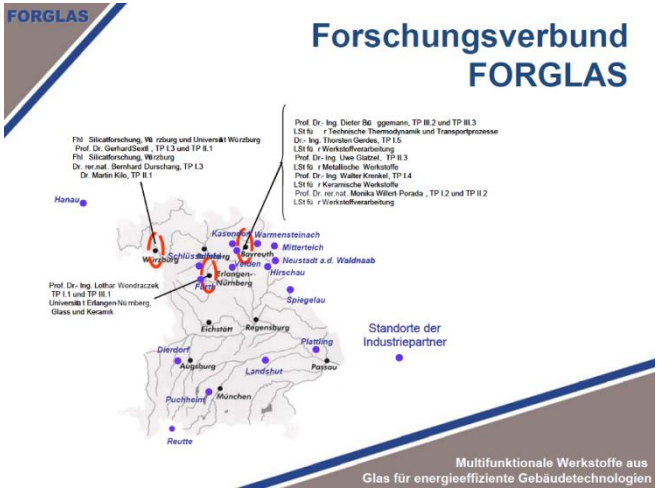
Result: weight loss in WHITE container glass melt

- pure molybdenum	17.0 mg/ electrode [1]
- $MoZrO_2$	14.9 mg/ electrode [1]

-13%

$MoZrO_2$ – a new material for GME

PLANSEE is member of the FORGLAS Project



FORGLAS

Project Status

Mo - $MoZrO_2$

UNIVERSITÄT BAYREUTH

Project Leader:
Marie-Christin Bölitz
University Bayreuht, Metallic Material

Werkstoffe Metallische

$MoZrO_2$ – a new material for GME

PLANSEE

Test procedures:

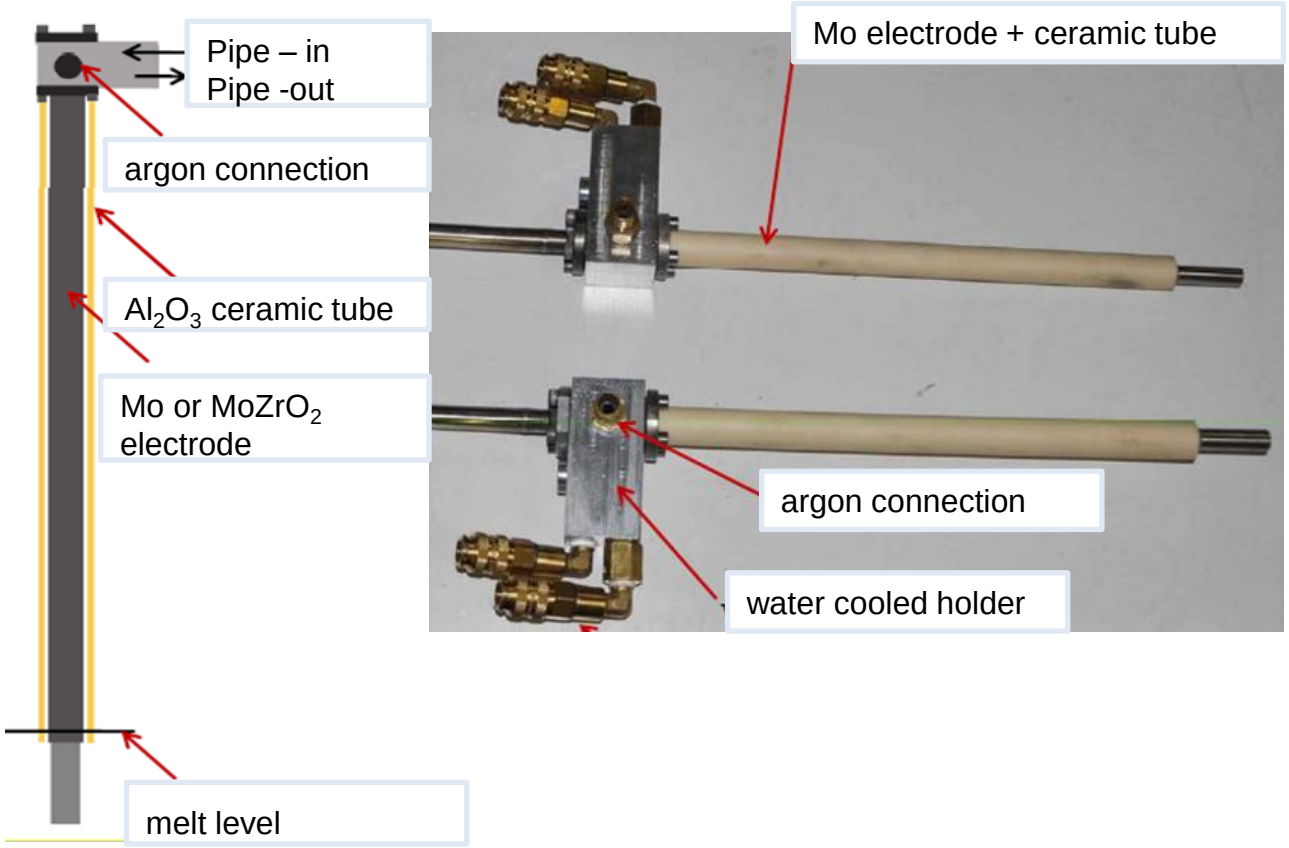
Molybdenum GME and $MoZrO_2$ GME

were immersed in molten soda-lime glass with antimony (Sb_2O_3) refining agent

- 24h at 1435°C, 50Hz, 1A/cm²
- 72h at 1435°C, 50Hz, 1A/cm²

$MoZrO_2$ – a new material for GME

Test procedures:



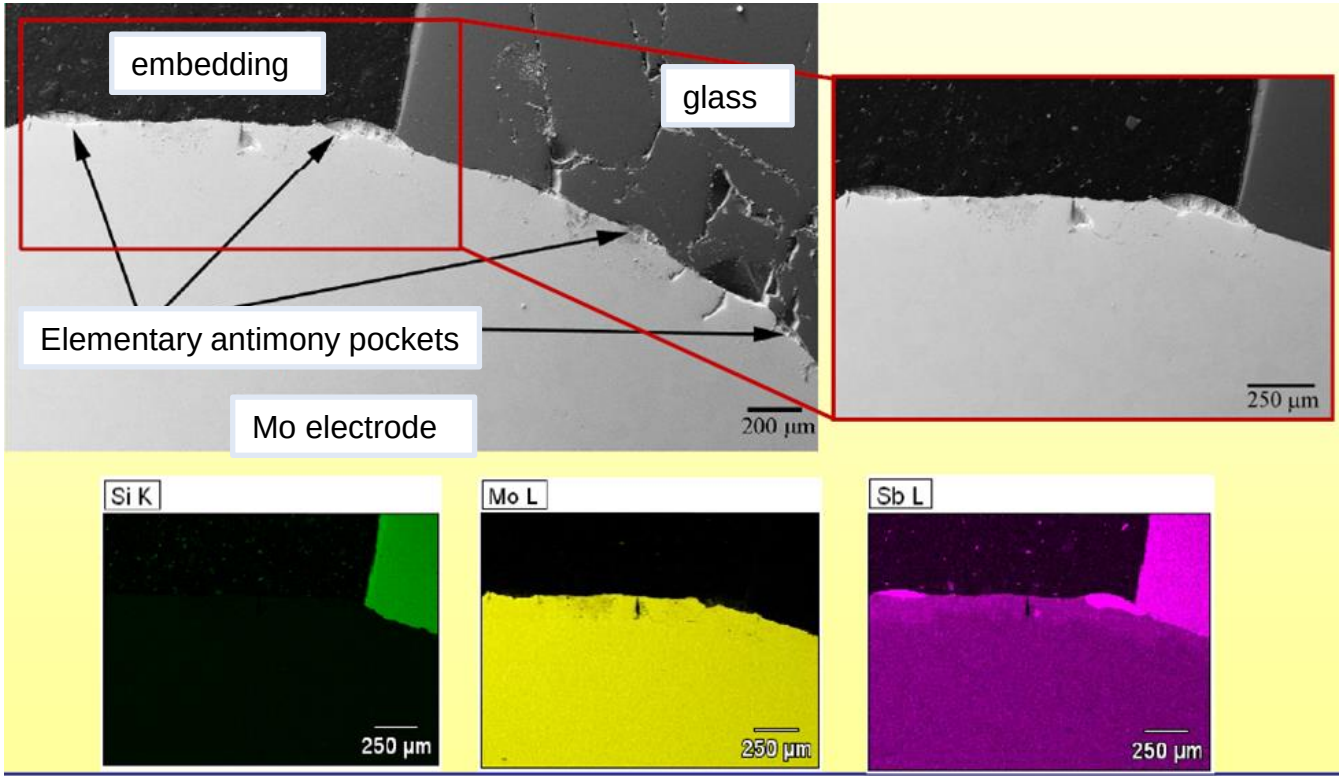




$MoZrO_2$ – a new material for GME

Molybdenum GME

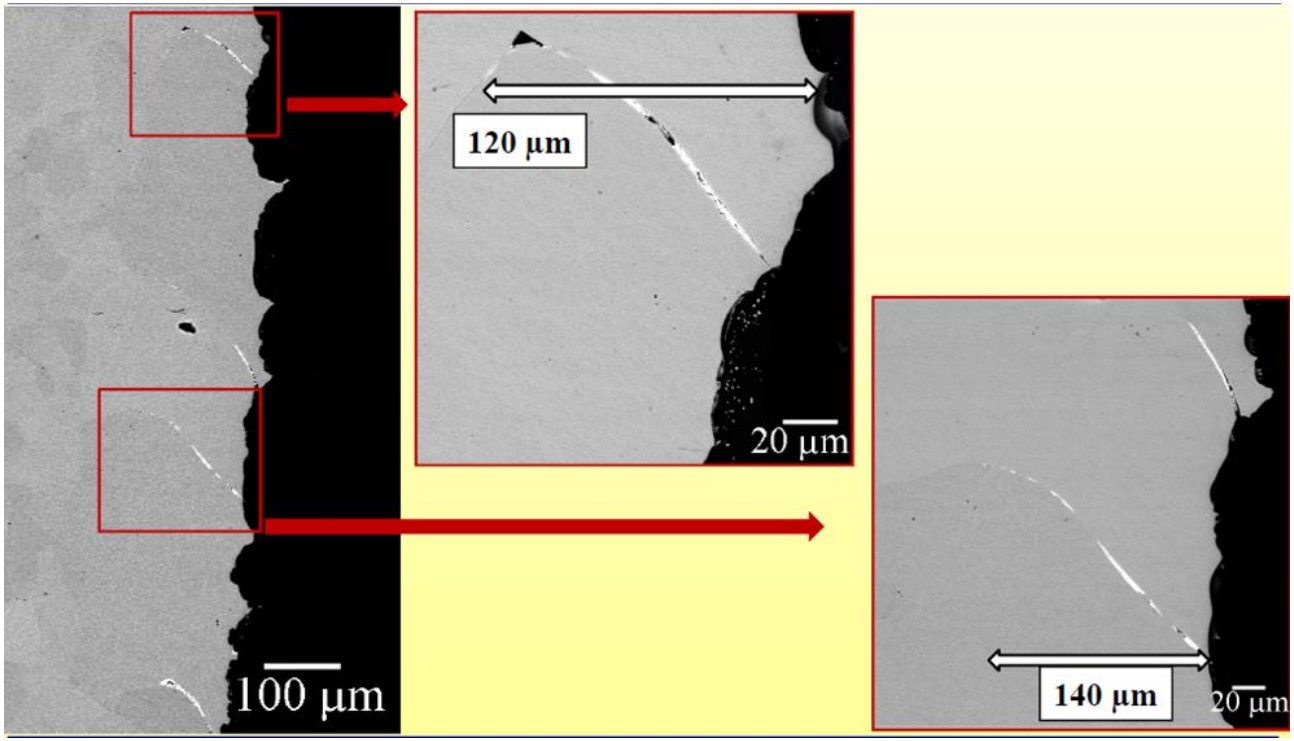
after **24h** in soda-lime glass with antimony (Sb_2O_3) refining agent at 1435°C, 50Hz, 1A/cm²



$MoZrO_2$ – a new material for GME

Molybdenum GME

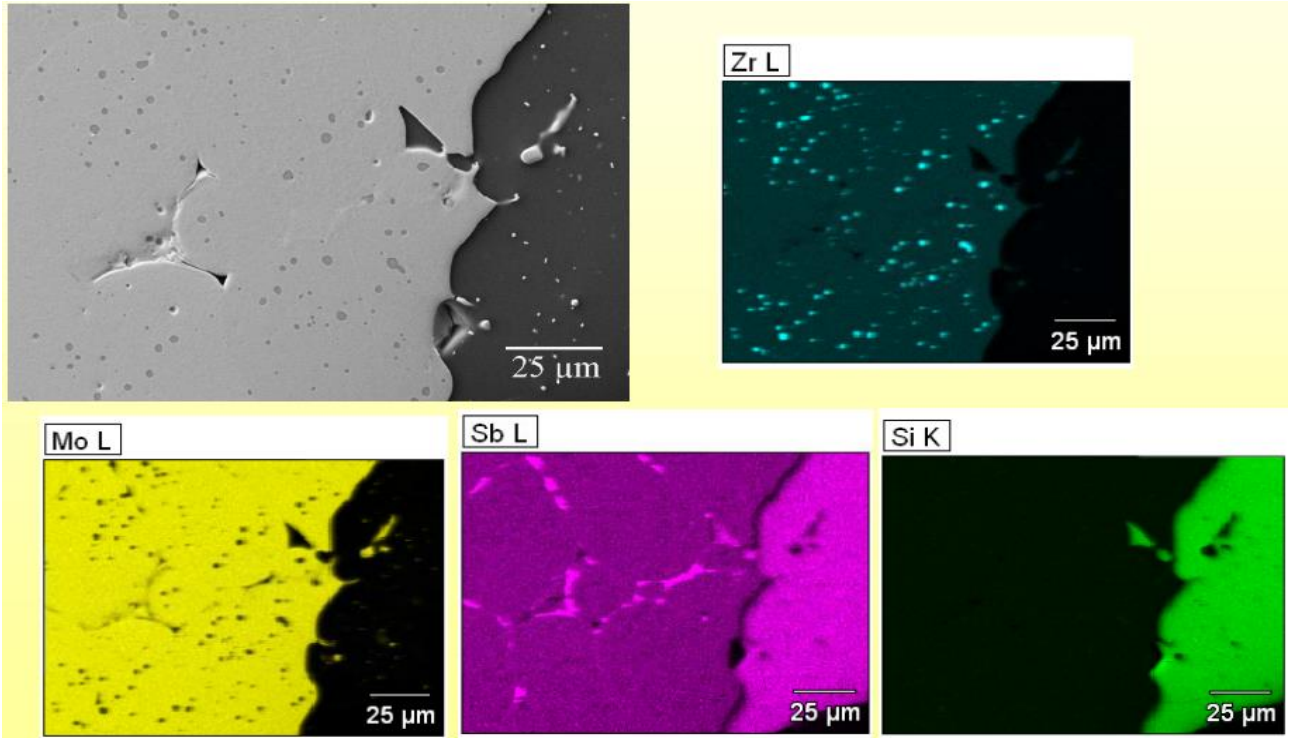
after **72h** in soda-lime glass with antimony (Sb_2O_3) refining agent at 1435°C, 50Hz, 1A/cm²



$MoZrO_2$ – a new material for GME

$MoZrO_2$ GME

after **72h** in soda-lime glass with antimony (Sb_2O_3) refining agent at 1435°C, 50Hz, 1A/cm²



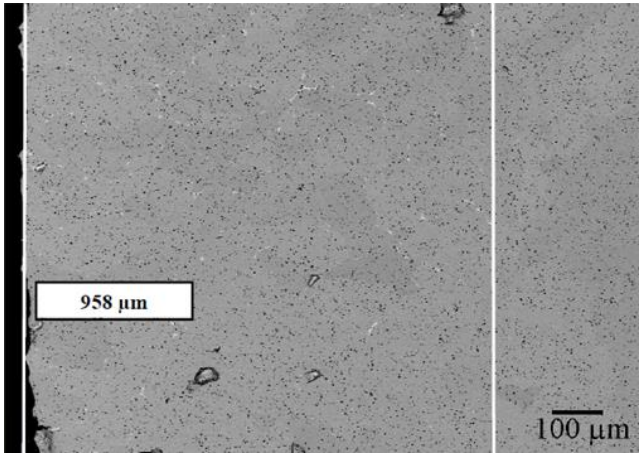
$MoZrO_2$ – a new material for GME

$MoZrO_2$ GME

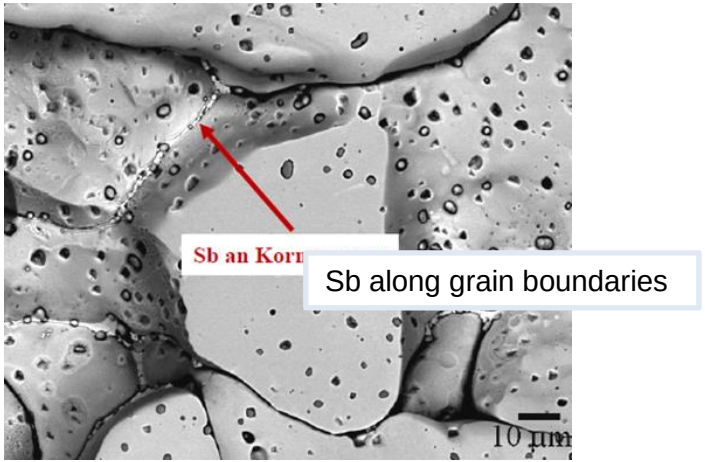
after **72h** in soda-lime glass with antimony (Sb_2O_3) refining agent at 1435°C, 50Hz, 1A/cm²

- Sb can be detected on the grain boundaries only
  (it can be clearly seen on the RE photo with the Z-contrast)

- after 72h in $MoZrO_2$ the antimony can be found only very finely distributed along the grain boundaries (whereas the antimony in Molybdenum forms “pockets”)



Antimony only detectable along the grain boundary on $MoZrO_2$ very finely distributed

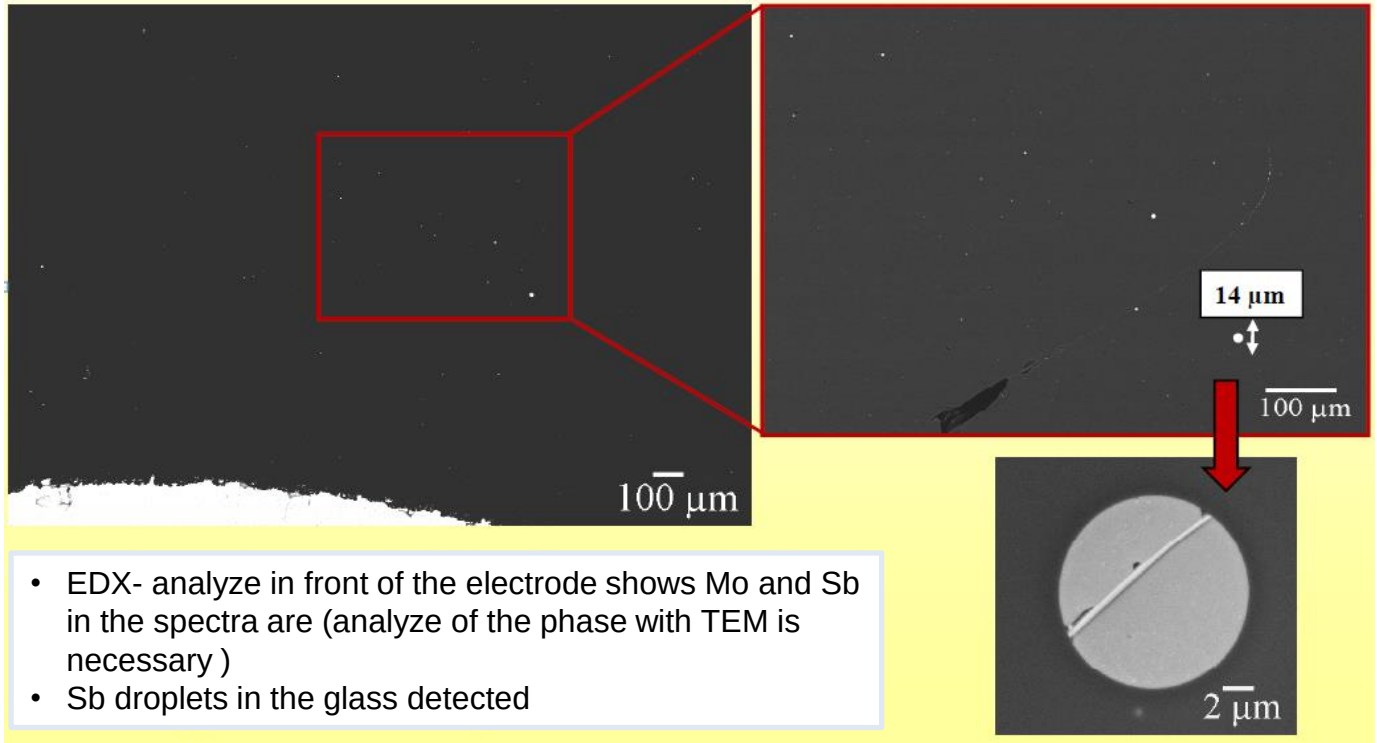


RE photo shows SB (white) along the grain boundaries

$MoZrO_2$ – a new material for GME

- Soda-lime glass with antimony (Sb_2O_3) refining agent

after test at 1435°C, 50Hz, 1A/cm² with Molybdenum/$MoZrO_2$ GME

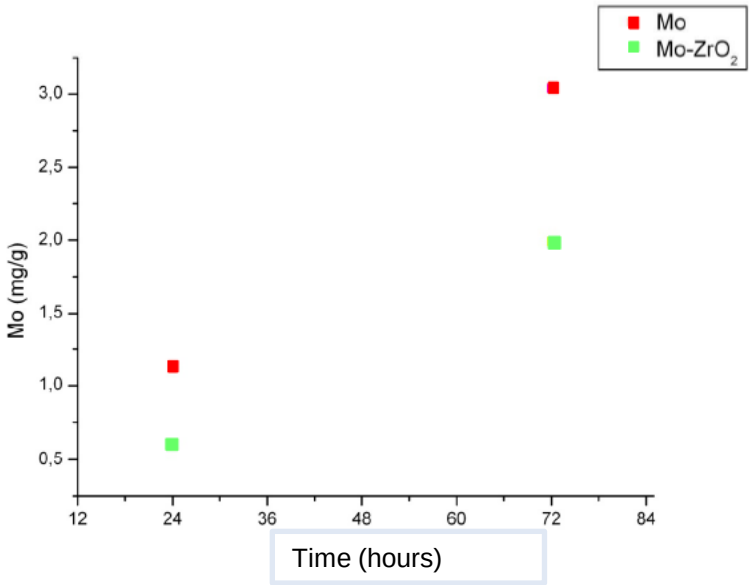


- EDX- analyze in front of the electrode shows Mo and Sb in the spectra are (analyze of the phase with TEM is necessary)
- Sb droplets in the glass detected

$MoZrO_2$ – a new material for GME

- Soda-lime glass with antimony (Sb_2O_3) refining agent

after test at 1435°C, 50Hz, 1A/cm² with Molybdenum/$MoZrO_2$ GME



- after 24h:
  $MoZrO_2$ = 0,60mg/g
  Mo = 1,12mg/g

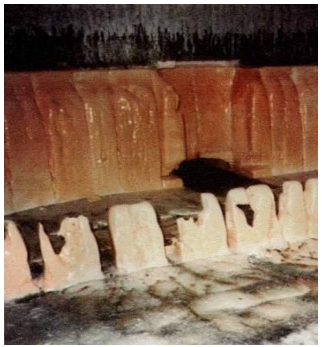
  -47% (MoZrO2 vs. Moly)

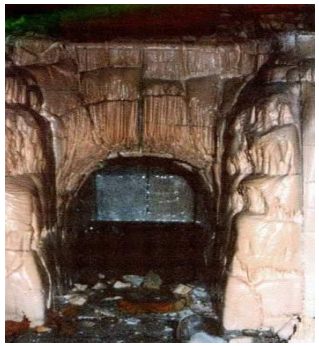
- after 72h:
  $MoZrO_2$ = 1,99mg/g
  Mo = 3,04mg/g

  -35% (MoZrO2 vs. Moly)

- History, facts and management, Sites, Market Units and products
- Research and development, Sustainability and additional benefits
- Materials, Production process
- Glass melting equipment & technology
- Glass melting electrodes
- **“GTR” Glass Tank reinforcement**
- Stirrer
- Quartz glass and Glass wool production

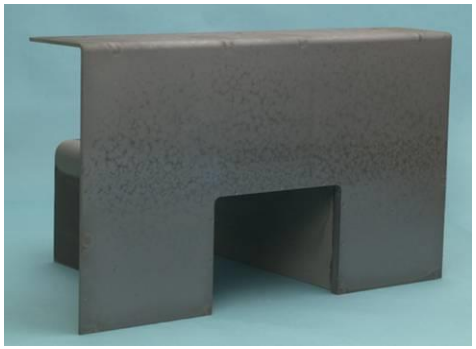
Molybdenum / Sibor®
Glass Tank Reinforcement





During the course of the glass tank's service life, the refractory bricks in critical areas such as doghouse, wall, bubbler and throat influence the quality of the glass and the service life.

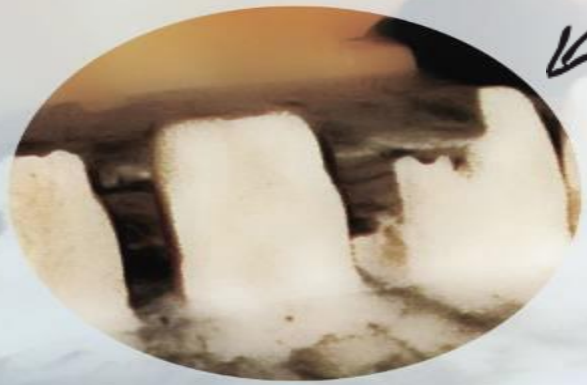
Solution:
GTR made out of Molybdenum & Sibor® coated





Severe attack from molten glass. Be prepared.

- Abrasion and erosion of the refractory bricks affect the quality of the glass and shorten the entire furnace campaign.

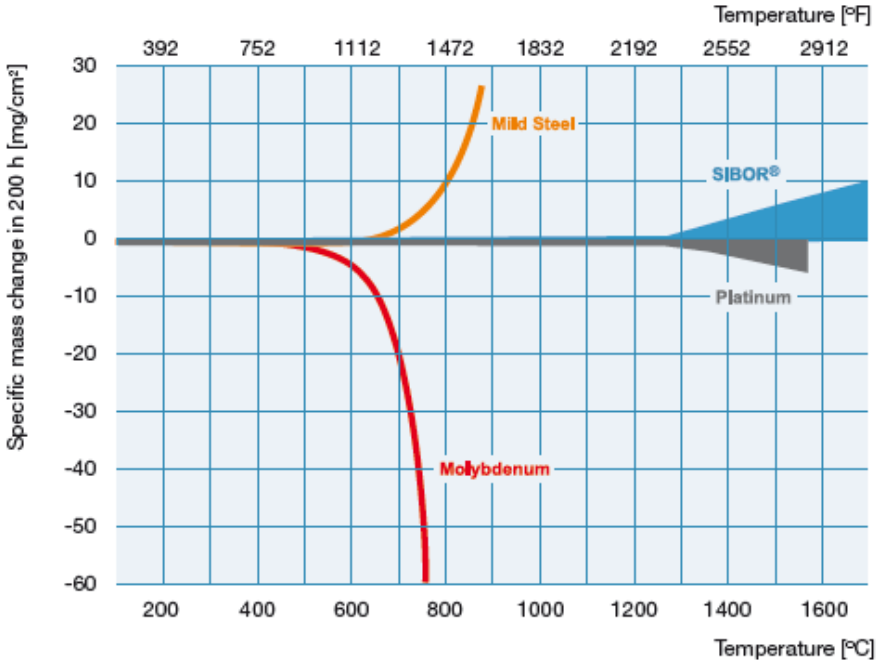


UNPROTECTED WALL AFTER COOLING DOWN THE TANK

Molybdenum / Sibor®
Glass Tank Reinforcement

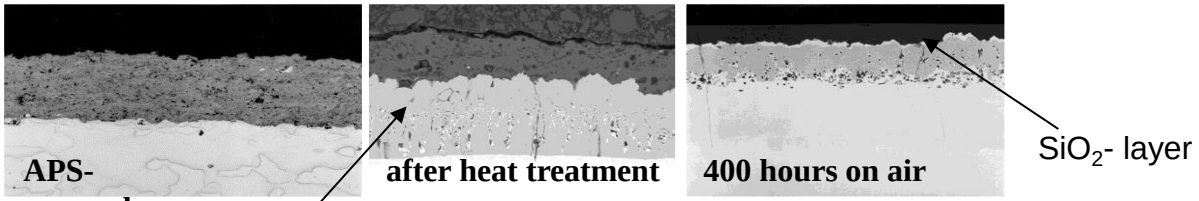
Sibor® - an oxidation protective coating for Molybdenum

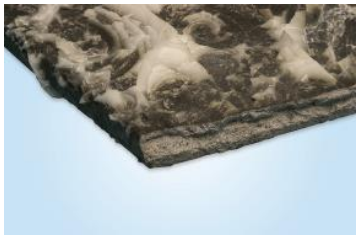
Protecting the material from oxidation during start-up, Sibor® coating clears the way.



Molybdenum / Sibor®
Glass Tank Reinforcement

Sibor® - an oxidation protective coating for Molybdenum



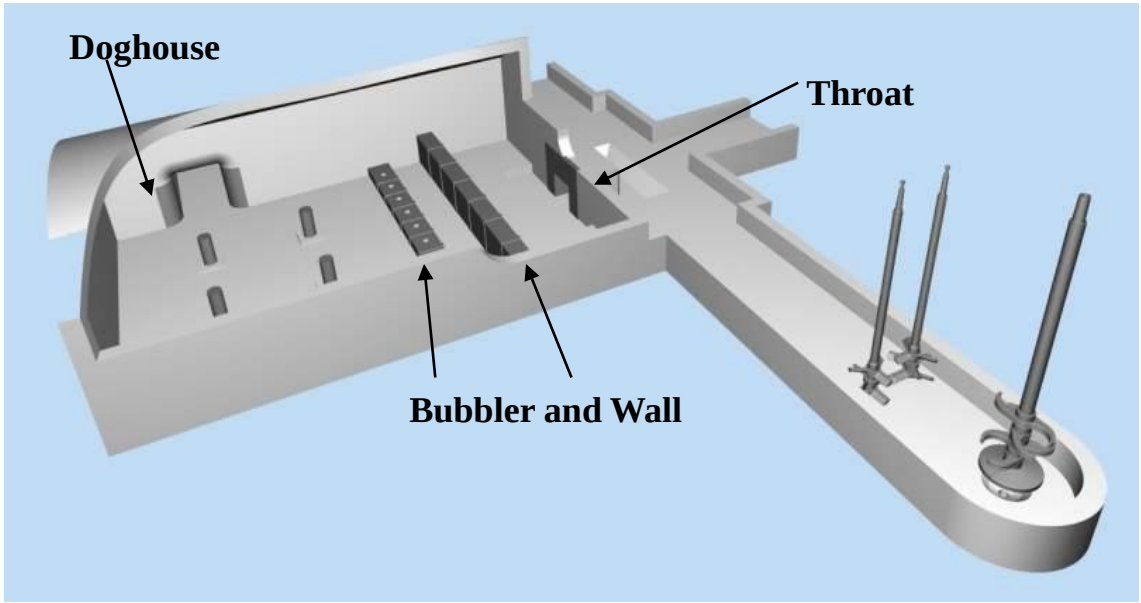


Mo-SHEET AFTER THE CAMPAIGN

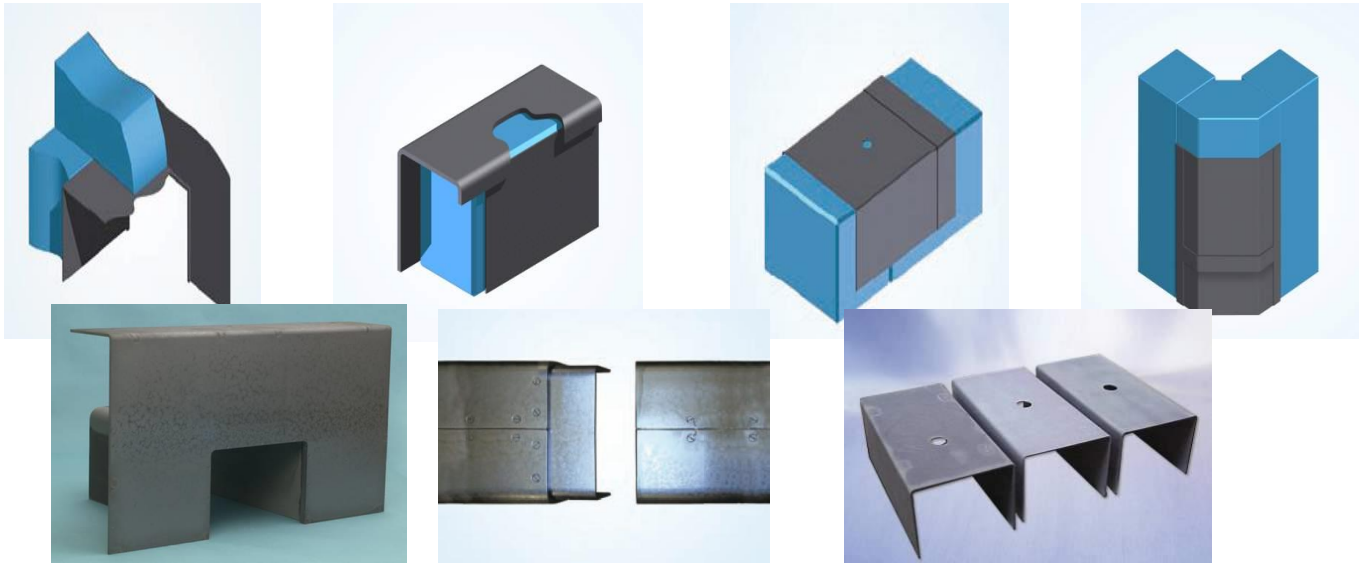
no oxidation, no discoloration, no contamination

Molybdenum / Sibor®
Glass Tank Reinforcement

GTR made out of Molybdenum with Sibor® coating for Throat, Wall, Bubbler and Doghouse



Molybdenum / Sibor®
Glass Tank Reinforcement



Molybdenum / Sibor®
Glass Tank Reinforcement

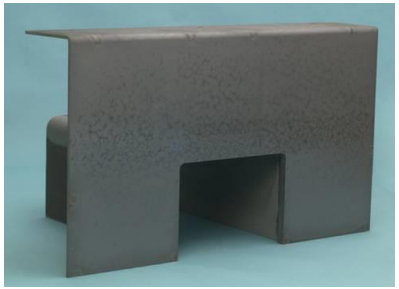
GTR made out of Molybdenum with Sibor® coating for Throat, Wall, Bubbler and Doghouse

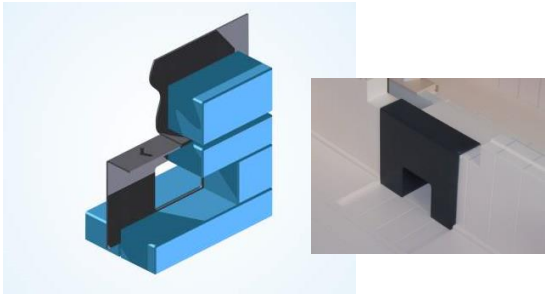
Characteristics:

- 6 to 14 mm thick Mo sheet
- Straightness of the sheet <1mm/m
- Tolerance on dimensions +/-0,8mm
- Sibor® - coating 180 +/- 30 µm thick (APS spraying)
- Multiple piece construction

PLANSEE

Throat protection: Classic design





The classic design with front plate and U-channel. Front plate protects the wall as well as the gaps in the neighboring bricks.

Molybdenum / Sibor®
Glass Tank Reinforcement

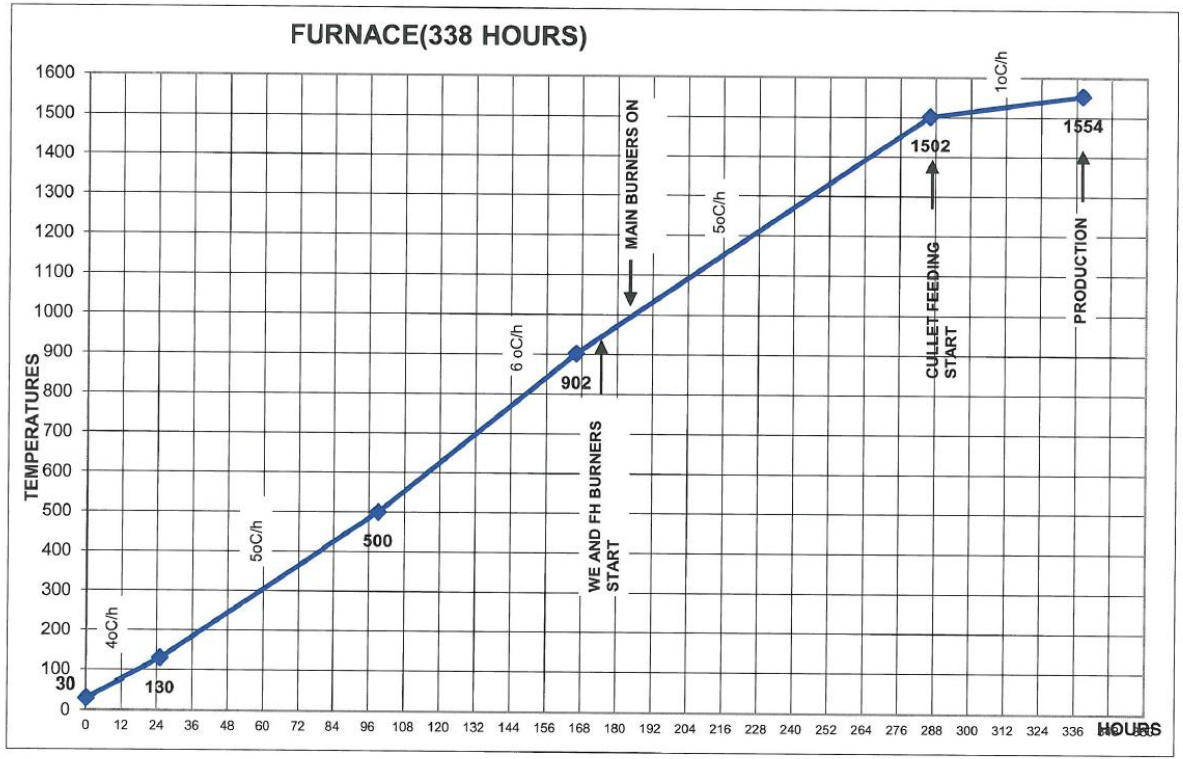


Molybdenum / Sibor®
Glass Tank Reinforcement

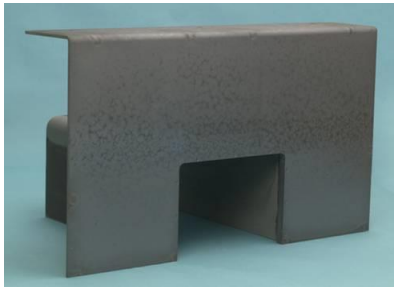


Molybdenum / Sibor®
Glass Tank Reinforcement

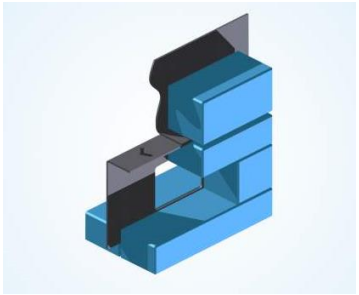
Temper Curves



Throat protection: Advanced design

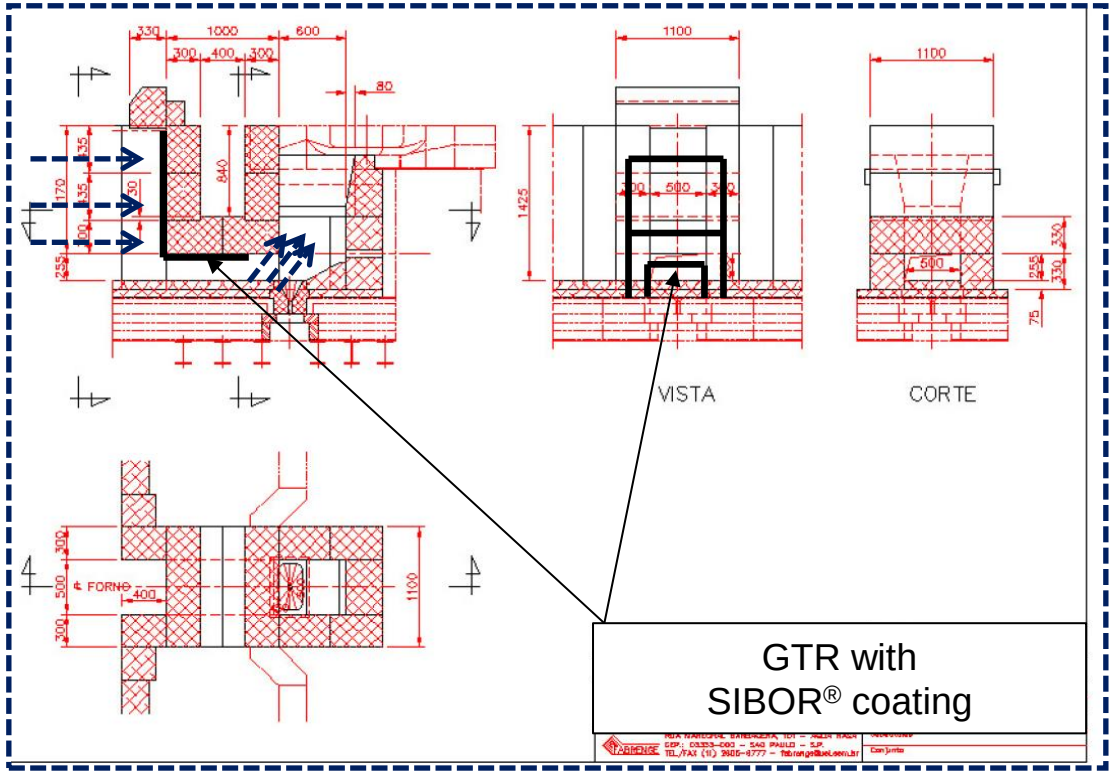




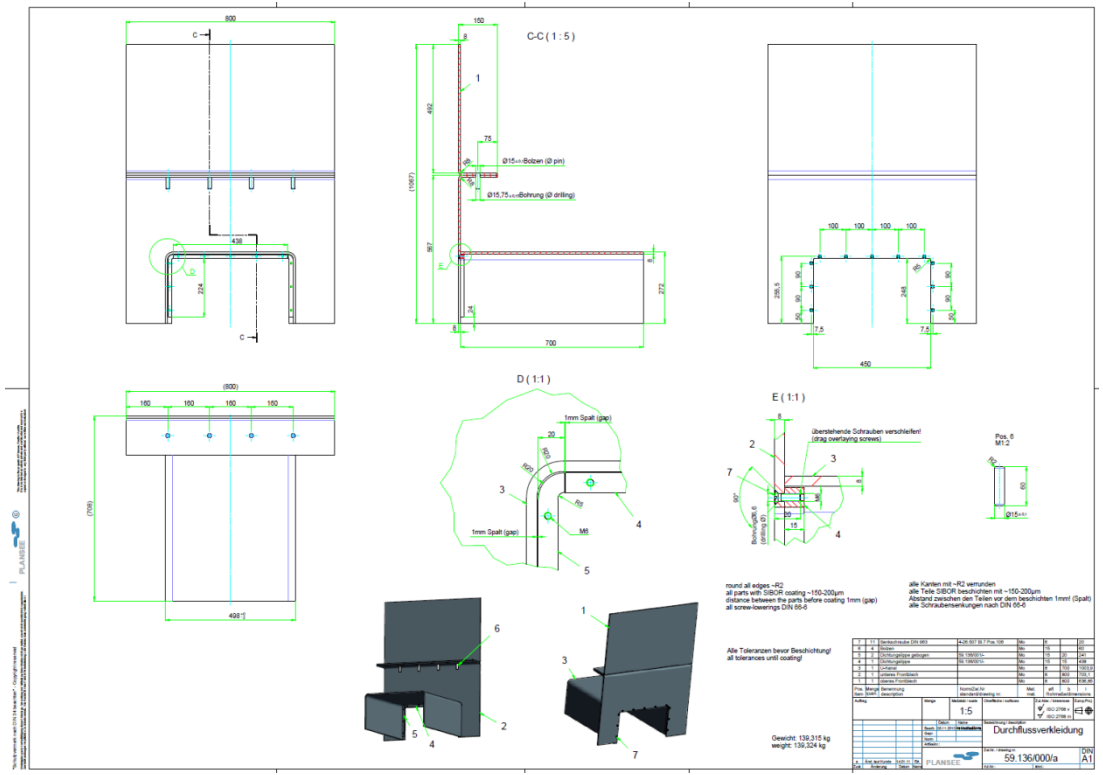


The advanced design with front plate, U-channel and L- shaped front plate protects the wall as well as the gaps in the neighboring bricks on top and at the side.

Molybdenum / Sibor®
Glass Tank Reinforcement

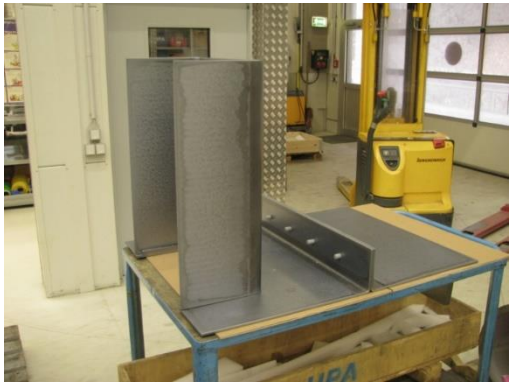


Molybdenum / Sibor®
Glass Tank Reinforcement



Molybdenum / Sibor®
Glass Tank Reinforcement









Molybdenum / Sibor®
Glass Tank Reinforcement





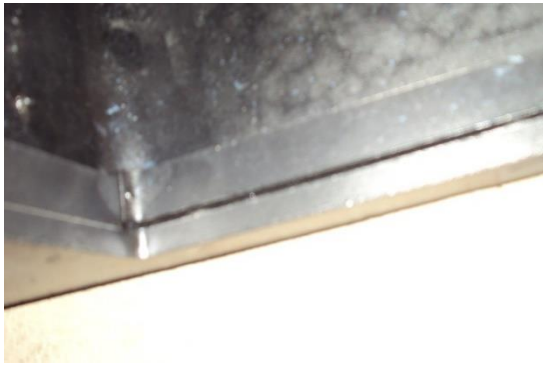




Molybdenum / Sibor®
Glass Tank Reinforcement









PLANSEE

Throat protection

In order to reduce that the Mo front plate can be washed out from behind in highly corrosive glasses such as borosilicate or opal glass, the

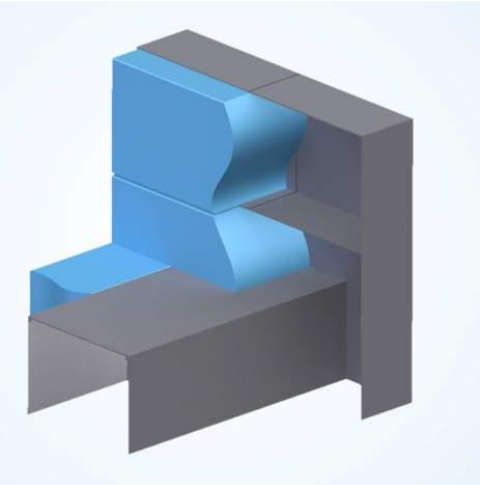
Box- Principle

can be applied

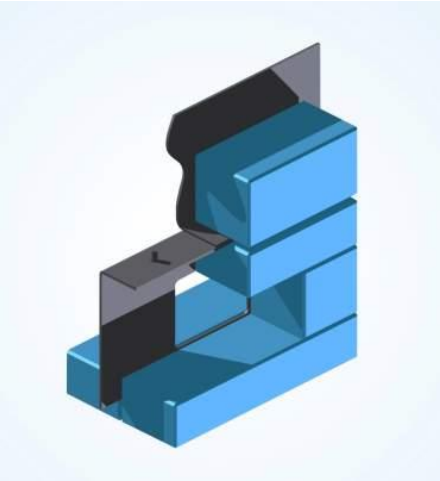
PLANSEE

Throat protection

With Box principle



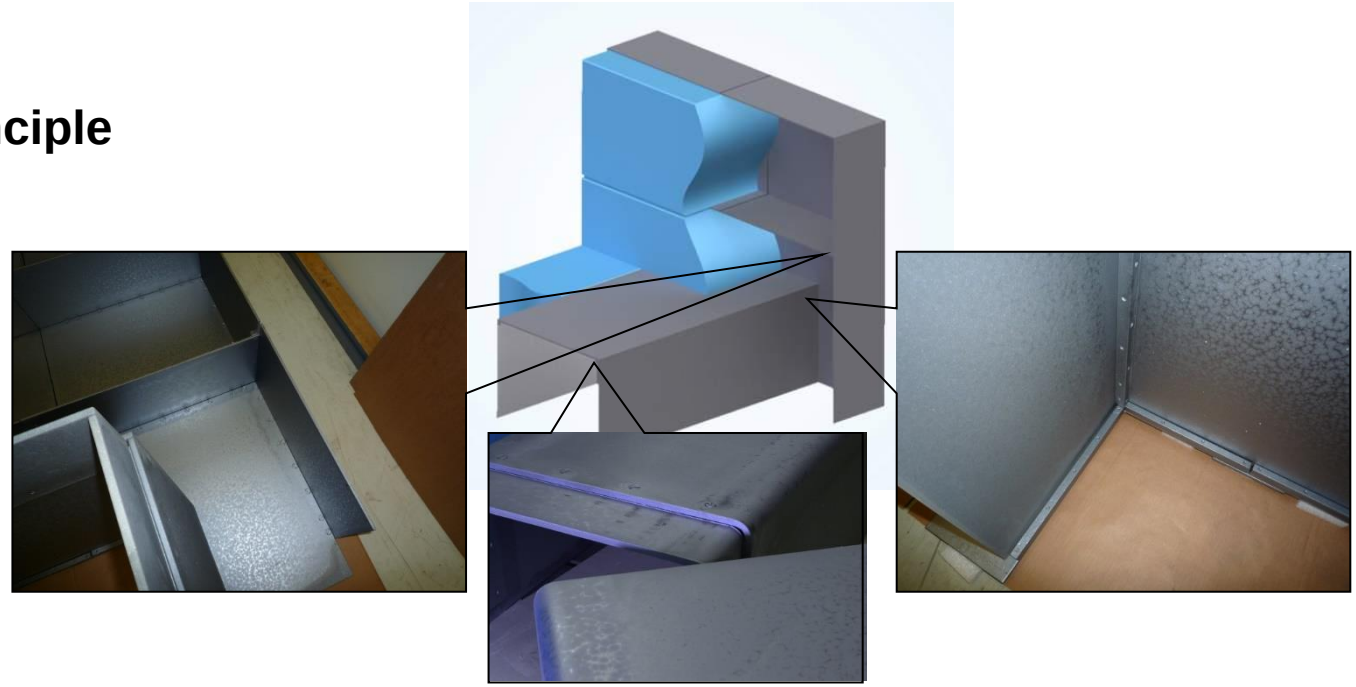
Without Box principle



Molybdenum / Sibor ®
Glass Tank Reinforcement

Throat protection

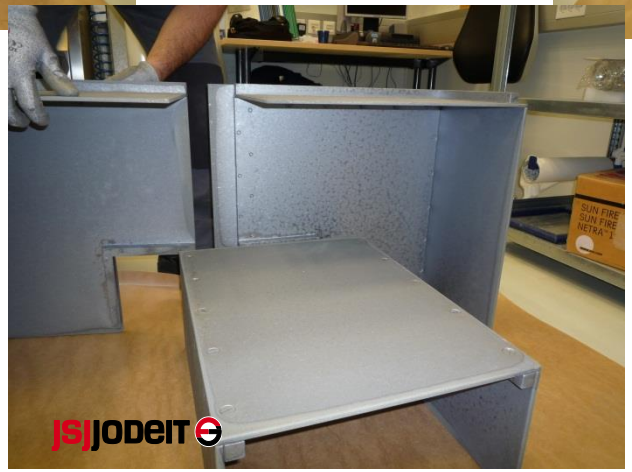
Box principle

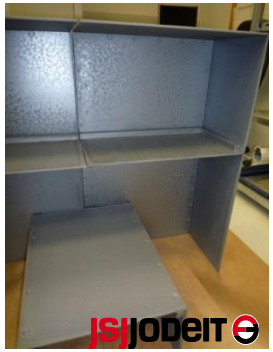


Molybdenum / Sibor®
Glass Tank Reinforcement









Molybdenum / Sibor®
Glass Tank Reinforcement



Molybdenum / Sibor®
Glass Tank Reinforcement

Advantages of the **Box Principle**

- Side “flaps” reduce washing out of the Mo front plate
- Multiple piece construction for easy assembly and handling
- Piece connections in 90°/screwed design leave less space for corrosive attacks
- The dimensional tolerances are tighter in comparison to the bent parts
- The 90°/screwed design offers an inner shape without radius. Therefore it is easy to fit to the bricks and reduce the need for brick shaping
- The Box Principle has already proved its quality in many campaigns in highly aggressive glasses

Molybdenum / Sibor®
Glass Tank Reinforcement

Weir Wall protection







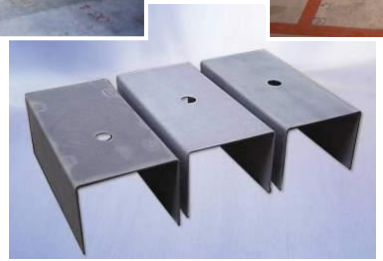


Molybdenum / SIBOR®
Glass Tank Reinforcement

Bubbler protection







References

Thermal Ceramics / FR

Verrerie du Courval / FR

Tableware producer / French

Borosilicate glass producer / French with English OEM

Holophane / USA

Alcan Packaging (former Wheaton) / USA

Crystalex / Czech Republic

Kavalier / Czech Republic

Opal- and Tableware producer / Germany

JSJ Jodeit / Germany

Pohris Fiber / Germany

Vidraria Anchieta / Brasil

….some which can not be named..

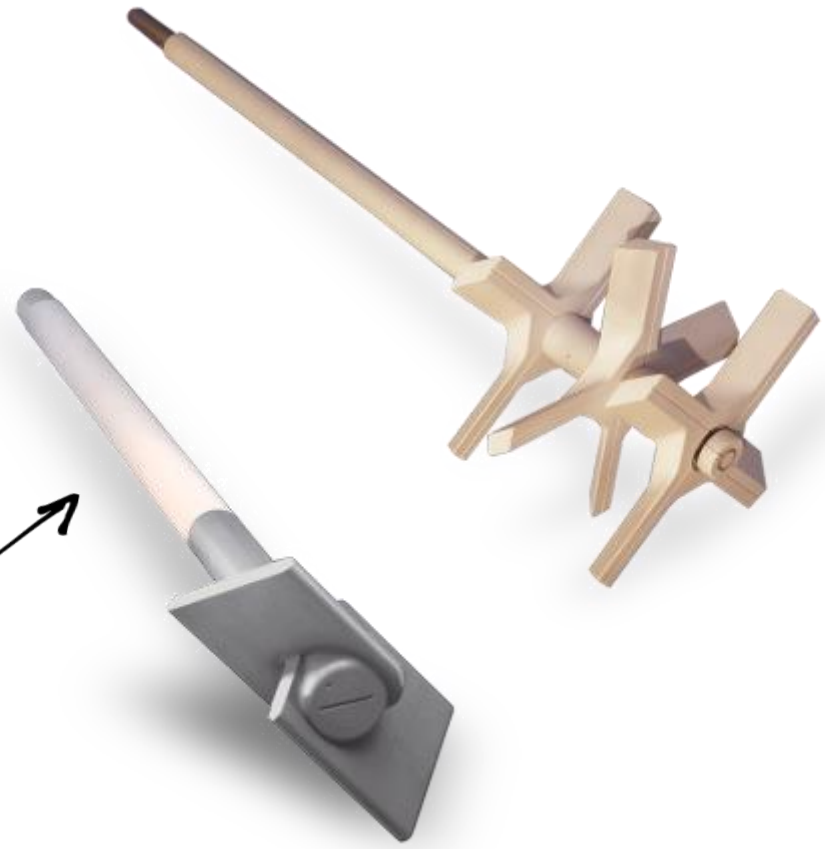
- History, facts and management, Sites, Market Units and products
- Research and development, Sustainability and additional benefits
- Materials, Production process
- Glass melting equipment & technology
- Glass melting electrodes
- “GTR” Glass Tank reinforcement
- **Stirrer**
- Quartz glass and Glass wool production

Molybdenum / Stirrer



Effective stirring.
Brilliant glass.

- high mechanical strength
- optimum thermal shock stability
- improved shaft to blade ratio
- no contamination



MOLYBDENUM CORES FOR PARTIALLY OR FULLY PLATINUM-CLAD STIRRERS

- History, facts and management, Sites, Market Units and products
- Research and development, Sustainability and additional benefits
- Materials, Production process
- Glass melting equipment & technology
- Glass melting electrodes
- “GTR” Glass Tank reinforcement
- Stirrer
- **Quartz glass and Glass wool production**

Effective stirring.
Brilliant glass.

- long lasting molybdenum and tungsten nozzles for glass, rock and ceramic wool spinning
  (with option of iridium or rhenium inserts)
- mandrel shafts and tubes for quartz glass production
  (riveted or single-piece)



References.
To name but a few.



Plansee Glass melting equipment.