

PLANSEE SE Reutte

Business Unit: Industries, Market Unit: Thermal Processes

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28th January 2014

“MoZrO₂– a new material for GME

“GTR” - Glass Tank Reinforcement Experience and Insights

Glassman South America 2014

Plansee Session

Fecomercio, Sao Paulo, Brazil

12th - 13th March 2014

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The key to high performance alloys: Pure powders.



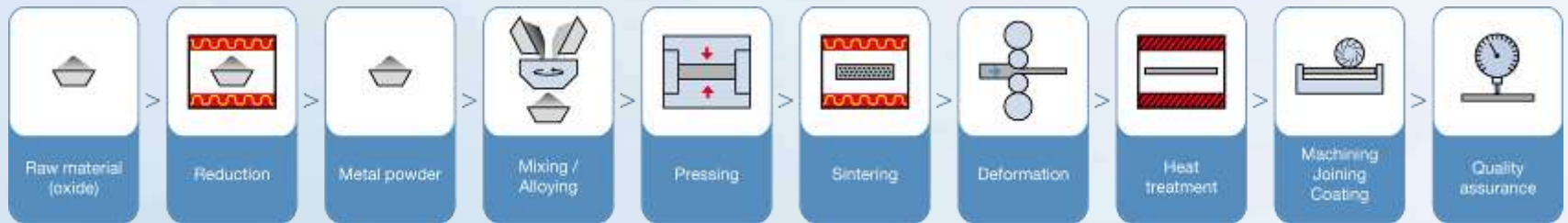
PLANSEE combines the advantageous properties of different metals: material solutions especially designed for customer needs.

Inhouse production.

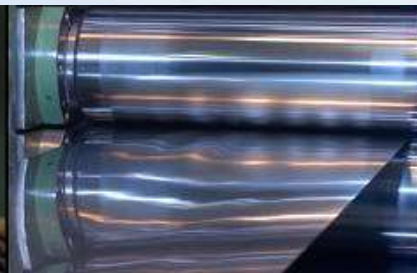
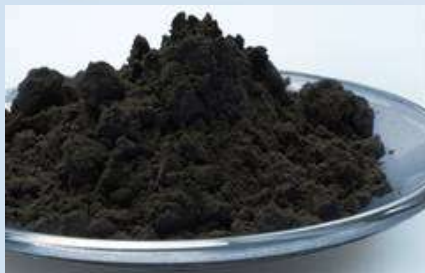
From powder to the final product.

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

For bubble free glass without any discoloration.



100 % TRACEABILITY



New Material for GME

Demands on a perfect GME:

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

New Material for GME

Demands on a perfect GME:

- PLANSEE GME:

-Guaranteed purity 99,97% typical 99,99%

-Guaranteed density >97% throughout whole diameter regardless to total diameter!

-Guaranteed coarse grain structure

-Guaranteed oxidation resistance with SIBOR[®] on request

New Material for GME

Demands on a perfect GME:

Shortly said:

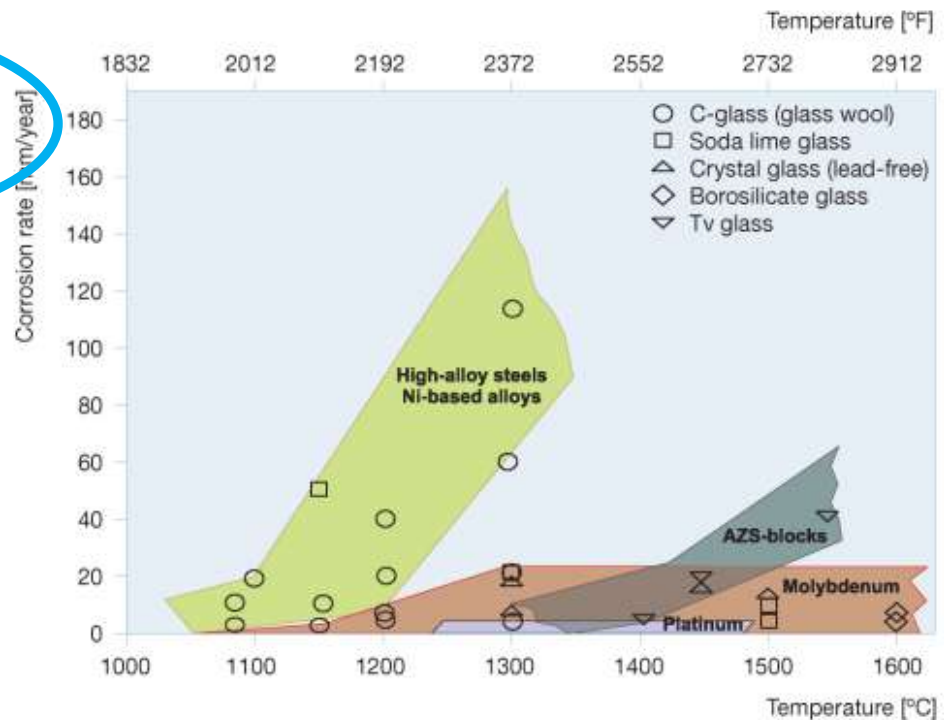
- Inexpensive
- Reliable
- Long lasting
- Easily available
- **Guaranteed performance by reliable supplier**

New Material for GME

Which materials can be used in a glass tank?

Refractory metals

- Molybdenum
- Tungsten
- Platinum

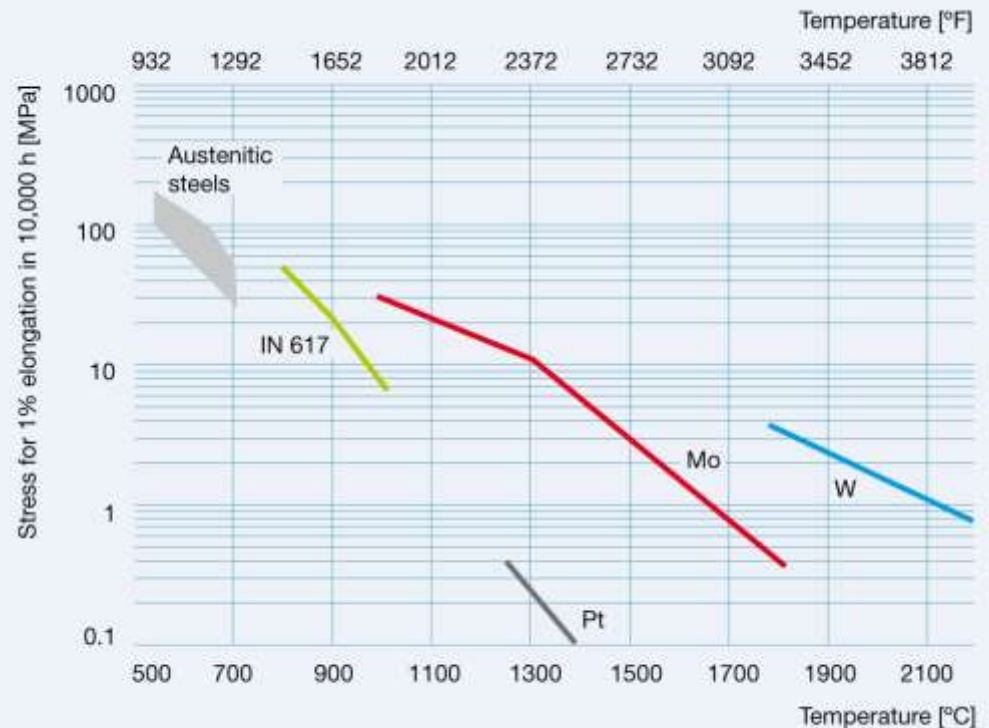


New Material for GME

Which materials can be used in a glass tank?

Refractory metals

- Molybdenum
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New Material for GME

Which materials can be used in a glass tank?

Refractory metals

Mechanical properties of Mo and Mo 5 Vol.-% ZrO ₂				
	Creep test at 1600 °C / 2912 °F in vacuum Creep stress of 15MPa	Notch tensile test at 800 °C / 1472 °F in vacuum		
	Creep Rate [s ⁻¹]	Tensile Strength [N/mm ²]	0.2-Proof Stress [N/mm ²]	Elongation [%]
Mo	4.4 x 10 ⁻⁶	226	97	16.9
Mo 5% ZrO ₂	9.5 x 10 ⁻⁷	335	246	6.3

Mean values of samples taken from the middle section and the edge of a rod, diameter 43 mm.



New Material for GME

MoZrO₂ - a new idea?

Not really!

- MoZrO₂ was already developed and tested years ago
- at the time it could not be produced in industrial scale due to the high mechanical force necessary
- after installing of new production equipment, **we are able to** produce MoZrO₂ in high volume

New Material for GME

MoZrO₂ - a new idea?



GFM 4 hammer forging machine with forging force of appr. 600t



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**

New Material for GME

What are the properties of MoZrO₂?

Mechanical-Technological Properties of Mo, W and Mo 5 Vol.-% ZrO₂

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

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

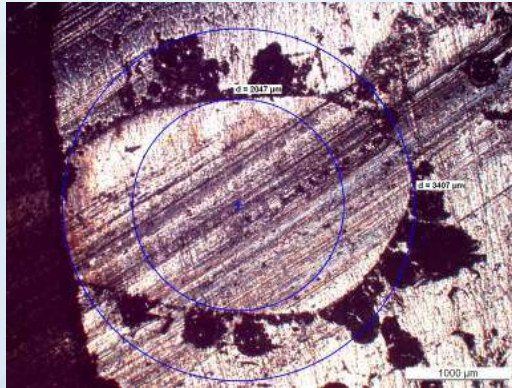
¹ Martinz/Matej/Leichtfried, 2001, 15th Plansee Seminar Reutte, A

² Matej et al, 2007, Glass Conference Teplice, CZ

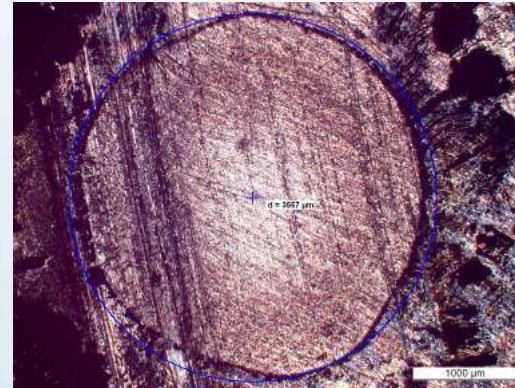
³ Gohlke et al, 1997, 14th Plansee Seminar Reutte, A

New Material for GME

Result: Increased corrosion resistance of MoZrO_2



Mo - Sb



Mo-ZrO₂ - Sb

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

$\text{Ø}43\text{mm}$

average decrease

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

New Material for GME

Increased corrosion resistance of MoZrO₂

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%

¹ Average out of 3 samples/ Martinz/Matej/Leichtfried 2003

New Material for GME

Increased corrosion resistance of MoZrO₂

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 |

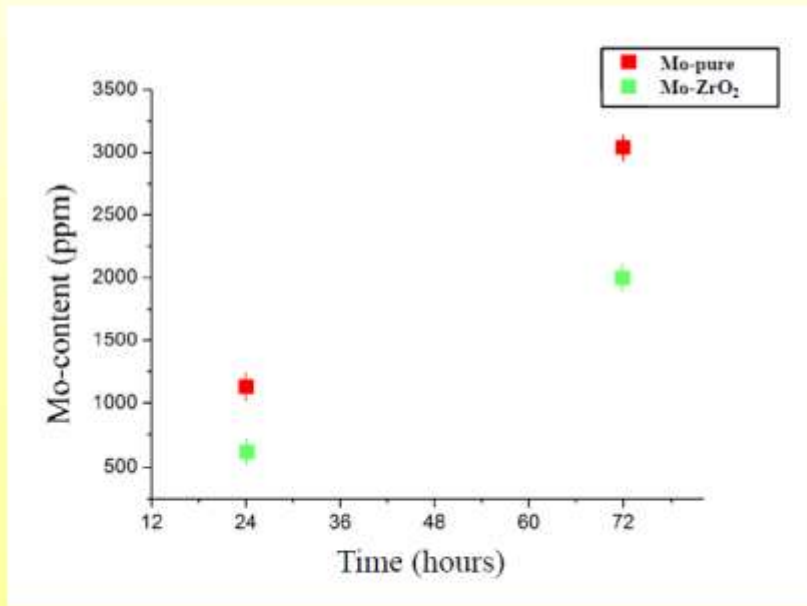
-13%

¹ Average out of 3 samples/ Martinz/Matej/Leichtfried 2003

New Material for GME



Mo concentration in glass after 24 h and 72 h - ICP-OES data



- Dark grey coloration of the glass
- Mo-ZrO₂ contains more Sb along grain boundaries than in pure Mo
- But Mo-ZrO₂ shows much lower concentrations of Mo in the glass:
 - **24 h**
Mo-ZrO₂=600 ppm and pure Mo = 1100 ppm
 - **72 h**
Mo-ZrO₂ = 2000 ppm and pure Mo = 3050 ppm

New Material for GME

MoZrO₂ GME.....

- Have a higher strength compared to regular pure Moly GME
- Show in all types of glasses and refining agents advantages compared to pure Moly GME
- Especially in Sb- refined glasses the dissolving of Moly into the glass is decreased
- Also the coarsing of grains in Sb refined glasses with the effect of drastical embrittlement of the GME and finally breaking is minimized
- Are produced exclusively by PLANSEE due to the most modern and powerful forging capabilities available

“MoZrO₂–
a new material for GME

“GTR” - Glass Tank Reinforcement
Experience and Insights

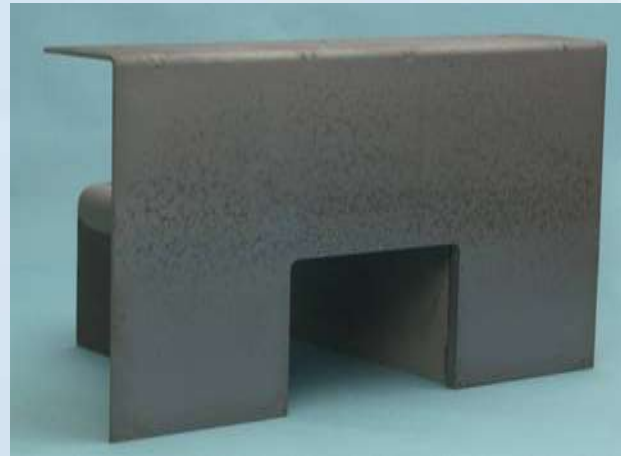
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Molybdenum / SIBOR® Glass Tank Reinforcement



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

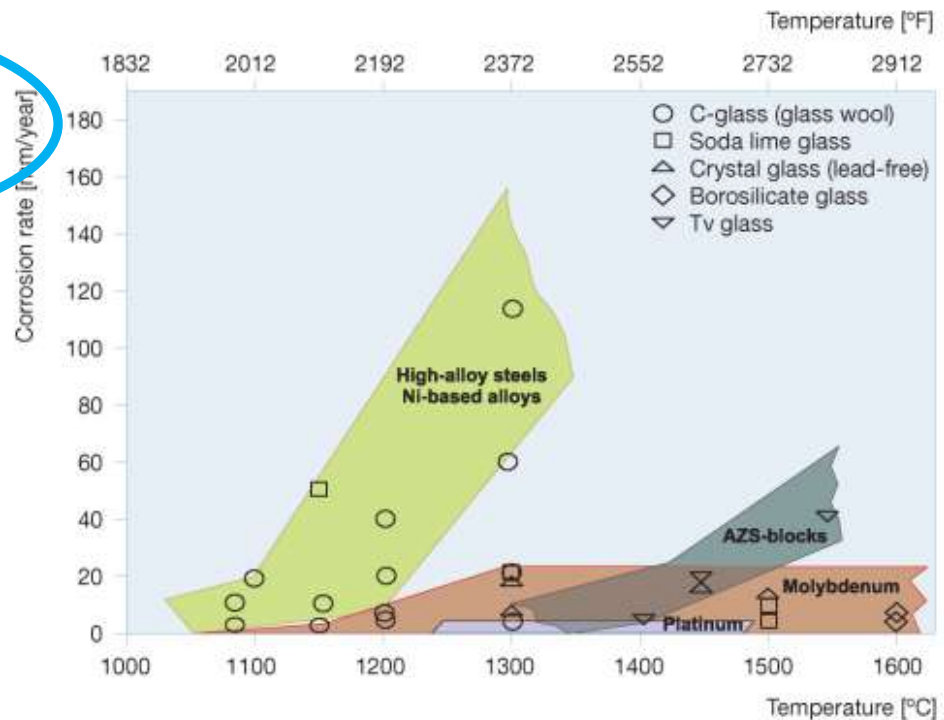


New Material for GME

Which materials can be used in a glass tank?

Refractory metals

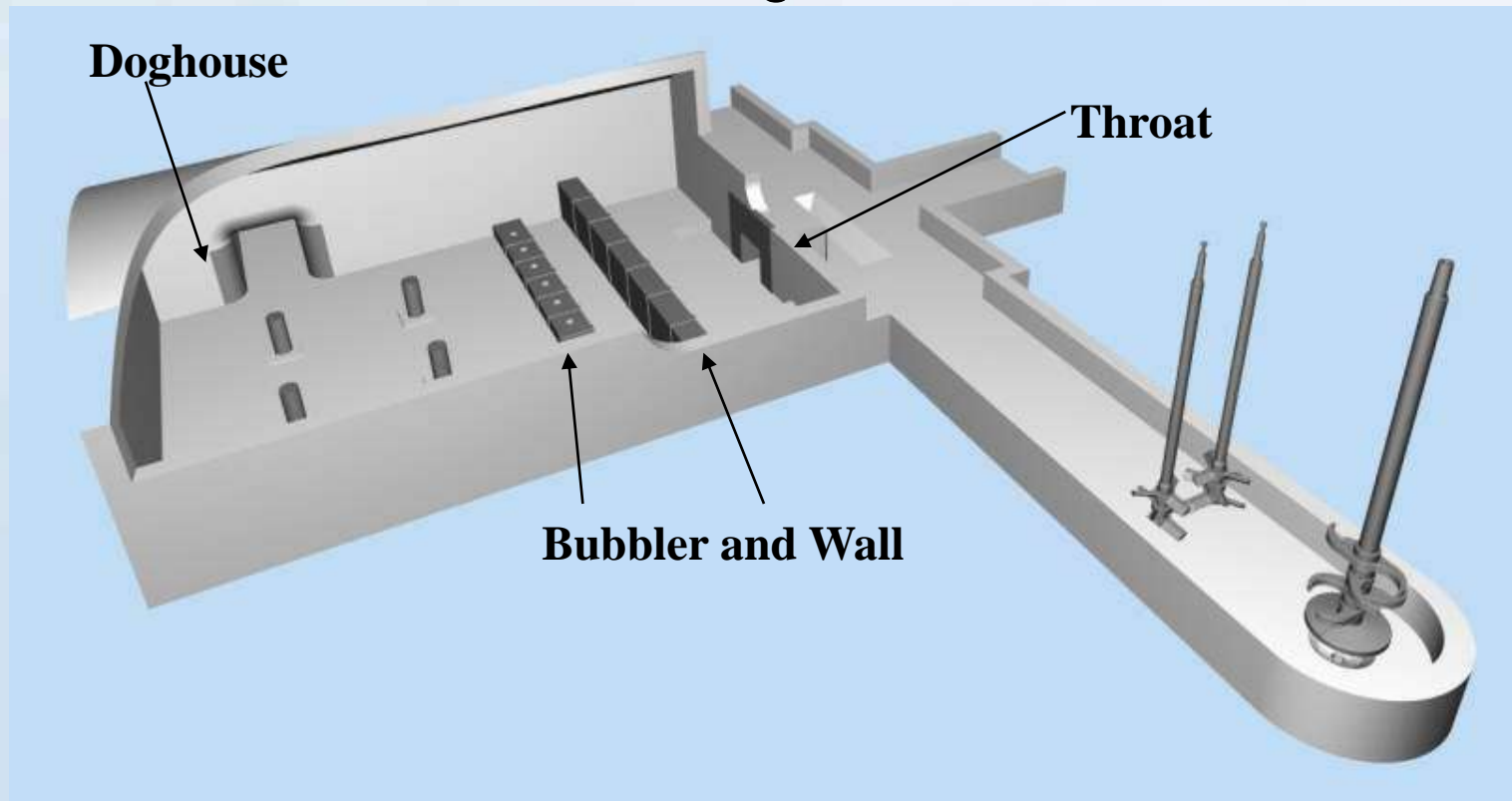
- Molybdenum
- Tungsten
- Platinum



Molybdenum / SIBOR®

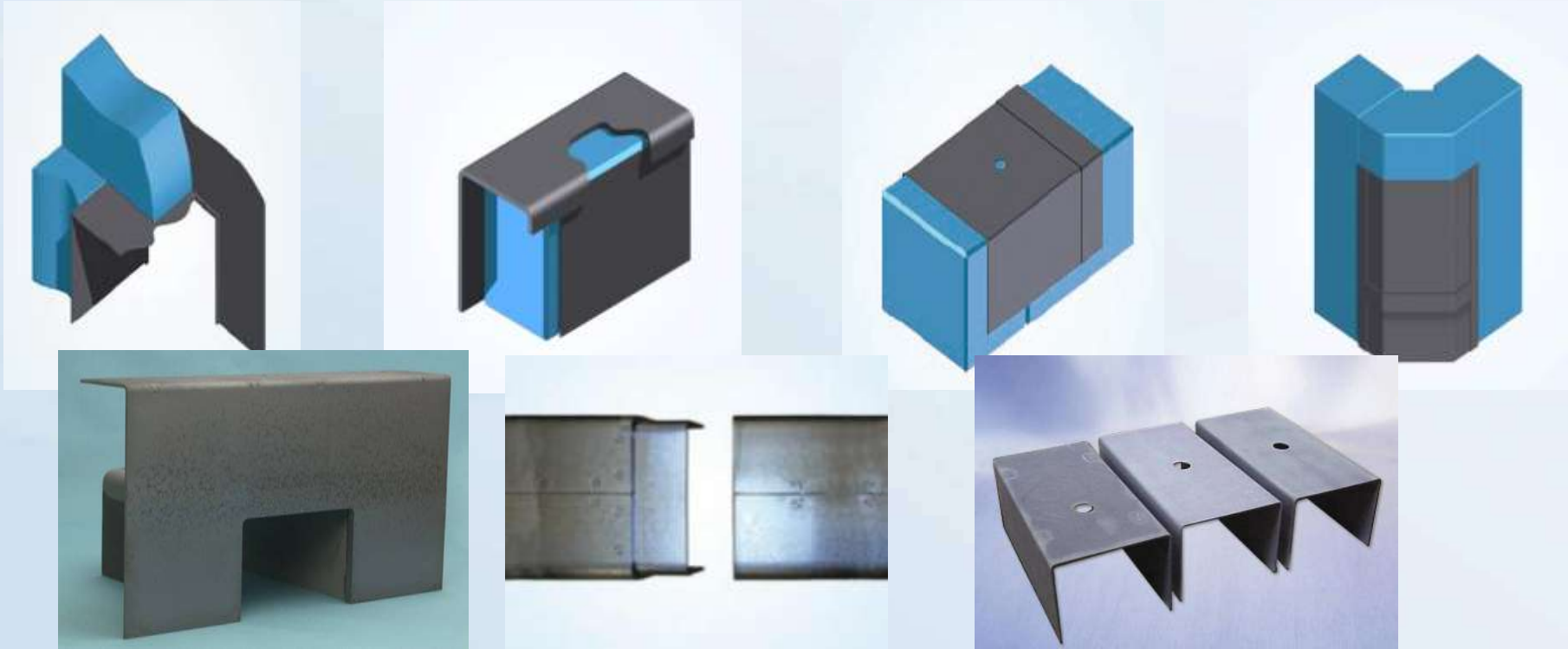
Glass Tank Reinforcement

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



Molybdenum / SIBOR[®] Glass Tank Reinforcement

GTR made out of Molybdenum with SIBOR[®] coating for
Throat, Wall, Bubbler and Doghouse



Molybdenum / SIBOR®

Glass Tank Reinforcement

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

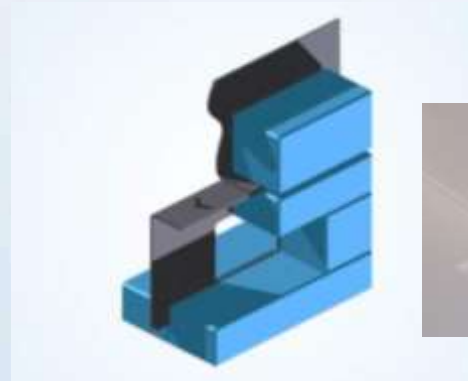
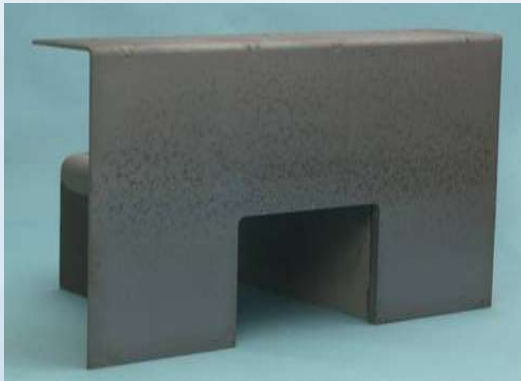
Characteristics:

- 6 to 14 mm thick Mo sheet
- Straightness of the sheet $<1\text{ mm/m}$
- Tolerance on dimensions $\pm 0,8\text{ mm}$
- SIBOR® - coating $180 \pm 30\ \mu\text{m}$ thick (APS spraying)
- Multiple piece construction

Molybdenum / SIBOR®

Glass Tank Reinforcement

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



Molybdenum / SIBOR® Glass Tank Reinforcement



Molybdenum / SIBOR®

Glass Tank Reinforcement

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

Molybdenum / SIBOR® Glass Tank Reinforcement



JSJODEIT 

Molybdenum / SIBOR®

Glass Tank Reinforcement

Throat protection

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



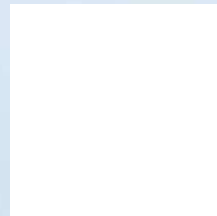
Molybdenum / SIBOR® Glass Tank Reinforcement

Bubbler protection



References.

To name but a few.



RESERVED FOR YOU!

PLANSEE Glass melting equipment

A step ahead in technology.