Non-oxidic Binding Systems of Refractory Products for Metal Melts*

W. Schoenwelski, J. Sperber, M. Bay

Decreased wear of silicon carbide bricks in a copper cathode furnace was observed during use as a result of in situ formation of oxinitrides. Different wetting behaviors of metal melts against non-oxidic materials (nitrides, SiC, carbon) were studied by experimental crucible test. Suitable combinations of ferrous and mainly non-ferrous metal melts and corresponding non-oxidic binders/additions have to be found experimentally and in practical application.

1 Introduction

Many different interactions and corrosion mechanisms between metal melts and refractory materials are very well known in literature and from practical experiences, for example the "corundum formation" in secondary aluminum furnaces (Fig. 1)

$$4\,Al_{met} + 3\,SiO_2 \rightarrow 2Al_2O_3 + 3\,Si$$

where aluminum reduces silica components of the ceramics to metallic silicon, thus becoming an oxide itself. This is combined with extreme densification and blackening (silicon). In this special case chemical additions like phosphate or barium sulfate being non-wetting agents can minimize this problem (Fig. 2).

A similar mechanism takes place with steel alloy metals, e.g. manganese and again silica [1]:

$$Mn + SiO_2 \rightarrow MnO_2 + Si$$

The compositions of metal melts are generally more defined than those of slags and other complex oxidic reaction products, so the interpretation of interactions is easier. Many of them can be explained by the *Richardson-Ellingham* diagram [2], similar explanations are manifested in the redox-potentials or electrochemical series [3], however you like to call them. They all have more or less the same background that under certain conditions base metals – as metals – are able to reduce more noble metals – as oxides or salts or other compositions – to the metallic state and become metals themselves. Silica seems to be the weakest component in standard ceramic materials, but theory also works in the rest of the series. Fig. 3 shows, where in a 99,5 % corundum brick alumina is reduced to aluminum by the 5 % Mg-part of the testing alloy.

The electrochemical activity is just one factor among many others for possible interactions between different materials. Beside temperature and (partial) pressure the activity (kinetics), pore structure and pore size distribution, atmosphere, surface tension = wettability and others play or can play a role in corrosions mechanics.

In this paper experimental work is described where literature is not as systematic as for oxide refractories: mainly for nitrides and its variations. Also other non-oxidic well-performing materials were tested as a reference: carbon and silicon carbide.

2 Experimental

The start of the study was induced by our observation of the performance of ceramic bonded silicon carbide bricks in a copper cathode furnace. The use of SiC-bricks is very common in furnaces for secondary copper of any kind, whereas in certain areas chrome-corundum bricks are more suitable. After the SiC lining was freshly installed, the wear started at a relatively high level, and reduced

Fig. 1 Corundum formation in an andalusite based brick after test with AlMg5-alloy

Fig. 2 Bauxite brick with high phosphate content after test with AlMg5-alloy

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Fig. 3 MgO/Spinel formation by the Mg-part of AlMg5-alloy after crucible test

Tab. 1 Comparison of phase-content of a lab-fired SiC-brick and a used brick from a copper cathode shaft furnace

	SiC-content [%]	Si_3N_4 [%]	Si_2ON_2 [%]
Lab-fired nitrided SiC-brick	80	7,5	7,5
Used SiC-brick from a Cu-cathode shaft furnace	60–80	up to 3,5	5–30

systematically with the lifetime of the furnace. After stop and breakout of the lining it surprisingly could be analyzed that remarkable amounts of silicon nitride and especially silicon oxinitride had been formed by the atmospheric conditions of the furnace (Tab. 1). A logical consequence was that this was an in situ formation of a self-protecting phase for the refractory, with increasing amount and stability during the furnace campaign. The performance of the nitride containing brick was better than the one of the pure ceramic bonded and even better than the one of the pure nitride bonded SiC-brick.

It seemed quite promising to examine, if there are other combinations of metal melts and non-oxides, mainly nitrides and its variations, which could be suitable for application.

Corrosion experiments were executed in crucibles of outer size 80 mm × 80 mm × 65 mm with a cylindrical hole ∅ 40 mm × 36 mm inside, under static conditions. Testing temperatures were adjusted to the application temperatures of the metals, and a little overheated to increase visible effects. Expressed in numbers temperatures were: 850 °C and 1000 °C for aluminum (Al), held for 72 h (melt overdose only in this case cast off the crucible after test); 1000 °C for lead (Pb), held for 72 h; and 1300 °C for copper (Cu), held for 12 h.

In one case also steel was tested at 1500 °C, held for 5 h.

All crucibles were filled to the maximum possible height with available metal scrap, final filling grade depending on scrap appearance. All were covered with a lid. In some cases – for Al all the time – crucibles were placed in a second container and protected by petroleum coke grains to simulate a reducing atmosphere. Where applicable not only the crucible materials themselves were tested, but a bottom disk made of silicon nitride.

3 Results and discussion

3.1 Aluminum

Fig. 4 shows a pure carbon crucible after the 850 °C Al-test as a reference for non-wettability and this is very well known for primary aluminum cells, pig iron and steel [4]. The still liquid melt could easily be cast out of the crucible at the end of the test. Fig. 5 shows that even SiC as the next well known non-oxide shows a good impression similar to a chemically treated standard ceramic (Fig. 2), although showing some infiltration. Fig. 6 shows the crucible with the Si_3N_4 bottom disk showing absolutely no infiltration

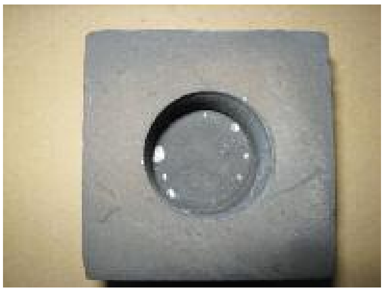

Fig. 4 Pure carbon crucible after test with AlMg5-alloy: melt completely cast off after test

Fig. 5 SiC crucible after test with AlMg5-alloy: just small infiltration

Fig. 6 SiC crucible with Si_3N_4 bottom disk after AlMg5-alloy test: no wetting

Fig. 7 SiC crucible, copper test, oxidizing conditions: corrosion visible

Fig. 8 SiC crucible, copper test, reducing conditions: remarkable reduced corrosion

Fig. 9 Nitrided SiC crucible, copper test, oxidizing conditions: only adherences of the metal

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Fig. 10 Nitrided SiC crucible, copper test, reducing conditions: no wetting

Fig. 11 SiC crucible, lead test, oxidizing conditions: heavy corrosion, formation of lead oxides/silicates

Fig. 12 SiC crucible, lead test, reducing conditions: remarkable reduced corrosion

Fig. 13 AC-brick crucible with Si_3N_4 bottom disk, tested with steel 5 h 1500 °C: total disappearance of the Si_3N_4

or even wetting. The cut disk can easily be pulled out of the metal residuals.

3.2 Copper

Copper is the metal we concentrated on in this test. The test is strongly atmosphere dependent. Pure ceramic bonded SiC under oxidizing conditions is slightly corroded (Fig. 7), but could still be removed as a disk after cooling. Under reducing conditions (Fig. 8) the corrosion was remarkably reduced. In situ nitrided SiC showed no corrosion or infiltration, but the metal still adhered to the crucible walls (Fig. 9). The remaining copper disk tested in the nitrided SiC crucible under reducing conditions fell off itself (Fig. 10).

3.3 Lead

The test is extremely atmosphere dependent. Under oxidizing conditions lead oxides and probably lead silicates are formed, which are aggressive and corrosive (Fig. 11). Under reducing atmosphere the corrosion remains weak (Fig. 12). The test was not continued with nitrided material for internal reasons.

3.4.Steel

This test was executed with a bottom disk made of silicon nitride in an alumina carbon brick crucible. The intensive reaction of Si_3N_4 with ferrous metals is described in literature [5] and can be confirmed by this test: the test has absolutely vanished and disappeared in the melt (Fig. 13). If any nonoxidic refractory material is suitable for steel melts, it is different to Si_3N_4. Here work has to be done and was already continued, promising alternatives have appeared.

4 Summary and conclusion

Non-oxidic refractory materials, especially nitrides, have been tested for their resistance against metals melts by home-made methods. The tests are still not finished in a systematic way and need scientific interpretation. Especially the role of the nitride has to be interpreted if it works as a binder, a support and/or an anti-wetting agent. Another question is, both for effectiveness and economic considerations. This will be made by a diploma thesis in the near future.

Nevertheless the first results are promising and there is a need for a systematic search for the fitting partners in these interactions. Refractories are one more step ahead on the way to high tech materials.

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