New Environmentally Friendly Carbon Bonded Alumosilicate Refractories: From Concept to Application

D. Cölle, M.P. Wiessler, C.G. Aneziris

Novel refractory composites within a newly developed carbon containing alumosilicate composition of defined granulometry are presented. The fundamental function of these composites is based on the granulation process approaches with more homogeneous macro- and microstructures, followed by flexible bonding. The material is characterized by high bonding strength and flexibility, combined with an effective oxidation inhibition. Furthermore, major factors to achieve a high slag penetration resistance are described. Concerning the focussed applications of these shaped materials, mainly in high corrosive areas of shaft furnaces, the obtained results of selected physical and chemical properties justify the replacement of commonly used refractory castables or ramming mixes based on the system Al_2O_3–SiC–C.

1 Introduction

"To be continued", refering to this argument from an outlook, a conception of a novel alumosilicate-carbon refractory material was introduced in 2007 [1]. Summarized, the objective is an application of prepared specific natural raw material fractions of high purity as main components of a high-temperature ceramic. In combination with selected carbon sources, composite materials with low wedding character and flexible bonding systems were postulated and confirmed in first examinations. Complementary, information and basic examinations are given in [2]. Furthermore, the technically proved main raw material is quasi indefinitely available. In contrast to this, completely synthesised Al_2O_3-SiC-C refractories are typically used in shaft furnaces, as a currently commercial practice, within the melting zone or iron and slag peripheries due to the high thermal stability, a specific strength profile and an adjusted abrasion and corrosion resistance. Slag amount and slag characteristics exert an important influence on the wear behaviour of these materials [3]. An exemplary construction type is illustrated in Fig. 1. The aim of current works intends to qualify selected modelling materials of an alumosilicate-carbon refractory for real conditions in shaft furnaces successively.

2 Basic arguments

Thermal stability is demanded up to temperatures near 1550 °C. By focussing on the well known wear mechanism, mainly initialized by decompositions of anti-wedding carbon structures and provoked through slag phases, a composite system with defined thermo-mechanically flexible volume units and visco-elastic peculiarities combined with an oxidation-protected carbon bond was assumed, in order to prepare alternatives to conventional materials. With increasing importance all necessary raw materials are prepared by imports independently with a long-term availability. Under consideration of material production and logistics, installing procedure and expected durability advanced economical and ecological aspects should be realized in the near future. Idea and conception of the alumosilicate-carbon composites is represented schematically in Fig. 2.

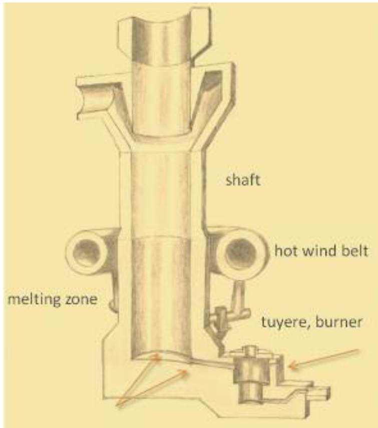

Fig. 1 Exemplary schematic representation of a shaft furnace (after EKW, Eisenberg/DE) with focus on essential, high-efficiency refractory demands up to and above the tuyere level, furthermore peripheries (see arrows)

So-called alumosilicate-carbon units as a granular material are defined to represent a complete homogeneous system of its own with high purity and reactivity to the surrounding others. Step by step it means: better workability in aqueous systems through the fixation of a hydrophilic alumosilicate-

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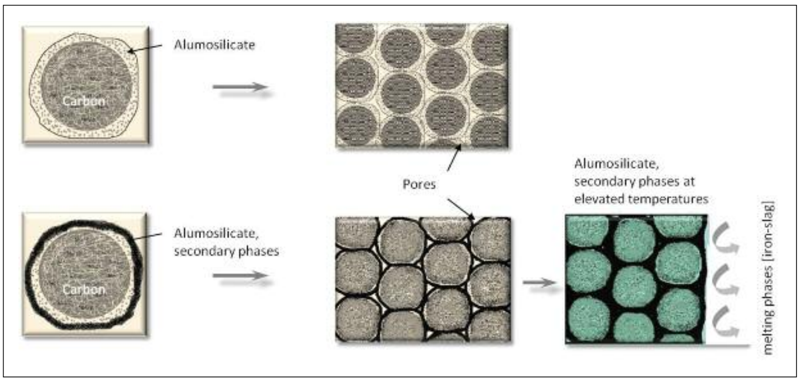

Fig. 2 **Schematic illustration of the composite conception**

based surface layer on carbon particles. The covered carbon particles stick together among each other through formation of an increased density with rising temperatures under retention of the necessary microporosity. The expected plastic behaviour of softening alumosilicate phases enables reduction of inner tensions. A compaction through infiltration of the porosity with low-viscous alumosilicate phases results in a reduction of the permeability with rising temperature to achieve the demanded oxidation inhibition. At least, an improved resistance against slag-metal attack should be evident.

3 Materials and methods

3.1 Characteristics

The basic alumosilicates are specified and exclusively prepared by *EKW GmbH*, Eisenberg in Palatinate/DE. The alumosilicate raw materials (AlumoSilicate, AS) used in this work are derived from a natural and regional limited well-defined and specified deposition. This raw material called "Eisenberger Klebsand" could formally be defined as kaolinized quartz sand (in technical terms: luting sand) and represents a sedimentary kaolinite, which originated through rock decay (primary residual clay), desolidification and rearrangements of the stratifications of variegated sandstone in the tertiary approximately 30 million years ago.

All the more significantly, the luting-sand deposit located in the geological region called "Eisenberger Becken" represents the biggest worldwide. Interrelated deposits of luting sands are very rarely to find caused by the nature of earth. The "Eisenberger Klebsand" mineral composition is characterized through approximately 80 % quartz and 20 % clay minerals, combined with nano-scaled crystalline and non-crystalline phases (Fig. 3).

The quartz grains covered with different kinds of kaolinitic minerals and also Al-Si phases in an amorphous stage with fractions of µm- and sub-µm scales [1, 4]. Essential characteristics of the specified alumosilicate fractions are summarized in Tab. 1, also re-

Tab. 1 **Characterisation of AlumoSilicates (AS)**

	AS $_{coarse}$	AS $_{fine}$
Grain size distribution	d_{10} = 10 µm d_{50} = 230 µm d_{90} = 650 µm	d_{10} = 0,7 µm d_{50} = 4 µm d_{90} = 25 µm
Mineralogical compostition	80 % quartz 20 % clay minerals	50 % quartz 50 % clay minerals + non-crystalline phases
Chemical composition	[mass-%]	
SiO_2	91,3	70,5
Al_2O_3	5,9	19,6
Fe_2O_3	0,2	1,1
TiO_2	0,2	0,9
K_2O	0,2	0,9
Na_2O	0,0	0,1
CaO	0,0	0,1
MgO	0,1	0,2

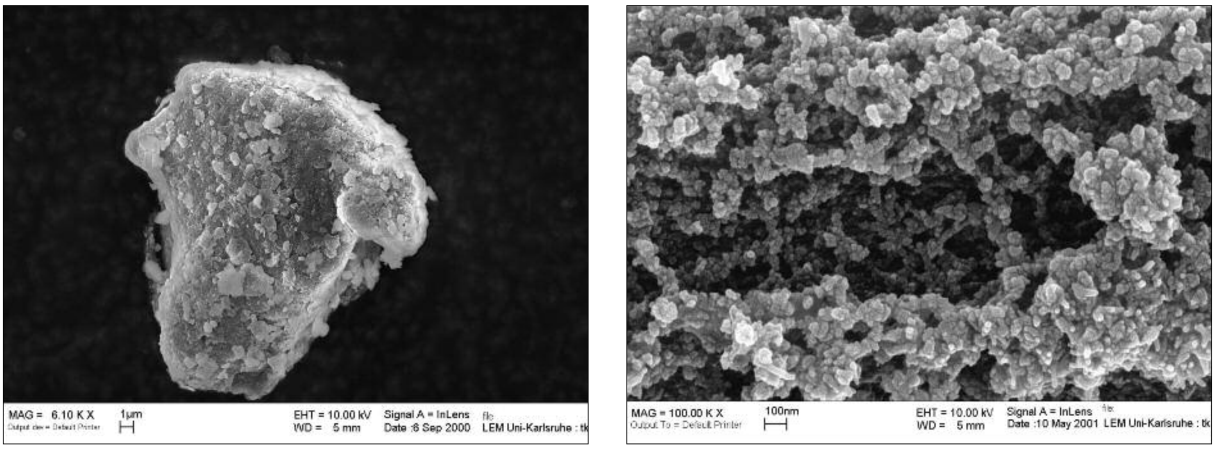

Fig. 3 **Typical, irregularly restricted grain represented the alumosilicate from "Eisenberger Klebsand", surrounded by clay particles (left side), structural construction of spherical Al-Si-gel phases of a loosely connected aggregate (right side)**

ferring to [5]. Already in a pure, untreated condition, the "Eisenberger Klebsand" in principle combines high adhesion with increased mechanical strength in a wide interval between room temperature and approximately 1700 °C.
Carbon agents and a specifically adapted carbonaceous binder system based on phenolic resins from *Momentive Specialty Chemicals GmbH*, Iserlohn-Letmathe/DE, following an approved practice [6, 7], were adjusted and optimized with a CARBOnaceousRESin, which is a high melting coal-tar resin. In contrast to the most frequently used resins, it forms a highly oriented graphite-like carbon structure after coking. This product from *Rütgers Basic Aromatics GmbH*, Castrop Rauxel/DE, was selected for producing the carbon bonding of the shaped alumosilicate-carbon composites produced. Coarse flaky graphite with high purity and low oxidation sensitiveness was applied to increase the total carbon content.
Finally, functional, nano-scaled additives were used to design and adjust the microphase evolution and oxidation-protection mechanism. In general, for the present shaped alumosilicate-carbon composites bulk-density values between 1,9 g/cm³ and 2,2 g/cm³ are characteristic, depending on the thermal treatment. The values of open porosity are clearly < 20 % after carburization and graphitization of the contained carbonaceous raw materials above 1000 °C.
Furthermore, the cold crushing strength achieves values > 30 MPa. Fig. 4 informs about the fundamental design of the composites. From this the typical chemical composition results of approximately 7 mass-% Al_2O_3 and 65 mass-% SiO_2 combined with a free carbon content of about 15 mass-%, also referring to [1].
After homogenisation all raw materials were granulated at room temperature in an R-type semi-production mixer (Eirich/DE) during a defined build-up agglomeration process as reported in [8]. Under consideration of the graphite wedding behaviour the surface tension was adjusted by batching additives in a suspension which was sprayed during mixing to improve the homogeneity of the granular material. Finally, the granular material was pressed by uniaxial procedures at 150 MPa to archive shaped composites of 230 mm × 114 mm × 64 mm and hardened for 2 h. The hardening temperature amounted to approximately 200 °C.

Specific	Alumosilicate (coarse)	Alumosilicate (fine)	Flaky graphite
	[mass-%]	[mass-%]	[mass-%]
	55 – 60	10 – 15	7 – 12
common	modified coal tar pitch powder	resin, hardener, wetting agent	Al-based additives

Fig. 4 **Fundamental composition of the alumosilicate-carbon composites**

3.2 Corrosion behaviour

To archive and evaluate fundamental microscopic corrosion effects under controlled conditions near to in-situ demands of shaft furnaces, industrial rotary furnace tests were conducted at *ThyssenKrupp Steel*, Duisburg/DE with a heating rate of 65 K/h up to 1550 °C / 80 h. Focussing the comparability, a negligibly reducing atmosphere at the gas-fired rotary furnace was adjusted (understoichiometric combustion). The set-up of the composites is given in Fig. 5.
Tab. 2 shows the chemical composition of the applied corrosion medium. A slag was taken from a shaft-furnace. An elevated corrosion potential is expected, especially with focus on the elements calcium, iron and manganese, leading to reduced constitutional or in-situ formed oxides and silicates. After the tests procedure post-mortem preparation and analysis of selected specimens were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX).

Tab. 2 **Typical slag specimen that was taken from the shaft furnace [mass-%]**

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Alkalines
31,1	6,8	17,4	1,3	0,6
CaO	**MgO**	**SO_3**	**MnO**	**P_2O_5**
30,7	4,5	5,2	1,9	0,2

Fig. 5 **Set-up of the composites, rotary furnace experiment, conducted at ThyssenKrupp Steel, Duisburg/DE. The evaluated alumosilicate-carbon compositions are signed with white coloured numbers**

4 Results and discussion
4.1 Observations

A low decarbonisation was expected due to the effective oxidation inhibition system, derived from first bases in [9]. Especially the preparation of carbon modifications like flaky graphite with alumosilicate (fine), pure or applied specific antioxidant additives represent a key function to form oxygen diffusion barriers within the inter-aggregate phases if the mullitization is completed, usually between 1100 °C and 1300 °C.
It should be noticed that the affection of the slag phases results in penetration depths only between 500 µm and 1500 µm in correspondence with a corrosion test > 50 h (Fig. 6 and Fig. 7). At this, iron indicates a relatively compact and thin accretion on the composition surface and does obviously not influence further reactions.
Theoretically, transformed FeO phases have an increased reduction potential to silicates to form low-melting iron silicates, e.g. fayalite. On the other hand, a higher iron valency could be expected until the phase equilibrium was achieved to stabilize the material surface. In context with calcium, the con-

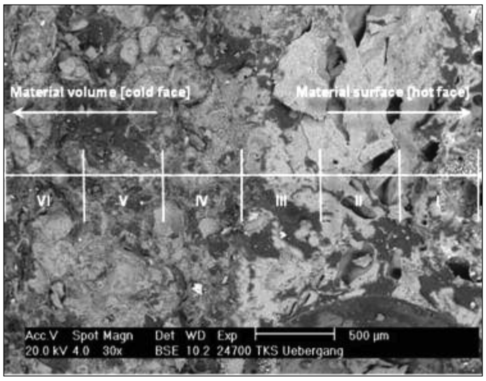

Fig. 6 Microstructure of the reaction profile related to slag-refractory interaction

tents of magnesium and manganese indicate reliably the expectant infiltration of the slag into the material volume. Its decrease proceeds rapidly above a penetrated scale thickness of 1000 µm and corresponds afterwards to the origin chemical composition of the alumosilicate-carbon composites as the values of Al and Si indicate.

4.2 Selected approaches

Under refractory points of view, the present fractions of a defined and prepared alumosilicate raw material indicate an increased reactivity at high temperatures with coexisting stability of mullite and cristobalite as reaction products. In addition, carbon contents like coarse-crystalline graphite could be coupled and consequently protected against oxidation or also layered in case of extremely fine dispersed carbon particles, e.g. carbon black. Sintering, with or without additives (antioxidants, sintering aids, mineralizers …) should densify the microstructure in presence of fluid phases (Fig. 8), also referring to Fig. 2. In consequence, the mutual diffusion velocity of gas phases (O_2, CO,

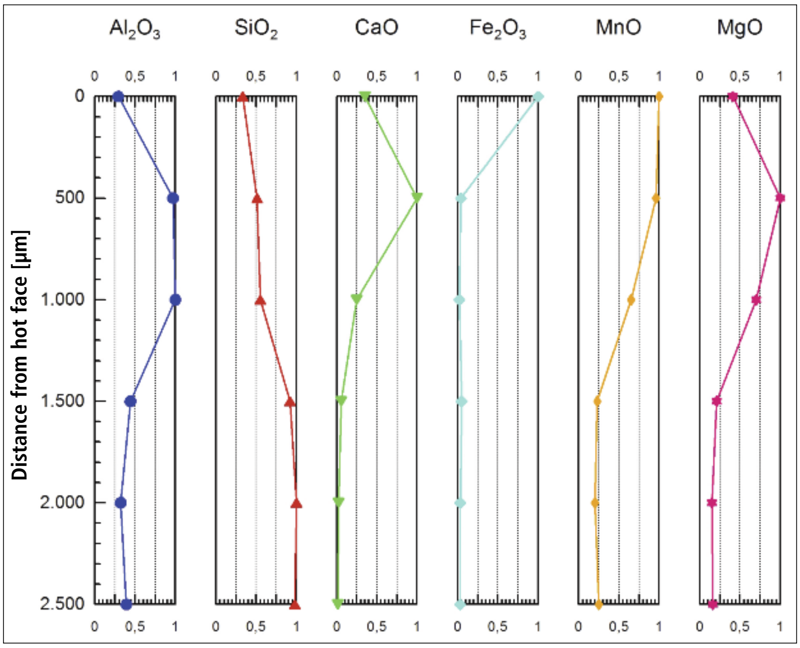

Fig. 7 Profile of essential penetration phases from slag components into the alumosilicate-carbon composition (normalized relative phase quantities) without consideration of the contained carbon

CO_2) will shift to lower values. In addition, Al-based additives support the stabilization of pure SiO_2 against carbothermic reduction following par example:

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \quad (1)$$

$$SiO_{(g)} + C_{(s)} \rightarrow Si_{(s)} + CO_{(g)} \quad (2)$$

In case of ambient reducing atmospheres at temperatures above approximately 1510 °C the carbon reacts with crystallizing mullite (thermodynamic instability) and forms SiC, alumina and mainly CO. The possibly increasing porosity could be easily regulated. Further densification of the structure and an improved wetting behaviour should result.

5 Conclusion

Due to the present refractory composites based on a granulated carbonaceous alumosilicate system, a new material as well as processing route has been performed. Approved low oxidation sensitiveness within the combination of the present raw material, additives and processing system are uniquely.

The granulation process results in more homogeneous macro- and microstructures followed also by flexible bonding mainly based on the combined ceramic as well as carbonaceous bonding mechanism. This argument could be supported by the statement that major wear mechanisms were related not only to chemical corrosion, erosion and oxidation, but also to the application conditions which promoted the attack during service. These conditions determined a decrease in the performance of the working lining due to grain segregation associated to the preparation conditions.

Furthermore, it was pointed out that inhomogeneous grain size distribution promotes mechanical strength decrease, apparent porosity increase and non-uniform chemical composition and phase distribution [10].

At last, interactions between corrosive phases and selected performed composites obviously result in a relatively slightly distinctive interface as a transition from the corroded surface to the unaffected bulk volume.

Finally, homogeneous processed granular materials with an approximation-wisely mono-modal particle size distribution have been realized as alumosilicate-carbon units for different kind of pressing routines to archive shaped composites.

A further important factor also by focussing the current global raw material situation, which joins with continually rising costs [11], could be expressed in an application as raw material for substitution or optimizing existing monolithic refractories, e.g. plastics,

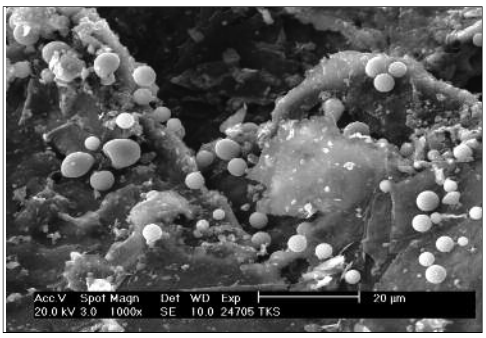

Fig. 8 Microstructure in detail taken from the cold face; typical amounts of silica-rich alumosilicate (spheroids), also referring to [1]

castables or gunning-shotcreting mixes, for sustainable refractory developments oriented on the lining and maintenance of shaft furnaces.

And last but not least, EKW was awarded with the "Innovation Award for Companies in the Raw Materials Industry" of the German state of Rhineland-Palatinate for outstanding performances in July 2010 for the development of a new carbon-bonded refractory composite on the basis of Eisenberger Klebsand, in cooperation with the *Technical University Bergakademie Freiberg, Institute of Ceramic, Glass and Construction Materials*/DE.

In consequence the demonstrated new material standard was transferred primarily into the production of high-alumina ramming mixes, silica-based gunning mixes and corrosion-stabilized castables.

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