DEVELOPMENT OF SELF-GLAZING CARBON-BONDED SIC CASTABLES

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ABSTRACT

The oxidation resistance is a key property during the application of carbon-bonded refractories and components. To prevent oxidation, a protective surface layer such as an externally applied glaze can be applied. However, for the glaze application and formation requires additional process steps, increasing fabrication costs. In recent studies, $Na_2B_4O_7$ was introduced as a self-glazing additive, resulting in the successful fabrication of carbon-bonded Al_2O_3 monoblock stoppers with self-glaze properties. However, this kind of self-glaze may not be suitable for inductively heatable carbon-bonded SiC-based refractory materials. The focus of this study was the application of the self-glaze approach developed for carbon-bonded Al_2O_3 functional bodies to SiC-based crucibles. Therefore, carbon-bonded SiC vibration flow castables, containing different glaze-forming additives such as microsilica, wollastonite and metallic silicon, and bonded with water-soluble resin binder were designed, manufactured, and carbonized at different temperatures. The physical and mechanical properties, as well as the microstructure as functions of the carbonization temperature, were investigated. The oxidation resistance was evaluated using thermogravimetry. A successful self-glaze formation was achieved using metallic silicon and wollastonite additions, whereby the water-soluble resin plays a decisive role.

INTRODUCTION

For carbon-containing refractory materials, protecting carbon from oxidation at high temperatures is a key issue that has to be faced. For this purpose, an externally applied glaze is commonly used, which protects carbon thanks to its high viscosity dense glassy layer.[1, 2] However, these glazes for carbon-bonded refractories need to fulfil several requirements. A very broad softening temperature range (between 500 – 1500 °C in the best scenario), a slightly higher thermal expansion coefficient than the carbon-bonded refractory substrate and good adhesion to it, presenting no point defects like pinholes, and being not permeable are the most important ones.[3]

Recent studies on self-glazing compositions were performed by Roungos et al., who designed Al_2O_3 monoblock stoppers with self-glazing and self-healing properties.[3, 4] The authors used boron, which is an undesirable addition in several applications due to its negative effect on the refractoriness and high-temperature properties.

In this study, boron-free additions were tested to achieve the self-glazing effect of casted carbon-bonded samples.

EXPERIMENTAL PROCEDURE

Castables were designed with a particle size distribution based on Dinger-Funk [5] using a q-value of 0.21, the compositions are shown in table I. For a god flow a q-value of 0.3 should not exceed. Moreover, investigations on castable mixtures flow behavior, described mixtures with a q-value < 0.25 a self-flow tendency, up to 0.3 rather a trend to vibration-flow behavior.[6]

Mixtures were prepared using:

- fine- and coarse-grained SiC up to 3 mm (Kempten, Germany) in different fractions;
- different carbon sources: natural graphite AF 96/97 (Kropfmühl, Germany), Carbores® P (Rütgers, Germany) and Carbon black MT N991 (Lehmann & Voss, Germany)
- as a binder, a water-soluble KOH-containing Bakelite® WhiteCast resin (Hexion, Germany), with the hardener H7 was used. The amount of carbon and binder addition was calculated based on the residual carbon content of approx. 10 wt.-% after carbonization at 1400 °C.
- microsilica (SiO_2), wollastonite (CaO-SiO_2), and metallic silicon (Si) (all supplied by ELKEM, Norway) additives and their combinations for the self-glazing properties.

Table I: Compositions for self-glazing SiC mixtures

Designation	SiC-A	SiC-B	SiC-C	SiC-D
	wt%			
SiC 0-3 mm	86.0			
Carbon black	4.0			
Graphite AF	1.34			
Carbores® P	4.66			
Wollastonite	5.0	5.0		5.0
Metallic Si	2.0	-	6.0	6.0
Microsilica	-	2.0	-	-
Whitecast	4.00			
Hardener H7	0.80			
Disp. agent	0.64			
Water	6.4	6.8	7.0	6.4

The mixing of the raw materials took place in a paddle (mortar) mixer (Toni Technik Baustoffprüfsysteme GmbH, Germany). For the determination of the mechanical and physical properties, bars with dimensions of 150x25x25 mm^3 and cylinders with a diameter and height of 50 mm were vibration-casted on a vibrating table.

Samples were carbonized with a program of 1 K/min up to 800 °C, every 100 K a half an hour dwell time, from 800°C with a heating rate of 3 K/min up to 1400 °C with a dwell time of 5 hours. Samples were placed in a retort filled with calcined petrol coke

grid. The cold modulus of rupture (CMOR) measurement of the carbonized samples were carried out according to the DIN EN 993-6.

The morphology of the SiC-C samples with different self-glazing additives was investigated using a scanning electron microscope XL-30 ESEM FEG (FEI). The glassy layer was locally analyzed with the aid of the electron backscatter diffraction technique (EBSD) to investigate the crystallography.

Open porosity of the carbonized specimens was measured by immersion in water according to DIN EN 993-1 (Archimedes' principle).

The oxidation resistance i.e. the self-glazing properties were evaluated using a modified thermogravimetric analysis (TGA). The mass loss of the samples was measured during a rapid heat up to 1400 °C with a 20 K/min heating rate.

RESULTS AND DISCUSSION

The flowability of the castables with the q-value of 0.21 with Bakelite® WhiteCast as binder was poor. Due to the hardener addition, the mass became sticky and vibration table had to be used. In table II the physical properties are listed for each composition. It can be seen that due to a higher water demand the composition SiC-C with 6 wt% of Si presents the highest open porosity and the lowest CMOR. A higher CMOR was expected since the formation of ß-SiC whiskers was observed in form of a blue/grey layer on the samples and in pores, see Fig. 1. It can be assumed that the high open porosity i.e. critical pore size due to the high water demand is responsible for the low CMOR.

Table II: Strength and open porosity of the samples carbonized at 1400 °C

Designation	CMOR in MPa	OP in %
SiC-A	9.74 ± 0.77	23.49
SiC-B	7.80 ± 1.18	22.08
SiC-C	6.85 ± 0.95	26.93
SiC-D	21.21 ± 1.04	23.70

The combination of microsilica and wollastonite (batch SiC-B) presented the

lowest open porosity, which was attributed to a good packing density since the grain size of the microsilica is in the submicron range. However, these samples presented only 1 MPa higher CMOR in comparison to batch SiC-C. Substituting the microsilica with metallic silicon increased the open porosity slightly, but due to the formation of secondary ß-SiC the CMOR also increased up to 9.74 MPa. In the case of the samples with wollastonite and increased metallic Si content, only a slightly higher open porosity was measured. Due to the formation of the ß-SiC, a CMOR of 21.21 MPa was achieved.

metallic Si, Al, boron nitride, silicon nitride etc.[7, 8], but were rather considered for the generation of a glassy layer on the surface of the samples. The idea behind this reaction is that the glass-building components are discharged from the microstructure and build a new, non-permeable layer. The high heating rate of 20 K/min was chosen to minimize the carbon loss.
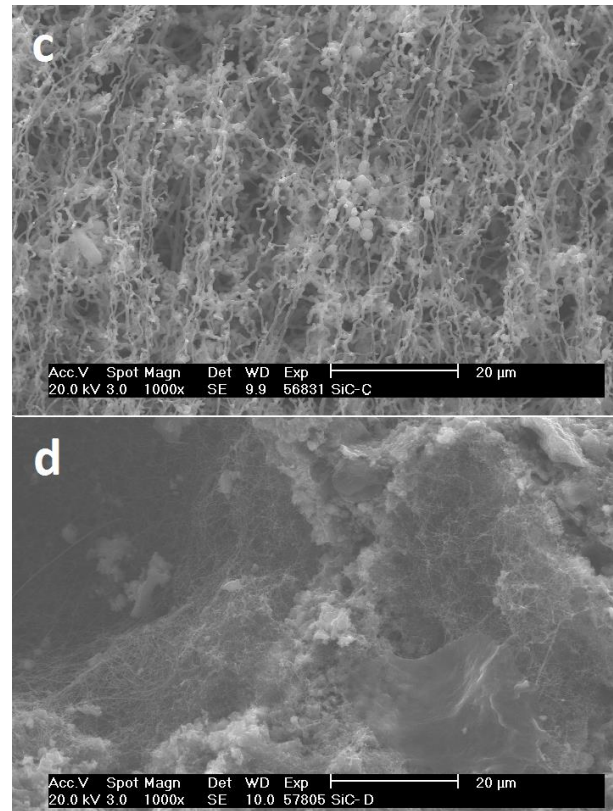

Fig. 2: SEM micrographs (SE mode) of the cross section of SiC-C (c) and SiC-D (d) samples.

Fig. 1: SEM micrographs (SE mode) of the cross section of SiC-A (a) and SiC-B (b) samples.

The microstructure of the samples can be observed in Fig.1 and 2. It can be seen how the silicon addition and consequently the ß-SiC formation affected the whole microstructure, the pores or just the surface. The wollastonite was detected as small spheres in the pores for sample SiC-D, see Fig. 3.

Oxidation tests were carried out to see the influence of the additives. In the present study, these were not used as antioxidants like
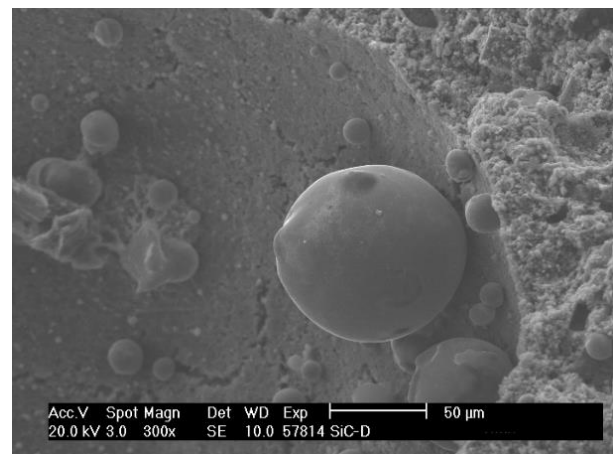

Fig. 3: SEM micrograph (SE mode) of a spherical particle in a pore of the SiC-D sample

As can be seen in Fig. 4, the highest mass loss of approx. 2.7 % took place up to 1200 °C and was followed by a mass increase of approx. 0.7 % for sample SiC-A (with 2 wt% Si addition). Against the expectations, sample SiC-C without wollastonite but with 6 wt% Si addition reveals a continuous mass loss during heat up and the dwell time of 1 hour. It can be assumed that the high open porosity is responsible for this phenomenon since the oxidation of the SiC grains occurs from 500–600 °C and should compensate the loss. This overlapping can be seen in the case of samples SiC-A, -B, and -D too. Sample SiC-B presented a mass loss of 1.65 %, sample SiC-D the lowest one of 1.48 %. For the samples SiC-A, -B, -D a mass increase of 0.7 % was detected. It was expected that this mass increase would be related to the glassy layer formation, however, this was only observed on the sample SiC-D.
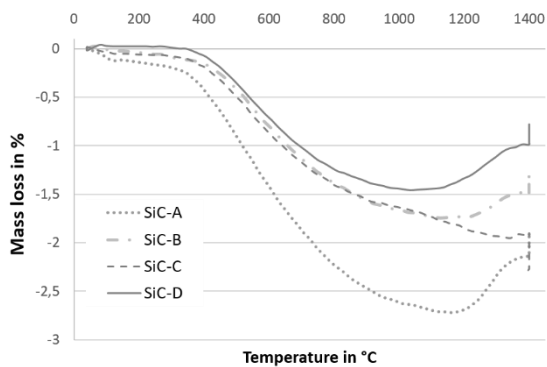

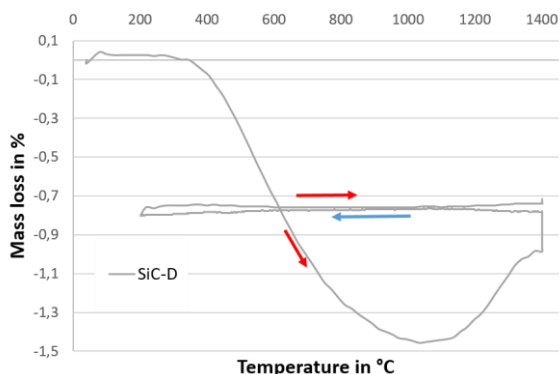Fig. 4: Thermogravimetric measurement of the SiC-A, -B, -C, -D samples

Fig.5: Thermogravimetric measurement of the SiC-D sample with repeated heat up.

The glassy layer stability and permeability were tested as shown in Fig 5. No further mass loss was measured for the sample during repeated heat up and dwell time of 1 hour up to 1400 °C. The glaze microstructure was analyzed utilizing SEM and EBSD, see Fig. 6 and Fig. 7. The structural analysis yielded a thickness of the glassy layer of approx. 50–100 μm.
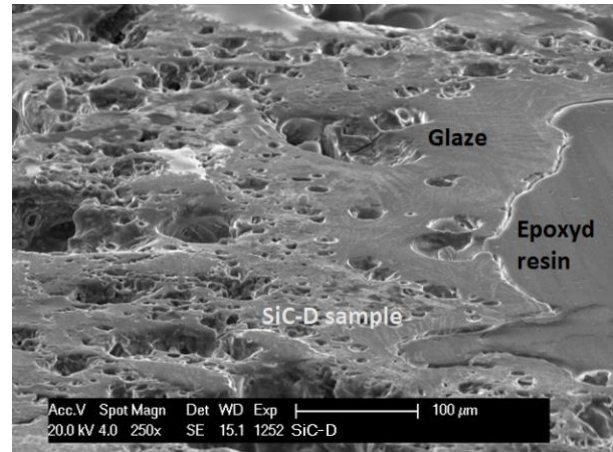

Fig. 6: SEM image (SE mode) of the cross-section of the SiC-D self-glazed sample
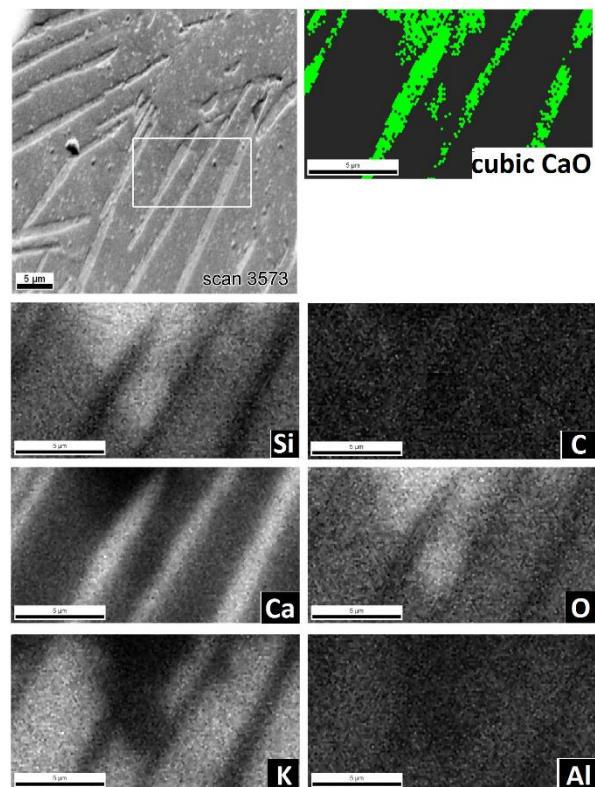

Fig. 7: SEM image of the glaze layer, element distribution, and EBSD phase analysis of the crystals in the amorphous phase (green: cubic CaO)

The elemental analysis revealed silicon, calcium, potassium, and oxygen as major elements, which was dedicated to the

wollastonite and water soluble resin addition. Within the amorphous phase, some needle-like crystals were registered. They could be identified employing EBSD as cubic CaO.

CONCLUSION

Boron-free carbon-bonded SiC vibration flow castables, with glass-forming additives were developed. It was found that microsilica addition besides wollastonite delays the oxidation in comparison to the same amount of metallic silicon addition. Samples with only 6 wt% metallic silicon addition showed continuous oxidation. However, only the composition containing 6 wt% Si in combination with wollastonite and the water-soluble resin presented a glassy non-permeable protective layer together with good mechanical properties and oxidation resistance. It was concluded that the addition of the water-soluble KOH containing Bakelite® WhiteCast resin is necessary for an effective glaze formation.

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