Investigation of Corrosion Mechanisms between Copper and Lead Melts with Various Refractory Materials

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In this article the different interactions between molten copper and lead and various refractory materials are investigated by crucible tests. The refractory bricks were chrome-corundum resp. chrome-zirconia-corundum bricks and silicate-bonded and nitride-bonded silicon carbide bricks. The test samples were analysed by:

- macroscopic investigation
- microscopic investigation
- scanning electron microscope (SEM)
- X-ray diffraction (XRD).

Corrosion mechanisms and reaction products were studied. For economic reasons not all tests and analyses were made for all samples, but for a reasonable selection.

For copper the results show that the corrosion resistance of chrome-corundum bricks can be improved if corundum is present in the form of white fused alumina instead of sintered alumina. Increasing the chromium content only helps if a considerable amount of it is prereacted with corundum to form ruby. Zirconia addition reduces Young's modulus, but has no influence on corrosion. Both silicate-bonded and nitride-bonded SiC shows good corrosion resistance with an advantage for nitride bond.

For lead the results are similar. For chrome-corundum the same graduation as for copper is observed, but lead chromates are formed having negative environmental effects. For SiC once again the nitride bond looks more promising, whereas silicate-bonded SiC under oxidizing conditions forms lead silicates. Like for aluminium [1] reaction mechanisms are strongly atmosphere dependent.

1 Introduction

This paper is a continuation of a paper published by Schönhof et al. [1] which described the interaction between aluminium melts and different refractory products. Consequently the investigations were extended to two other most common non-ferrous metals, copper and lead in this case.

Tab. 1 Properties of Al, Cu, Pb

	Melting Point	Viscosity η [mPa*s]	Surface Energy [10^{-3} N/m]	Density [g/cm³]	Electro-negativity	Valency
Al	660 °C	1,3 (at MP) 1,04 (at 750 °C)	914 (at MP) 835 (at 850 °C)	2,7	1,61	3
Cu	1084 °C	4 (at MP) 3,2 (at 1200 °C)	1300 (at MP) 1280 (at 1300 °C)	8,94	1,9	2, 1
Pb	327 °C	2,65 (at MP) 1,15 (at 900 °C)	468 (at MP) 370 (at 1050 °C)	11,34	1,8	4, 2

Copper and lead have different properties from aluminium, related to melting point, viscosity, surface tension, density, electronegativity and ionic charges (Tab. 1). Therefore a couple of different interactions between metal melts and refractories should be expected.

Common refractory products for secondary copper production are chrome-corundum bricks or SiC-bricks, depending on type of furnace and position. For lead furnaces mostly basic bricks (magnesia or chrome-magnesia) are used for the working lining, although outside the furnaces, e. g. for runners, the whole selection of refractories has been tried with more or less success.

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This work deals with the interactions of non-basic refractories with these metals, and what improvements can be made in detail.

2 Experimental

Corrosion tests were made in accordance to preliminary standard DIN CEN/TS 15418:2006-09 in crucibles 80 mm × 80 mm × 65 mm with a bore 40 mm ∅ and 35 mm deep. Bores were filled to the max but always the same amount of metals; corrosion tests took place at 1300 °C/12 h for copper and 1050 °C/72 h for lead. All crucibles were covered with a lid, one part in oxidizing atmosphere (ox), another part with graphite foil placed between lid and crucible surface (red. step 1), and the third part totally surrounded in a bed of petcoke grains (red. step 2). So different steps of oxygen partial pressure, although not quite defined, could be realised.

In fact under reducing conditions step 2 no interaction between metals and refractories was detected at all. So any examination of this part of the test series did not make sense. All examinations for reducing conditions (=red.) that are described in the following are related to step 1, under graphite foil.

The brick qualities that have been used for the tests are characterised by their chemical composition (Tab. 2).

For comparison reasons some older tests have been taken into observation just for a macroscopic view, consisting of pure corundum and magnesia-chrome.

This work is a part of a bigger diploma thesis, and for time and economic reasons not all tests were made with all qualities and not all examinations with all samples, but for a reasonable selection listed in Tab. 3–4.

Tab. 2 Qualities of tested bricks

	Main Raw Material	Type of Bond	Chemical Composition [%]					
			Al_2O_3	Cr_2O_3	ZrO_2	P_2O_5	SiO_2	SiC
CK 9	sintered alumina	chem.-ceram.	86	9		2	2	
CZK 5	fused alumina	chem.-ceram.	85	5		1,4	5	
CZK 15	fused alumina	chem.-ceram.	77	15	4	1,5	2	
SC 90	silicon carbide	silicate	2				5	92
SCN 70	silicon carbide	nitride	3				2	70

Tab. 3 Executed tests with copper

Sample	Tests	Examinations
CK 9	ox. / red.	mac. (both), mic. (red.), XRD
CZK 5	ox. / red.	mac. (all), mic. (ox., red.), SEM (ox., red.), XRD (red.)
CZK 15	ox. / red.	mac. and mic. (both), XRD (red.)
SC 90	ox. / red.	mac. (all), mic. (ox., red.), SEM (ox.), XRD
SCN 70	ox. / red.	mac. (all), mic. (ox.)

Tab. 4 Executed tests with lead

Sample	Tests	Examinations
CK 9	ox. / red.	mac, mic. (both), XRD
CZK 5	ox. / red.	mac. (all), mic. (ox., red.), SEM (ox.), XRD (ox.)
CZK 15	ox. / red.	mac., mic., XRD (both)
SC 90	ox. / red.	mac. (all), mic. (ox., red.), XRD (ox., red.)
SCN 70	ox. / red.	mac. (all), mic. (ox., red.), XRD (red.)

Fig. 1 Cu-crucible test of CK 9 in oxidizing atmosphere

Fig. 2 Cu-crucible test of CK 9 in reducing atmosphere

3 Results

3.1 Copper

3.1.1. CK 9

The crucibles have massively been attacked. Under oxidizing conditions the crucible was nearly totally destroyed (Fig. 1). Under reducing conditions the appearance was not much better (Fig. 2). Microscopic observation showed that the matrix but also the coarse grains are attacked, but in a different degree (Fig. 3 – 4). Obviously chemical

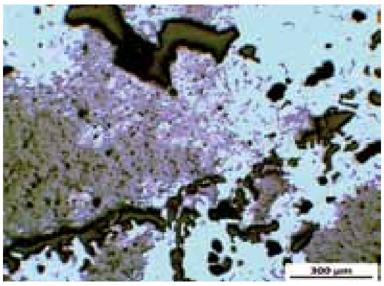

Fig. 3 LM-micrograph of Cu-test of CK 9 in reducing atmosphere

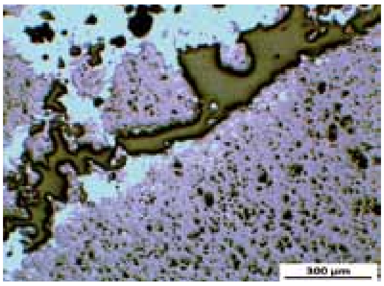

Fig. 4 LM-micrograph of Cu-test of CK 9 in oxidizing atmosphere

Fig. 5 **Cu-crucible test of CZK 5 in oxidizing atmosphere**

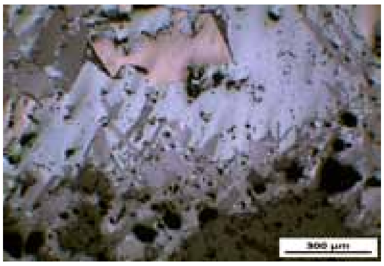

Fig. 6 **LM-micrograph of Cu-test of CZK 5 in oxidizing atmosphere**

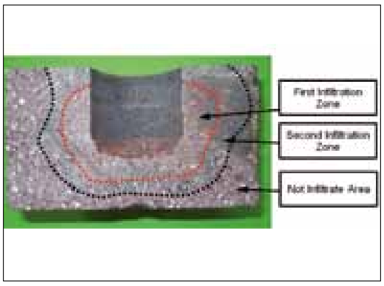

Fig. 7 **Cu-crucible test of CZK 5 in reducing atmosphere**

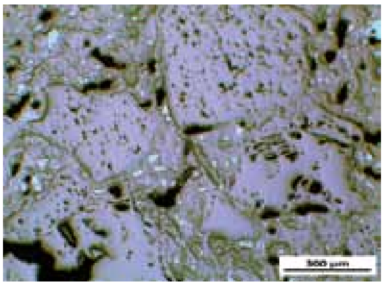

Fig. 8 **LM-micrograph of Cu-test of CZK 5 in reducing atmosphere**

Fig. 9 **Cu-crucible test of CZK 15 in oxidizing atmosphere**

Fig. 10 **Cu-crucible test of CZK 15 in reducing atmosphere**

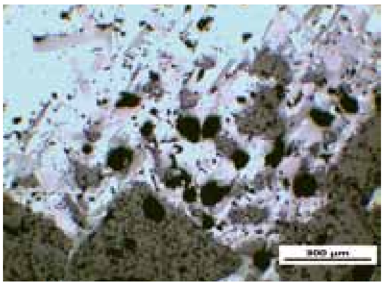

Fig. 11 **LM-micrograph of Cu-test of CZK 15 in oxidizing atmosphere**

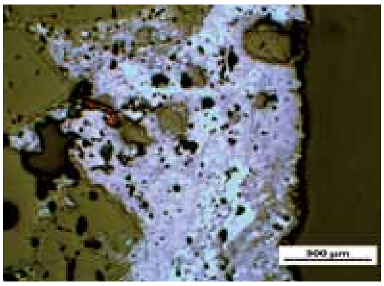

Fig. 12 **LM-micrograph of Cu-test of CZK 15 in reducing atmosphere**

attack is reinforced by the porosity of the sintered alumina grains.
XRD of the crucible materials – no big difference between reducing and oxidizing – showed the formation of CuO, $CuAlO_2$ and $CuCr_2O_4$. The last one suggests that in the brick matrix there is still a certain amount of free chromium oxide present. This may also be related to the relatively lower firing temperature of this kind of brick.

3.1.2 CZK 5

Under ox. conditions the copper has visually totally reacted, with oxygen coming from the air as well as with refractory components (Fig. 5). Reaction products are partly crystalline with a columnar shape, others are more isometric, but most of it seems to be amorphous or has a homogenous matrix-like structure (microscopic picture Fig. 6). SEM-analyses show that the slag-matrix is Cu_2O, the columnar shaped crystals are $CuAlO_2$ and the isometric shaped crystals are a mixed spinel $Cu(Al, Cr)_2O_4$. The mechanism behind it explains, why there is no attack of copper to alumina refractories under real reducing conditions: As a first step copper has to oxidise to copper oxides, these can attack the alumina and "ruby" phases to form the above mentioned phases.
Under slightly red. conditions two zones of infiltration have built up in the brick matrix, one with a lighter colour and one somehow darker (Fig. 7). The rest of copper metal could easily be removed as a block. Microscopic pictures confirm the optical expression, there is an intensive infiltration of copper and a formation of reaction products in situ and with the refractory matrix, but not with coarse refractory components (Fig. 8).
XRD shows the formation of mostly $CuAlO_2$ beside a high portion of alumina still present, and a minor part of $Cu(Cr, Al)_2O_4$. $CuAlO_2$ is a metastable phase which should transfer to $CuAl_2O_4$ during cooling below 800 °C, but the cooling rate was obviously too high for this reaction.
As a conclusion the corrosion mechanism of chrome-corundum refractories for copper melts is:

- infiltration of the metal
- oxidizing of the metal to copper oxides
- formation of $CuAlO_2$ and subsequently Cu–Al, Cr-spinel, destroying the brick structure.

The lower the partial pressure of oxygen is, the lower is the danger is to start this process by forming copper oxides.

3.1.3 CZK 15

This quality was included in the test series to see the influence of a higher Cr_2O_3-content and if there in an influence of free ZrO_2 on corrosion (ZrO_2 in CZK 5 is present in a different form).
Under ox. conditions more copper slag remains in the crucible and the infiltration zone is smaller compared to CZK 5 (Fig. 9). The same is the case for red. conditions (Fig. 10).
Microscopic pictures show a similar corrosion mechanism than for CZK 5: reducing does not attack the coarse grains, oxidizing also coarse WFA-grains are corroded (Fig. 11–12).

XRD of the red. sample shows as reaction products $CuZrO_3$, again $CuAlO_2$, and a metallic alloy Al_2Zr_3. Probably this intermetallic phase could have formed by the combined reaction:

$$3\,Cu + 2Al_2O_3 \rightarrow 3CuAlO_2 + Al$$
$$2\,Cu + 3ZrO_2 \rightarrow 2CuZrO_3 + Zr$$
$$2\,Al + 3\,Zr \rightarrow Al_2Zr_3$$

The formation of zirconates concludes that zirconium oxide is not more corrosion resistant than the other components. The presence of more Cr_2O_3 does not influence the corrosion mechanism, but obviously leads to a lower reaction rate. The "ruby" component (mixed crystal $Cr_2O_3 - Al_2O_3$) seems to be more stable than the single oxides, so the firing temperature should be high enough to form this phase.

3.1.4 SC 90

Fig. 13 Cu-crucible test of SC 90 in reducing atmosphere

Fig. 14 Cu-crucible test of SC 90 in oxidizing atmosphere

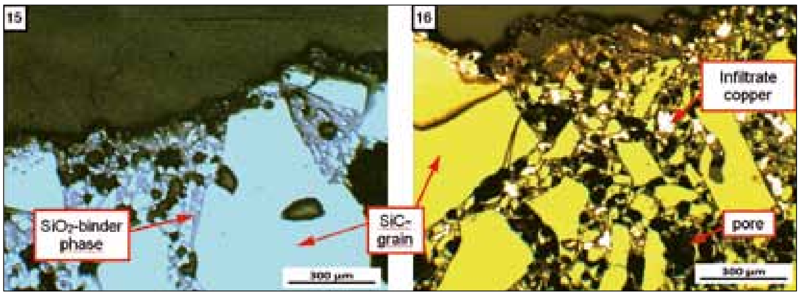

Fig. 15–16 LM-micrograph of Cu-test of SC 90 in reducing atmosphere

There is absolutely no reaction visible for reducing conditions (Fig. 13), oxidising there is some small surface reaction (Fig. 14). This is confirmed by microscopic pictures (Fig. 15–16), where only small droplets of metallic copper inclusions can be detected ox. SEM and XRD of the ox. tests show a small zone of SiO_2 on the refractories surface (Fig. 17), protecting the SiC grains from mechanical disintegration. Microanalysis shows that the copper droplets inside contain some silicon.

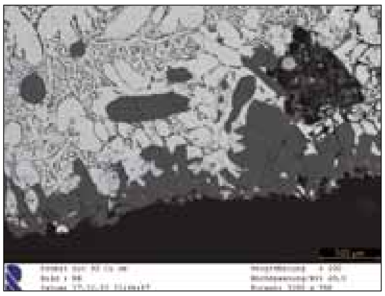

Fig. 17 SEM of Cu-test of SC 90 in oxidizing atmosphere

Fig. 18 Cu-crucible test of SCN 70 in reducing atmosphere

It can be concluded that the corrosion mechanism takes place in three steps:

- SiC oxidises on the surface, forming a dense mechanically protecting layer of SiO_2
- SiO_2 is reduced by copper, forming Cu–Si-alloy and Cu_2O
- surface SiC grains disintegrate, if oxygen has access new SiO_2 is formed.

The kinetics of this process seems to be very slow. As SiC grains are not corroded themselves, reinforcement of the matrix should improve the resistance of the refractory.

Fig. 19 Cu-crucible test of SCN 70 in oxidizing atmosphere

Fig. 20 Pb-crucible test of CK 9 in oxidizing atmosphere

3.1.5 SCN 70

The behaviour of nitride bonded SiC is slightly better but similar to ceramic bonded SiC: absolutely no wetting under reducing conditions (Fig. 18), just sticking and a small oxidised surface when oxygen has access (Fig. 19). The microscopic picture shows that the protecting layer is about three times thicker than for SiCs 90. Nitriding is one of the possible reinforcement measurements for improving the binding matrix like mentioned above.

3.2 Lead

3.2.1 CK 9

Similar to copper, lead destroys the structure of the crucibles heavily under ox. conditions, under red. conditions the effect is smaller but still destructive (Fig. 20–21).

Fig. 21 Pb-crucible test of CK 9 in reducing atmosphere

Fig. 22 Pb-crucible test of CZK 5 in oxidizing atmosphere

Fig. 23 Pb-crucible test of CZK 5 in reducing atmosphere

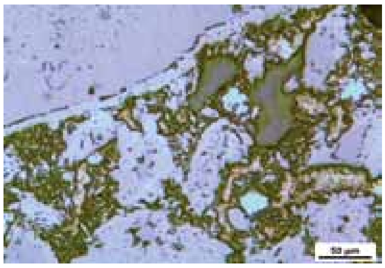

Fig. 24 LM-micrograph of Pb-test of CZK 5 in reducing atmosphere

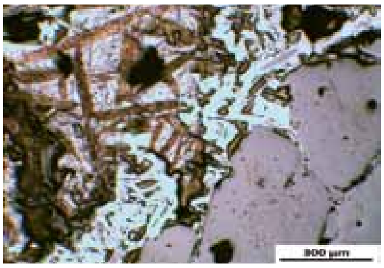

Fig. 25 LM-micrograph of Pb-test of CZK 5 in oxidizing atmosphere

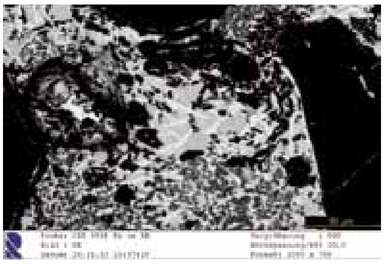

Fig. 26 SEM of Pb-test of CZK 5 in reducing atmosphere

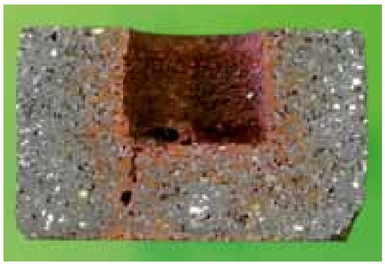

Fig. 27 Pb-crucible test of CZK 15 in oxidizing atmosphere

Fig. 28 Pb-crucible test of CZK 15 in reducing atmosphere

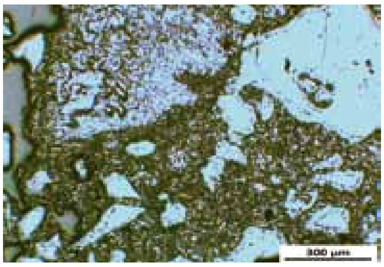

Fig. 29 LM-micrograph of Pb-test of CZK 15 in reducing atmosphere

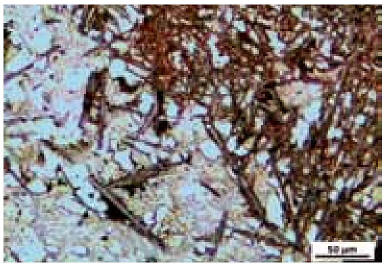

Fig. 30 LM-micrograph of Pb-test of CZK15 in oxidizing atmosphere

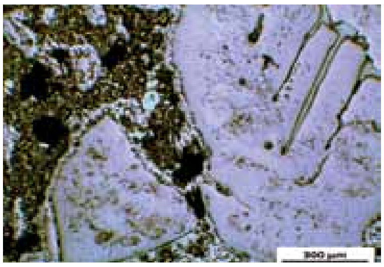

Fig. 31 LM-micrograph of Pb-test of CZK 15 in reducing atmosphere

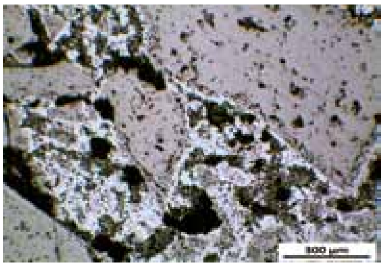

Fig. 32 LM-micrograph of Pb-test of CZK 15 in oxidizing atmosphere

Microscopic observation again shows that red. mainly the matrix is attacked, whereas ox. also the coarse grain (tabular alumina) is attacked. XRD shows in both cases the formation of lead chromate Pb_2CrO_5, which means again unreacted fine chromium oxide is more attacked than coarse fused alumina grain.

3.2.2 CZK 5

The same picture appears for the high-fired fused alumina grain based material. Oxidizing: the crucible is infiltrated and a big layer of lead oxide has formed on the surface of a residual metal rest (Fig. 22). Reducing: the crucible is infiltrated and the rest of metal could be poured out after the test (Fig. 23). Under the microscope one can see needle-shaped crystals, a glassy matrix and largely uncorroded chrome-corundum coarse grains in the reaction zone (Fig. 24–26). SEM and XRD identify lead silicate $Pb_{11}Si_3O_{17}$, lead chromate Pb_2CrO_5 and PbO and a lot of amorphous phase to be present, whereas only disproportional small amounts of alumina have come into solution. Deductively mainly the matrix is attacked, consisting of chromium oxide and silicate phases, and alumina is much more stable.

3.2.3 CZK 15

So it was not a surprise that the higher chromium content and the presence of zirconia in this sample was not an improvement. Oxidizing: the crucible was corroded and the lead complete vanished, infiltrating the refractory (Fig. 27). Reducing: the crucible was infiltrated to about 20 mm, some corrosion and cracks appeared in this zone (Fig. 28). The microscope shows that the high-chromium matrix and the zirconia containing grains are totally destroyed (Fig. 29–30), but the alumina grain have only a seam of reaction (Fig. 31–32). This is more or less both for reducing and oxidizing conditions the case. XRD identify lead zir-

Fig. 33 Pb-crucible test of SC 90 in oxidizing atmosphere

Fig. 34 Pb-crucible test of SC 90 in oxidizing atmosphere

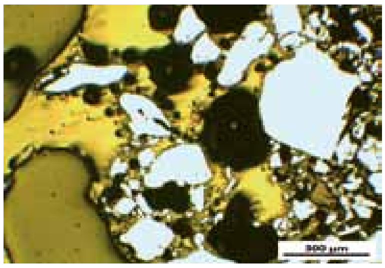

Fig. 35 LM-micrograph of Pb-test of SC 90 in oxidizing atmosphere

Fig. 36 Pb-crucible test of SCN 70 in oxidizing atmosphere

Fig. 37 Cu-crucible test of MCr

Fig. 38 Pb-crucible test of MCr

conate $PbZrO_3$ and lead chromate Pb_2CrO_5 as reaction products. Consequently neither Cr_2O_3 nor ZrO_2 are suitable refractory components for liquid lead applications.

3.2.4 SC 90

Under oxidizing conditions a lot of lead silicate glass is formed, overboils out of the bore and covers the whole crucible surface (Fig. 33). As the glassy phase "seals" and protects against oxygen access, residuals of metal remain on the crucible bottom and corrosion mainly takes place in the upper parts (Fig. 34). The microscope exhibits the dissolution of the silicate matrix by lead oxide and the SiC grains remain unattacked, but are washed away by the melt (Fig. 35). XRD shows no crystalline reaction products, what confirms that it is amorphous.
There is absolutely no infiltration or corrosion visible under reducing conditions.

3.2.5 SCN 70

The nitride-bonded SiC-brick again shows no wetting, so no corrosion or infiltration. Examinations did not make sense resp. did not indicate any structure changes.
In the zone of the melt formation under ox. conditions (Fig. 36) there is erosion visible, but under the microscope the mechanism of "washing out" the SiC-grains cannot be observed. This indicates that a similar corrosion mechanism like for silicate bonded material must take place, but to a much lower degree. The nitride bond is much more resistant to lead attack that silicate. In XRD only refractory components are present.

3.2.6 Comparison to other refractories

Just for comparison reasons older crucible test have been paid attention too, namely magnesia chromite bricks and pure corundum. The magnesia chromite brick was totally infiltrated by both metals and the crucible content completely vanished (Fig. 37 and 38). The same happens with lead and pure corundum (Fig. 39). In all cases no corrosion or erosion is visible. The authors could not test if there is any influence of this infiltration on the thermomechanical properties of the bricks, but they estimate there is. All we could see is that some new phases are formed with the magnesia chromite brick; gueggenite $MgCuO_x$ in the case of copper and some undefined lead compounds in the case of lead. Only the pure corundum treated with lead does not show new reaction phases, only glassy lead oxide PbO.

Fig. 39 Pb-crucible test of KE 99

4 Conclusion and summary

The results are summarised in the following tables.
Consequences:
- Chrome-corundum bricks are suitable for copper melts, if the chromium oxide

Tab. 5 Summary of copper tests

Brick Type	Infiltration	Corrosion	Most Stabile Phase	Reaction Phases	Application Recommended	Remarks
CK 9	strong	strong	corundum	$CuAlO_2$ $CuCr_2O_4$	no	totally destroyed
CZK 5	remarkable	ox. = minor red. = no	corundum	$CuAlO_2$ $CuCr_2O_4$	limited	
CZK 15	minor	ox. = minor red. = no	corundum	$CuAlO_2$ $CuZrO_3$	yes	zirconia just improves TSR
SC 90	no	no	SiC	–	yes	silica bond weakest point
SCN 70	no	no	SiC, Si_3N_4, Si_2ON_2	–	yes (1.)	good resistance but expensive

is trapped in the corundum to form ruby. Fused grains and low porosity must be preferred against sintered raw materials. High firing temperatures must be sought, because high contents of free Cr_2O_3 do not help. Zirconia addition reduces Young's modulus, but has no positive effect on corrosion. Silicon-carbide materials, especially nitride bonded, show better results.

- Chrome-corundum bricks are not suitable for lead melts. Lead chromates are formed. Zirconia again has no positive influence on corrosion, lead zirconates are formed. Silicon-carbide materials, especially nitride bonded, show better results.
- For both metals, as already concluded for aluminium, low oxygen partial pressure down to zero reduces corrosion down to zero.

Tab. 6 Summary of copper tests

Brick Type	Infiltration	Corrosion	Most Stabile Phase	Reaction Phases	Application Recommended	Remarks
CK 9	strong	strong	corundum	Pb_2CrO_5	no	totally destroyed
CZK 5	remarkable	mean	corundum	Pb_2CrO_5, $Pb_{11}Si_3O_{17}$, PbO	no	
CZK 15	ox. = strong red. = remarkable	mean	corundum	$PbZrO_3$, Pb_2CrO_5	no	
SC 90	no	minor	SiC	lead silicate	yes	silica bond weakest point
SCN 70	no	minimal	SiC, Si_3N_4, Si_2ON_2	–	strongly yes	good resistance but expensive

Reference

[1] Schönhof, V.; et al.: Interactions between Molten Aluminium and Various Refractory Materials. refractories WORLDFORUM **6** (2014) [4] 76–82