SIBOR®

A New Oxidation-Protective Coating for Molybdenum Parts in the Glass Industry

A Step ahead in Technology.

PLANSEE

PLANSEE is the world's leading manufacturer of high performance powder metallurgical products. We develop and manufacture advanced products made of refractory metals and metallic composite materials.

Guaranteed oxidation-protection of molybdenum

Due to their unique characteristics molybdenum and molybdenum alloys are used in the glass industry for glass melting electrodes, stirrers, gobbers, parts of glass tanks and other products for the manufacture of glass. Compared to ceramic materials molybdenum shows superior corrosion- and creep-resistance, leading to an increase in the service life of the components and improved glass quality.

Unprotected molybdenum starts to react with oxygen at approximately 400 °C / 752 °F and forms a yellow, sublimating oxide at higher temperatures. This reaction excludes its use above temperatures of 500 °C / 932 °F in atmospheres containing oxygen. After years of intense research PLANSEE has developed a ground-breaking solution to the problem of how to protect molybdenum against oxidation: the patented SIBOR® coating.

SIBOR® allows the use of molybdenum over long periods in oxidizing atmospheres at temperatures of up to 1.700 °C / 3092 °F. Guaranteed oxidation-protection for isothermal lifetimes:

5000 h at 1250 °C / 2282 °F
500 h at 1450 °C / 2642 °F
50 h at 1600 °C / 2912 °F

no oxidation – no discoloration – no contamination

Silica-forming coating with sealing effect

SIBOR® is a silicon-based coating and builds a silica-surface layer on the protected component. The very hard and dense coating constitutes a diffusion barrier against the base material and creates a SiO_2 sealing wherever it is exposed to air. As the up-tempering of a glass tank takes place in an environment containing oxygen, SIBOR® can reliably protect molybdenum parts against damage until the glass is molten.

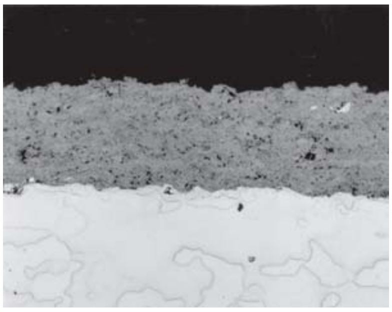
Applications in glass melting

Whereas molybdenum is highly resistant to dissolution in molten glass, SIBOR® dissolves within just a few days. This property is very useful in the heating-up of glass tanks, with SIBOR® providing the protection against the oxidizing gas atmosphere until the molten glass covers the part. Coated glass melting electrodes can be fixed conveniently at their final positions in the cold glass melting tank before heating with burners starts. The same applies to SIBOR®-coated molybdenum throats and front shields, which help to maintain an accurate and controlled glass flow over longer periods due to lower corrosion rates than unprotected ceramic blocks. Mo reinforcements for walls, bubble makers and doghouses are also regularly protected with SIBOR®.
SIBOR® is dissolved by the molten glass within a short period of time so that effects such as glass discoloration or bubble-formation do not occur during normal melting operation.

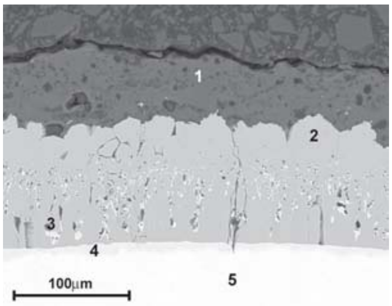
Advantages of SIBOR®

Compared to ceramic, intermetallic, platinum and other metal alloy solutions, SIBOR® stands out with:

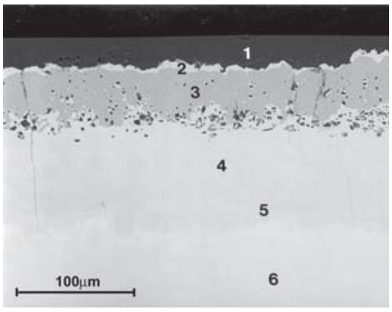
- Versatile application possibilities at very high temperatures
- Excellent long-term stability on oxidizing atmospheres
- Quick dissolution in the glass
- Prevention of oxidation at temperatures up to 1700 °C / 3092 °F (coating starts to soften above 1800 °C / 3272 °F)
- Corrosion-protection against aggressive gases, salts, molten salts and molten metals
- Allows fast heating and cooling processes without limitation (as SIBOR® is a diffusion and compound layer)
- Self-healing effect protecting parts against premature failure
- No glass discoloration or bubble-formation during melting operation.



Micrograph of a cross section of as-coated SIBOR®, thickness 150 µm



SEM (BS-mode) of a heat-treated SIBOR® coating; EDX: 1 - Si (molten SIBOR®); 2 - Si, 4 - Mo, (Si); 3, 5 - Mo



SEM (BS-mode) cross section of an oxidized SIBOR® coated Mo-sample (168 h in air at 1450°C). EDX: 1 - SiO_2; 2 - Mo, Si; 3 - Si, Mo; 4 - Mo, Si, B; 5 - Mo, (Si); 6 - Mo

SIBOR® coating process

SIBOR® is a highly efficient coating for molybdenum materials which is based on silicon and boron. It is applied by advanced coating technologies. The molybdenum surface is sandblasted before SIBOR® is sprayed on by means of APS (Atmospheric Plasma Spraying) in combination with a robotic system.
During the subsequent heat treatment, SIBOR® reacts with the base material and forms a dense and stable layer (see micrographs) which, depending on the application, is 200 to 400 µm thick and consists of molybdenum-silicide compounds with a SiO_2 surface sealing. The surface is dark grey before, and distinctly brighter after the heat treatment process. Its structure is amorphous to polycrystalline before the heat treatment and composed of additional Mo-Si-B-containing diffusion zones afterwards.
As molybdenum is unforgiving of any (even local) defect in the coating process, it is essential to thoroughly supervise and double-check the various manufacturing steps, including final inspection and measurement of the thickness (by eddy current method). Package, shipment, and unpacking have to be done with care.

Dimensions available

The maximum dimensions for SIBOR®-coated parts are: 1000 x 640 x 600 mm. Larger assemblies can be produced by using a multi-part design.

Coating requirements

Molybdenum / SIBOR® allows a wide variety of designs. Nevertheless, certain engineering and production principles must be observed.

- The parts to be protected must be designed according to the coating requirement. Sharp edges and small bending radii have to be avoided. In the case of inner coatings the length/diameter ratio has to be checked.
- All machining work must be completed before the coating is applied. However, the joining-together of already-coated parts is still possible.
- In order to avoid chipping of the coating, only very limited bending of the finished parts is allowed. This procedure requires elevated temperatures and can only be done at PLANSEE.

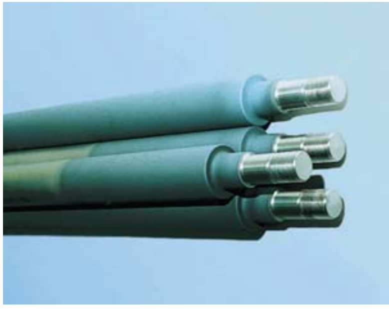
Further application fields of SIBOR® on molybdenum

Due to its outstanding mechanical properties at high temperatures in combination with the new type of protection against oxidation and corrosive media, SIBOR®/ molybdenum has beneficial characteristics which are also used for applications in furnace industry and waste incineration.

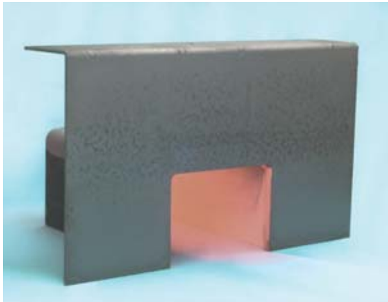
- SIBOR® allows the use of high-temperature-resistant molybdenum materials in the high-temperature-processing and furnace industry at temperatures of up to 1700 °C / 3092 °F in atmospheres containing oxygen. Typical components are thermocouple protection tubes, gas lances, burner components and shielding. Even complex and joined components such as annealing boxes and rotary furnaces can be protected with SIBOR®.
- In waste incineration plants SIBOR®-coated molybdenum parts are found in critical corrosion areas of the combustion chamber and boiler. The corrosion rate of molybdenum/SIBOR® at 450 - 550 °C / 842 - 1022 °F in chloride-corrosion conditions is very low. Therefore it is possible to use molybdenum/SIBOR® as anchors and hooks, nozzles and protection tubes or cladding material in the combustion or exhaust chamber.

PLANSEE products and service

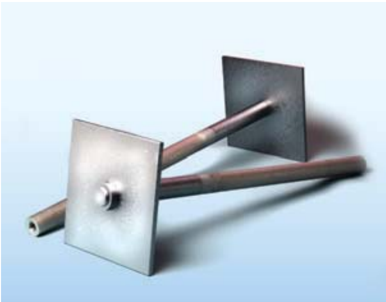
PLANSEE provides a wide range of products and services for parts and components made of molybdenum and molybdenum alloys. A team of experienced engineers and application technicians supports our customers in matters of material selection and choice of appropriate design. All products are produced to the highest quality, meeting ISO 9001 standards, on state-of-the-art machinery.



Glass melting electrodes with SIBOR® coating



Molybdenum throat channel protection fully coated with SIBOR®



SIBOR®-coated molybdenum plate electrode

Properties of SIBOR® on molybdenum

The following table presents application-relevant properties of as-deposited SIBOR® on molybdenum (200 µm SIBOR® on 2 mm molybdenum sample, density of the coating approximately 80 %).

Physical properties of SIBOR®

	SIBOR®	Mo
Density [g/cm³]	2.2	10.22
Coefficient of thermal expansion CTE [1/K] [1]	$3.3 \cdot 10^{-6}$ (100 °C / 212 °F), $4.5 \cdot 10^{-6}$ (600 °C / 1112 °F), $9.8 \cdot 10^{-6}$ (1000 °C / 1832 °F), $8.9 \cdot 10^{-6}$ (1200 °C / 2192 °F)	$5.3 \cdot 10^{-6}$ (20 °C / 68 °F), $5.8 \cdot 10^{-6}$ (1000 °C / 1832 °F), $6.5 \cdot 10^{-6}$ (1500 °C / 2732 °F)
Thermal conductivity [W/(m·K)]	6.0 (100 °C / 212 °F), 5.9 (600 °C / 1112 °F)	118 (100 °C / 212 °F), 110 (600 °C / 1112 °F)
Hardness [2]	486 ± 50 HV0.1 (20 °C / 68 °F)	220-280 HV10 (20° / 68 °F)
Heat capacity cp [J/(g·K)]	0.83 (100 °C / 212 °F) and 0.99 (600 °C / 1112 °F)	0.26 (100 °C / 212 °F) and 0.28 (600°C)
Temperature conductivity [cm²/s]	0.033 (100 °C / 212 °F), 0.025 (800 °C / 1472 °F)	0.449 (100 °C / 212 °F), 0.357 (800 °C / 1472 °F)
Specific electrical resistivity [mW·m] [3]	$3.2 \cdot 10^{+5}$ (100 °C / 212 °F), $3.2 \cdot 10^{+5}$ (1000 °C / 1832 °F)	0.1 (100 °C / 212 °F), 0.25 (1000 °C / 1832 °F)

[1] according to our experience the system SIBOR® on molybdenum can be heated to temperatures of about 1650 °C / 3002 °F without delamination.

[2] SIBOR® is a brittle but strongly adherent coating; it should be treated like a glass coating.

[3] according to our customers experience SIBOR®-coated glass melting electrodes work like uncoated ones during electrical heating of the glass melt.

Oxidation behavior and interaction with other materials

- oxidation behavior (Mo+SIBOR®):
  SIBOR® coated molybdenum can be heated slowly (as slow as about 5°C hour) in annealed condition in oxidizing atmospheres. The lifetimes of the protective system under isothermal conditions – after an initial ramp – are:
  about 50 hours at 1600 °C / 2912°F
  about 500 hours at 1450 °C / 2642 °F and
  about 5000 hours at 1250 °C / 2282 °F.
  This outstanding behavior of SIBOR® can be explained by the slow growth of a Mo-Si-B-phase with low diffuseness for Si in the Mo-coating-interface and the formation of a shock-resistant boron-modified SiO_2 glass passivation layer on the surface of the coating.

- interaction with other materials of glass-making equipment:
  Laboratory experiments and customers‘ experience have so far revealed that direct contact with platinum must be avoided due to formation of low melting eutectics. Zircon-mullite is the most appropriate ceramic material for long-term contact with SIBOR® under oxidizing conditions.

- interaction with molten glass (SIBOR®):
  Immersion experiments in borosilicate glass at 1450 °C / 2642 °F show that dissolution is not yet complete after 200 hours; however, the generation of bubbles containing gaseous reaction-products (such as SiO) does strongly decrease after about 24 hours. Dissolution experiments under a.c. loading (1A cm²) showed the following results: in C-glass (1300 °C / 2372 °F) the SIBOR® coating is dissolved within about 2 weeks, in green glass at 1400 °C / 2552 °F in about 1 week with formation of some bubbles. Bubbling and dissolution (H^2 and CO) are mainly caused by the reaction of Si, B and C with hydroxyl groups within the glasses; In the case of the green glass the reaction of the sulfate and iron-III-oxide also makes a minor contribution. White glass (1400 °C / 2552 °F) is dissolved most quickly – namely, within half a week, also with accompaniment of bubbling. In this case, it is mainly bubbles filled with CO_2, N_2, H_2S and COS that are formed by the reaction of the sulfate with H_2/CO. The direct reaction of sulfate with SIBOR® also contributes significantly to the dissolution of the coating.

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