

Corrosion behaviour of chromium-free ceramics for liquid slag removal in Pressurized Pulverized Coal Combustion

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Abstract

The corrosion behaviour of HfO_2 , HfSiO_4 , ZrSiO_4 , NiAl_2O_4 and, for comparison, a commercial Cr_2O_3 -containing ceramic was investigated under Pressurized Pulverized Coal Combustion (PPCC) conditions at 1450°C in the presence of liquid slag. Although Cr_2O_3 -containing ceramics show sufficient corrosion resistance, they have the main disadvantage of vaporisation of toxic Cr(VI) -species. Among the investigated chromium-free ceramics, HfO_2 and HfSiO_4 showed relatively good corrosion resistance in laboratory investigations. The stability of the latter one depends not only on the microstructure of the ceramic but also on the slag composition. Technically produced ceramic balls of HfO_2 and ZrSiO_4 performed very well in the liquid slag separator of a PPCC test facility.

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1. Introduction

The limitation of fossil fuel resources and the necessity of reducing CO_2 emissions require an increase in efficiency of power plants by using combined cycle power systems. Up to now, efficiencies in excess of 50% are only achievable by using ash free fuels such as natural gas or oil in combined cycle power plants. Coal, however, constitutes 80% of the world's total fossil fuel resources. Today, coal is mainly utilised in steam power stations. Even if supercritical steam parameters are used, these coal-fired power plants only reach efficiencies below 50%, so that further development is essential, e.g. in coal-based combined cycle processes for improved efficiency.

The Pressurized Pulverized Coal Combustion (PPCC) combined cycle (Fig. 1) is a coal-fired combined cycle concept able to achieve efficiencies about 4% below that of gas-fired combined cycle systems.^{1,2} In it, coal is burned in a slag-tap furnace at $1500\text{--}1700^\circ\text{C}$ and at 15–20 bar. The hot flue gas is directly used for driving a gas turbine having a gas inlet temperature of $\geq 1200^\circ\text{C}$ (ISO) and a real flue gas temperature of $\geq 1400^\circ\text{C}$.

The residual thermal energy of the gas stream leaving the gas turbine is finally transferred to a steam cycle.

Gas cleaning related to fly ashes and alkali metals is a necessary prerequisite for the direct use of combustion gas in advanced gas turbine systems. In the case of PPCC, the flue gas is routed through a column of ceramic balls for slag separation and an alkali removal unit at an average temperature of 1450°C before entering the gas turbine and the steam cycle (Fig. 1). In the liquid slag separator, the liquid ash droplets deposit on the ceramic balls forming a thin film on the surface of the balls which flows down the separator column. Thus, the ceramics are always exposed to a flowing film of fresh slag with no solidified layer of slag formed to protect the ceramics from slag interaction or vaporisation of volatile species. The highly corrosive slag can react with the ceramic balls causing corrosion and wear. Liquids from coal combustion contain high concentrations of SiO_2 , Al_2O_3 , and Fe_2O_3 , as well as alkali and alkaline earth oxides, which penetrate the refractory structure and interact with it. The conditions in the slag separator system demand the following properties of the ceramics: high corrosion resistance in flue gas (CO_2 , H_2O , O_2 , SO_2) at $T > 1400^\circ\text{C}$; thermodynamic stability in the liquid slag; very low solubility in the liquid slag; no formation of low-melting eutectic mixtures with slag components; as well as low porosity, high density, and high homogeneity.

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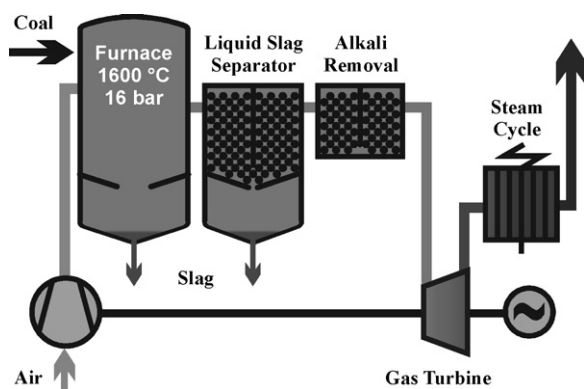


Fig. 1. Schematic flow diagram of the Pressurized Pulverized Coal Combustion (PPCC) combined cycle process.

Because of these requirements, many technical refractories are not suitable for liquid slag separation. SiC and Si₃N₄, for example, are not suitable because these non-oxide ceramics form SiO₂ in contact with the hot flue gas, which is dissolved by the slag.³ In the field of technical ceramics only Cr₂O₃-containing ceramics show sufficient corrosion resistance in the PPCC test facility.^{4,5} These refractories also showed a high corrosion resistance against coal slags in reducing coal gasifier atmospheres.^{6,7} The main disadvantage in oxidising atmosphere in the PPCC is the vaporisation of toxic Cr(VI)-species.^{8,9} Thermodynamic calculations showed that especially the alkali oxides increase the Cr vaporisation. About 1 kg Cr₂O₃ evaporates/1 MWh thermal power under PPCC conditions assuming equilibrium.⁸ Even though the exact amount of evaporated Cr₂O₃ was not determined in the PPCC test facility, the condensation of significant amounts of Cr₂O₃ at cooler parts of the facility was observed. Therefore, other chromium-free ceramic materials that could perform satisfactory in the PPCC environment were researched.

2. Experimental

The corrosion behaviour of hafnium oxide (HfO₂), hafnon (HfSiO₄), zircon (ZrSiO₄), nickel aluminate (NiAl₂O₄) and, for comparison, a commercial Cr₂O₃-containing ceramics (ICP-OES analysis: 31.0% Cr₂O₃, 27.0% Al₂O₃, 22.1% ZrO₂, 11.7% SiO₂, 1.4% Fe₂O₃, 0.6% MgO, 0.2% TiO₂) which was in use in the PPCC test facility in Dorsten, Germany, were investigated for slag interaction. Hafnon, zircon, and nickel aluminate were prepared by repeated milling and sintering of the pure oxides. Pellets (8 mm in diameter and 3 mm height) of the ceramic materials were prepared by one-dimensionally pressing with 20 kN followed by sintering at 1500–1700 °C for 24 h. The samples prepared are listed in Table 1.

Laboratory tests of refractory/slag interactions were conducted in platinum crucibles, in which 0.3 g ceramic powder or ceramic pellets were completely covered with 2.1 g slag from the PPCC test facility (ICP-OES analysis: 36.2% SiO₂, 27.0% Al₂O₃, 14.4% Fe₂O₃, 9.1% CaO, 2.5% MgO, 2.1% Na₂O, 1.2% K₂O) or a synthetic slag with 41% SiO₂ and the same concentration of the other oxides as in the slag from

Table 1
Samples for corrosion tests.

Sample	Sintering temperature (°C)	Density (g/cm ³)	Relative density (%)
One-dimensional pressed samples			
Cr ₂ O ₃ -ceramic	1500	3.50	
NiAl ₂ O ₄	1500	3.81	95
ZrSiO ₄	1600	4.15	88
HfSiO ₄	1600	4.74	68
HfSiO ₄	1700	5.86	84
HfO ₂	1600	8.69	90
Cold isostatically pressed samples provided by Eggerding Deutschland			
NiAl ₂ O ₄	1640	4.05	101 ^a
ZrSiO ₄	1640	4.20	90
HfSiO ₄	1640	5.80	83 ^a
HfO ₂	1640	9.47	98

^a Not single phase.

the PPCC test facility. Fig. 2 shows a schematic representation of the experimental set-up for the tests with ceramic powders. The ceramics were exposed to the slag at 1450 °C in pure oxygen at atmospheric pressure for 500 h in the case of powder tests and for 50 h in case of tests with pellets. Pure oxygen was used because Fe₂O₃ is the stable oxide under typical operational conditions in PPCC at a total pressure of 16 bar. The test temperature was much higher than the melting point of the slag. After the testing of pellets was finished, the crucibles were turned upside down and heated up to 1450 °C again so that the molten slag could drip off from the pellets. After the annealing experiments, the slag was investigated by chemical analysis (ICP-OES) to determine the solubility of the oxides in the slag. The ceramic powders were investigated by X-ray diffraction (XRD). The pellets were investigated by ceramography, XRD, optical microscopy, and SEM.

One disadvantage of the pellet tests is the saturation of the slag with refractory components,¹⁰ which is different compared to the situation in the slag separator system. Therefore, commercially produced ceramic balls (Table 1), provided by Eggerding Deutschland, were tested in the laboratory and exposed in the liquid slag separator of the 1 MW_{th} test facility in Dorsten² for up to 500 h.

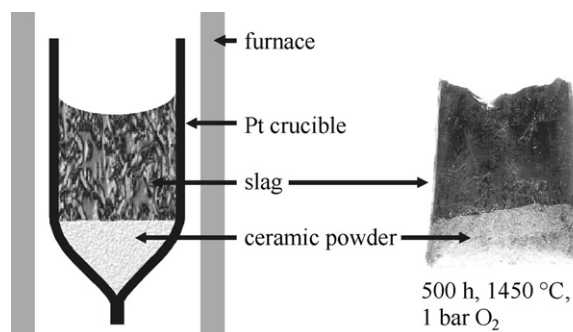


Fig. 2. Experimental set-up for the powder tests of different ceramics in liquid coal slag.

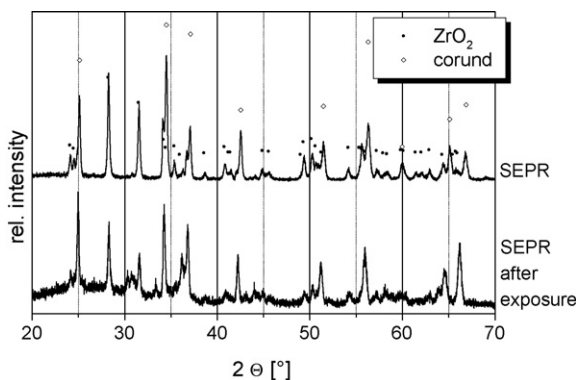


Fig. 3. XRD patterns of Cr_2O_3 -ceramic powder before and after 500 h of exposure to coal slag at 1450°C .

3. Results and discussion

3.1. Laboratory investigations of the commercial Cr_2O_3 -containing ceramic

For comparison, the corrosion behaviour of a commercial Cr_2O_3 -containing ceramic which shows high corrosion resistance in the PPCC test facility was investigated. One reason for corrosion resistance of Cr_2O_3 can be found in the phase diagram of the Cr_2O_3 – SiO_2 – Al_2O_3 system at 1700°C .¹¹ It shows only solid phases and immiscibility of Cr_2O_3 and SiO_2 . There are no low-melting eutectic mixtures with the other main components of the slag, e.g. with iron oxide, solid sesquioxides are formed; and with magnesia, a stable spinel is formed. The powder tests confirmed the stability of the $(\text{Cr},\text{Al})_2\text{O}_3$ corundum phase (Fig. 3). In contact with slag, the fraction of Al_2O_3 in the “corundum” phase slightly decreased, which can be shown by the shift in the lattice parameters. The chemical analysis of the slag shows that most of the ZrO_2 is dissolved in it. Up to 6% ZrO_2 but only 0.2% Cr_2O_3 was soluble in the PPCC slag. In case of a ceramic body, the dissolution would take place much more slowly because of the relatively small surface area, compared to a powder. Fig. 4 shows a one-dimensionally pressed specimen after 50 h exposure to original slag and its cross-section. The

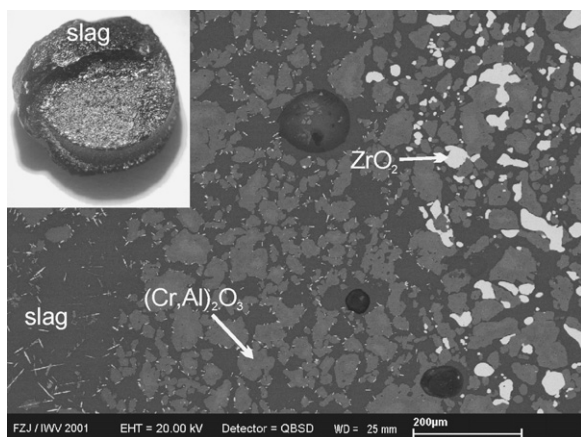


Fig. 4. Photo and SEM picture (BSE) of the cross-section of the Cr_2O_3 -containing ceramic after 50 h exposure to coal slag at 1450°C .

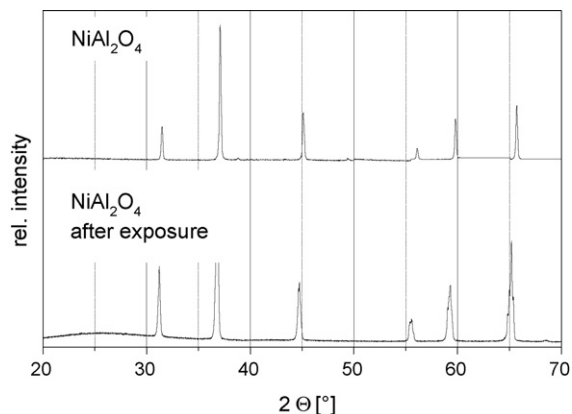


Fig. 5. XRD patterns of NiAl_2O_4 before and after 500 h of exposure to coal slag at 1450°C .

contour of the specimen was not damaged during testing, but there was a zone up to 1 mm thick on the sample surface where ZrO_2 was completely dissolved out of the ceramic body by the slag. Since this refractory is normally manufactured from the molten state, and therefore, very dense with very few pores at the surface, it indicated a very high corrosion resistance in the PPCC test facility, although it contains high amounts of soluble components such as ZrO_2 and Al_2O_3 .

3.2. Powder tests with chromium-free ceramics

The thermodynamic stability of Cr_2O_3 against slag components seems to be the main reason for the high corrosion resistance of Cr_2O_3 -containing ceramics. Moreover, the microstructure and porosity of the material are the important factors for corrosion resistance. Ceramics made of materials with comparable low slag solubility similar to Cr_2O_3 should show similar corrosion resistance.

The phase diagrams of ZrO_2 and HfO_2 with SiO_2 and Al_2O_3 show immiscibility with SiO_2 ^{12,13}; with zircon and hafnion being the stable phases over a wide temperature and composition range. Most of the eutectic mixtures with other slag components have melting points above 1450°C . NiAl_2O_4 is a stable phase in the NiO – Al_2O_3 – SiO_2 system.¹⁴ The lowest eutectic melting point in this system is above 1450°C . For this reason, it was tested in addition to the silicates.

Figs. 5 and 6 show the XRD patterns of NiAl_2O_4 and HfSiO_4 before and after 500 h of exposure to the PPCC slag. The XRD patterns of zircon look very similar to those of hafnion. After this length of exposure time, the thermodynamic equilibrium should be reached. Only NiAl_2O_4 spinel remains as a stable phase. After exposure, the spinel shows only a small shift in the lattice parameters. NiO has a solubility of about 2% in PPCC slag, as the chemical analysis of the slag revealed. The stability of hafnion in coal slags depends on the SiO_2 content of the slag. Hafnion is not stable in the PPCC slag with about 36% SiO_2 , decomposing completely into HfO_2 and SiO_2 . In the synthetic slag containing 41% SiO_2 hafnion is almost completely stable, with a small amount decomposing. The oxides have solubilities of 6.2% in the case of ZrO_2 and 0.4% in case of HfO_2 . ZrO_2 itself cannot be

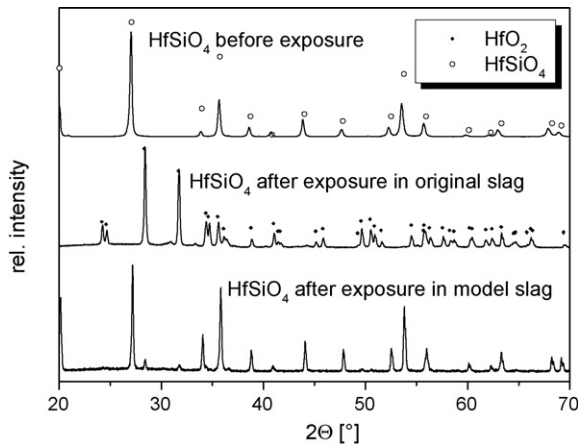


Fig. 6. XRD patterns of HfSiO₄ before and after 500 h exposure to coal slag at 1450 °C.

used because the phase transformation during heating up leads to high inner stresses and fracture of the refractory. Stabilised ZrO₂ is unsuitable because the stabilising elements are highly soluble in the slag, e.g. >9% Y₂O₃ as powder dissolved in the PPCC slag. In case of HfO₂, the phase transformation occurs at higher temperatures in comparison to ZrO₂.¹⁵ Therefore, it was considered in the following corrosion tests.

All oxide materials tested have higher solubilities in the slag than Cr₂O₃. However, the main loss of Cr₂O₃ is caused by vaporisation. In Fig. 7 the maximum loss of ceramic material per MWh thermal power of a PPCC plant calculated from the obtained solubility data (assumption: coal with 30 GJ/t, 8% ash, 10% of the ash into the liquid slag separator) is compared. If thermodynamic equilibrium is reached, the loss of Cr₂O₃ by vaporisation is higher than the consumption of ZrO₂, NiO and HfO₂ by dissolution. Even if the liquid slag film at the surface of the ceramic spheres decreases the vaporisation of Cr₂O₃ by two orders of magnitude, the theoretically determined loss is still similar to that of HfO₂.

3.3. Laboratory corrosion tests on ceramic pellets

One-dimensionally pressed ceramic pellets of hafnium, zircon, hafnium oxide, and NiAl₂O₄ were exposed to the PPCC slag for 50 h. In addition, hafnium and hafnium oxide were exposed to the synthetic slag. After the corrosion test, the NiAl₂O₃-

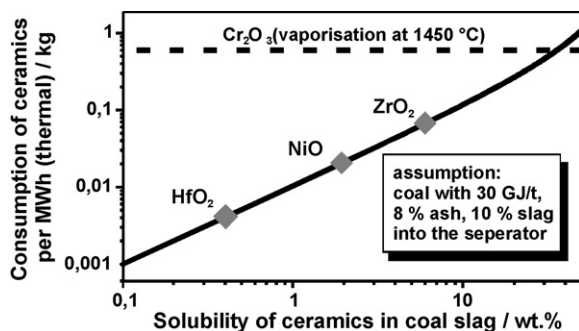


Fig. 7. Thermodynamically calculated consumption of ceramics in the liquid slag separator.

pellet was completely covered and infiltrated by slag. It was not possible to distinguish between ceramic body and slag in the cross-section. Fig. 8 shows the other specimens and their cross-sections after the corrosion test. The edges of the zircon specimen are rounded. The contours of the hafnium oxide and hafnium specimens are not damaged. The main reason for this should be the higher solubility of ZrO₂ in the slag. The surfaces of all ceramics got rougher due to the slag attack, with zircon showing the strongest increase in roughness. The cross-sections confirm that the surfaces of the hafnium oxide and hafnium specimens are much better preserved than the surface of the zircon specimen. In contrast to the hafnium oxide and hafnium specimens, there are pits in the surface of the zircon specimen which appear to have been pores before dissolution of the material. The zircon specimen has a very porous penetration zone with a thickness of 1.5 mm and more. In case of the two hafnium specimens, the cross-sections show the samples sintered at 1700 °C having a finer and more homogeneous microstructure. They also have a higher density. The 1600 °C sample has a density of 4.7 g/cm³ (68% relative density). The 1700 °C specimens have densities of 5.9 g/cm³ (84% relative density). After exposure to the PPCC slag, the hafnium specimen with rough microstructure has a penetration zone of 1–1.5 mm, the sample with fine microstructure has one of about 0.5 mm. A lower porous material fired at higher temperature led to a more homogeneous microstructure with less penetration, and therefore higher corrosion resistance. XRD measurements and SEM investigations (Fig. 9) in combination with EDX analysis show the silicates decomposing into oxides in the slag penetration zone resulting in the formation of relatively large HfO₂ grains and dissolution of SiO₂ into the slag. In the inner zone the silicates are stable. However, there is also little corrosion attack observable in the main body. The grains are rounded. Slag elements, e.g. Fe, can be identified throughout the ceramic material. However, this does not seem to have any influence on the mechanical stability of the refractory material at this time. The 1700 °C hafnium specimen, which was exposed to the synthetic slag with a higher amount of SiO₂, has a penetration zone of 0.1 mm maximum, since hafnium is almost stable in this slag. In contrast to the specimens exposed to PPCC slag, the silicate in the penetration zone of the specimen exposed to synthetic slag was not completely decomposed into the oxides. This confirms the great influence of slag composition, especially SiO₂ activity, which was already found in the powder tests. However, this result also confirms that the stability of a refractory, especially hafnium, depends on the coal quality. The hafnium oxide specimens do not show any remarkable corrosion attack regardless of slag composition.

3.4. Corrosion tests on technically produced ceramic balls

Technically produced ceramic balls of NiAl₂O₃, ZrSiO₄, HfSiO₄, and HfO₂ were tested in the laboratory and exposed to liquid coal slag in the liquid slag separator of the 1 MW_{th} test facility in Dorsten for up to 500 h. All ceramics showed higher corrosion resistance in comparison to chromium-free and low-chromium ceramics tested earlier in the test facility.⁵ Most of earlier tested samples had been completely dissolved in the slag

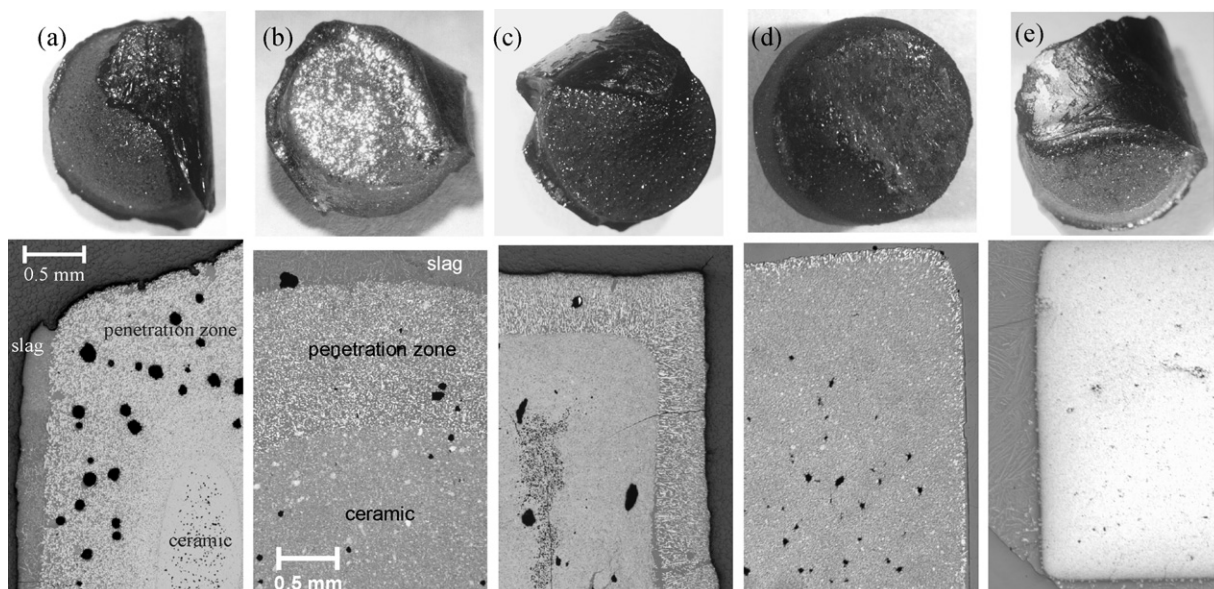


Fig. 8. Photos and SEM pictures (BSE, all taken at the same magnification) of cross-sections of the samples after 50 h of exposure to slag at 1450 °C; (a) zircon sintered at 1600 °C, PPCC slag; (b) hafnon sintered at 1600 °C, PPCC slag; (c) hafnon sintered at 1700 °C, PPCC slag; (d) hafnon sintered at 1700 °C, synthetic slag; (e) hafnium oxide sintered at 1600 °C, PPCC slag.

during one test run. HfO_2 showed the highest corrosion resistance in the present test runs. Fig. 10 provides a photo of the balls before and after exposure.

The NiAl_2O_4 balls were delivered containing cracks visible on the surface of the samples. The corrosion attack started at these cracks in the laboratory test. The cracks were filled with slag and the edges were rounded. Sound surface areas exhibited no macroscopic corrosion attack. Due to the replacement of iron into the spinel lattice, the balls became nearly black. However, this interaction did not seem to influence the mechanical properties of the material, since no further cracking was observed. The balls exposed in the liquid slag separator for 200 h showed severe corrosion attack. Cracks became deep holes due to the dissolution of the NiAl_2O_4 into the slag. At sound surface areas on the sample, the slag penetrated up to 2 mm into the ceramic, causing swelling and spalling. Due to this results and the relatively high solubility of NiO in the slag, this material was determined to

be not suitable as substitute for Cr_2O_3 -ceramics in liquid slag separation.

The HfSiO_4 balls had a relative density of 83%. As XRD investigations reveal, the ceramic contains a noticeable (>5%) amount of unreacted SiO_2 and HfO_2 beside HfSiO_4 . In addition, there were cracks and pits at the surface of the ceramic where slag could easily penetrate into the ceramic. In comparison to the HfSiO_4 -pellets, the technically produced balls showed poor corrosion resistance in the laboratory tests. The originally white ball was coloured brown due to the slag penetration. The number of cracks at the surface increased. Layers approximately 100 μm thick were detached from the surface. Results after 200 h of exposure in the liquid slag separator indicated further sample destruction. The balls were completely penetrated by slag and were very porous, as the broken ceramic in Fig. 10 shows,

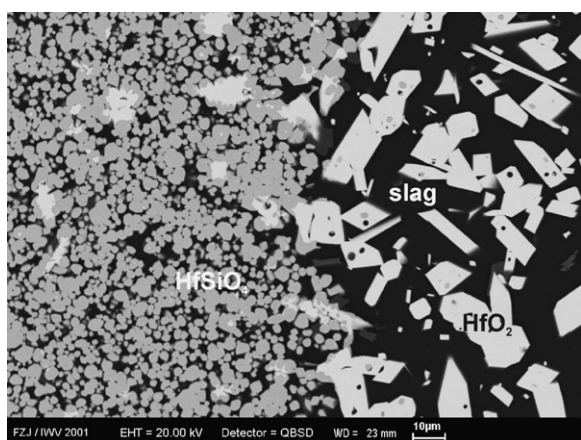


Fig. 9. SEM picture (BSE) of the cross-section of a hafnon specimen after 50 h of exposure to coal slag at 1450 °C.

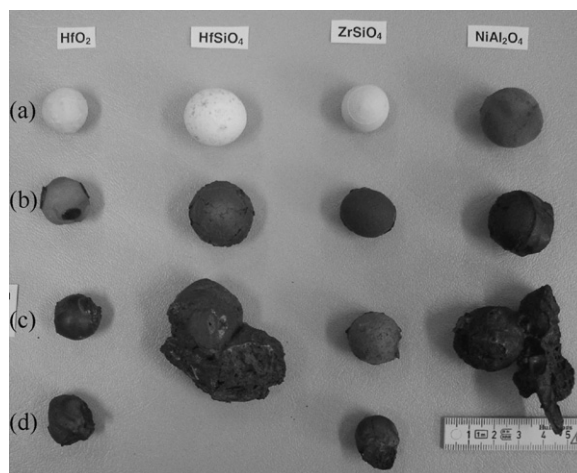


Fig. 10. Photo of technically produced ceramic balls (a) before, (b) after 100 h of exposure to coal slag at 1450 °C in laboratory tests and after (c) 200 h and (d) 500 h in the liquid slag separator of the test facility in Dorsten, Germany.

and became swollen. Thus, the technically produced ceramic is not suitable for use in the liquid slag separator. However, it is possible that ceramic balls with homogeneity like the pellets produced in the laboratory would behave much better.

The HfO₂ balls had a relative density of 98%, showing no cracks or pits at the surface. After exposure to coal slag in laboratory tests, no corrosion attack was observed. The surface of the ceramic was slightly brown coloured by the slag. However, the slag almost completely dripped off the ceramic. This poor wetting behaviour prevents plugging of the slag separator. The same result was found after 200 h of exposure to coal slag in the liquid slag separator of the test facility. Even after 500 h of exposure to coal slag in the test facility, very little corrosion attack in terms of increased roughness of the surface was observed. The slag penetrated about 0.1 mm into the ceramic.

The ZrSiO₄ balls had a relative density of 90%. They were very homogeneous, with no visible defects at the surface. In contrast to the HfO₂ balls the surface of the ZrSiO₄ balls was slightly rougher. After the laboratory test, very little corrosion attack was observed. The surface was slightly brown coloured by the slag, which penetrated 100 µm maximum into the ceramic. The wetting behaviour was similar to that of the HfO₂ balls. Thus, the technically produced ceramic behaves much better than the one-dimensionally pressed pellet. The exposure tests in the liquid slag separator confirmed the relatively high corrosion resistance of the zircon balls. After 200 h of exposure, the roughness of the surface slightly increased. After 500 h of exposure, the ZrSiO₄ balls were smaller due to the dissolution of material into the slag, causing them to decrease in size from about 2 cm in diameter to about 1.8 cm. This large decrease is a result of the relatively high slag solubility of ZrO₂ in comparison to the low solubility of HfO₂, which was not dissolved to the extent of ZrO₂. The penetration zone, in which the ZrSiO₄ decomposes into oxides, had a thickness of up to 1 mm. It is remarkable that the wettability of the material has not changed. Although the consumption of ZrSiO₄ balls is higher than that of HfO₂ or Cr₂O₃ balls, it has to be considered, that zircon is much cheaper than the other materials and, in contrast to Cr₂O₃, is not detrimental to the environment.

4. Conclusions

The corrosion behaviour of HfO₂, HfSiO₄, ZrSiO₄, NiAl₂O₄ and, for comparison, a commercial Cr₂O₃-containing ceramic was investigated in the presence of molten slag from a PPCC test facility in pure oxygen at 1450 °C. In addition, the ceramics were exposed in the liquid slag separator of the PPCC test facility for up to 500 h.

Cr₂O₃-containing ceramics show sufficient corrosion resistance because the (Cr,Al)₂O₃ corundum phase is stable in contact with slag components, because there are no low-melting eutectics and the solubility of Cr₂O₃ in the slag is very low.

Among the investigated chromium-free ceramics, HfO₂ and HfSiO₄ showed relatively good corrosion resistance in the laboratory investigations. The solubility of HfO₂ in the slag is about 0.4%. Therefore, the consumption of Hf-ceramics by dissolution should be less than that of Cr₂O₃-ceramics by vaporisation

under equilibrium conditions. The stability of HfSiO₄ depends mainly on the microstructure of the ceramic and on the slag composition, with less corrosion occurring with higher SiO₂ content of the slag. HfO₂ is stable regardless of the slag composition. The main disadvantage of Hf-materials is the high price of the raw material.

During exposure tests in the liquid slag separator of a PPCC test facility, the technically produced ceramic balls of HfO₂ and ZrSiO₄ performed very well. Both ceramics showed small amounts of corrosion after 500 h of exposure. In contrast to Cr₂O₃-ceramics, which still behave better, the new ceramics are environmentally friendly. Thus, these materials may be an alternative for use in a slag separator. However, the overall annual costs will decide upon the favourable material.

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