Contribution to the Characteristic Improvement of Carbon Bonded Doloma Refractories by Addition of TiO_2

V. Stein, Chr. G. Aneziris, E. Guéguen, K. Hill

The production and application of carbon bonded refractories is linked with environmental harmful emissions in the broadest sense. Amongst the aspect of environmental friendly refractory systems this work has observed and shown the interaction of functional ceramic material TiO_2 with the organic binder system in doloma carbon refractories. The focus of the present work lays on increased residual carbon content of the binder resin and furthermore improved mechanical and physical properties due to TiO_2-addition. This offers the feasibility to reduce the total carbon content without downgrading the brick properties. This aspect has not been observed yet and is of high interest with respect to reduced emissions and environmental friendly refractories.

1 Introduction

Doloma carbon bricks with graphite contents of approximately 2 mass-% are widely used in the production of stainless steels in AOD (Argon Oxygen Decarburisation) or in VOD (Vacuum Oxygen Decarburisation) vessels as lining material. The application of doloma refractories is connected with metallurgical benefits such as high oxidic stability of its oxides, and the ability to bond sulphur from the hot metal. Directly linked with the production and application of carbon bonded refractories is the aspect of environmental harmful emissions as well as emissions of greenhouse gasses like CO_2. Based on the *Kyoto Protocol* and the *German Federal Emission Control Act* it is a general aim to reduce emissions [1, 2]. The binder makes the adherence of the oxide grains possible. The residual carbon content of the resin in combination with graphite and carbon black is lowering the steel and slag wetting due to the surface occupation of the fines [3–5]. The addition of primary carbon (graphite and carbon black) increases both the carbon content and the slagging resistance and elasticity and is decreasing the thermal expansion, cold crushing strength and bulk density of the products. *Yamaguchi et al.* and *Rakszawski et al.* found out, that refractory oxides like TiO_2, ZrO_2 and MgO are able to improve the oxidation resistance of graphite due to an interaction mechanism. That stabilizes the graphite structure [6, 7]. This leads to the assumption that the introduction of TiO_2 into doloma carbon refractories over the phenol binder system can cause an effect on the residual carbon content of the resin. The actual residual carbon content of typical novolak resin used for doloma carbon brick production lays at approximately 45 mass-%. An increased carbon content could result in the reduced emission of harmful pyrolysis gases and furthermore in an improvement of the mechanical properties. An increased carbon content of the binder resin will lead also to the feasibility to reduce the binder resin content or reduce the primary carbon content while the properties of the products are not decreased. This is a real chance to reduce emissions in more than one way.

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2 Experimental

As raw materials (Tab. 1), commercially available dead burnt doloma (Magnesita Refractories GmbH/DE) with a density of 3,23 g/cm³, graphite flakes with a specific

Tab. 1 Used raw materials

Raw material	Density [g/cm³]	Purity
Doloma	3,23	59,2 % CaO + 38,3 % MgO
Graphite flakes A/F	2,26	96,0 % carbon
Carbon black N990	1,90	99,8 % carbon
TiO_2 (anatase)	3,67	>97,0 %

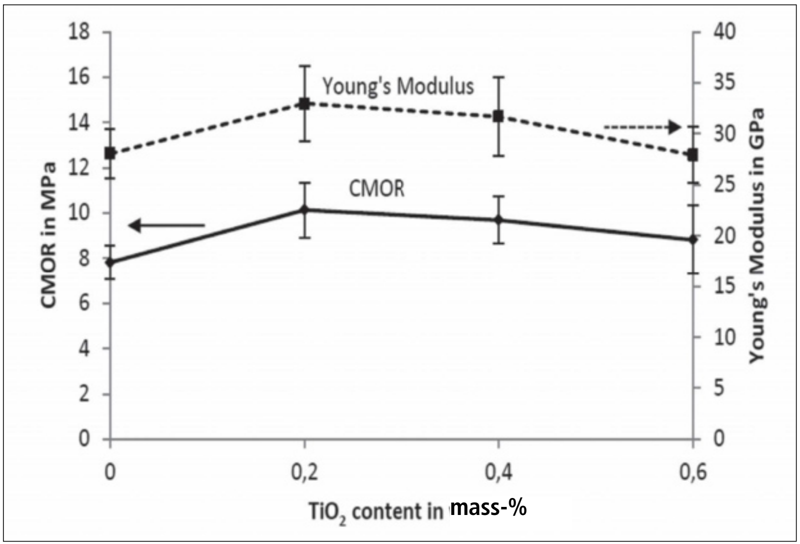

Fig. 1 CMOR and Young's modulus as function of TiO_2 content after firing at 1000 °C

Tab. 2 Physical properties of doloma-carbon samples containing TiO_2

	Reference	0,2 mass-% TiO_2	0,4 mass-% TiO_2	0,6 mass-% TiO_2
BD 1000 °C [g/cm³]	2,85 ± 0,02	2,85 ± 0,01	2,86 ± 0,02	2,87 ± 0,01
AP 1000 °C [%]	13,97 ± 0,70	13,54 ± 0,22	13,55 ± 1,11	13,08 ± 0,39
C-content 1000 °C [mass-%]	3,49 ± 0,03	3,88 ± 0,06	4,01 ± 0,07	3,93 ± 0,03

surface area of 11 m²/g and a carbon content of 96 mass-% C (*Graphit Kropfmühl*/DE) and carbon black with a specific surface area of 12 m²/g and a carbon content of 99,8 mass-% (*Cancarb Ltd.*/CN) were used. The used titania was an anatase powder (*Tronox*/DE) with a specific surface area of 90 m²/g and a TiO2-content larger than 97 mass-%.

At first a resin slurry was prepared. Therefore, the liquid resin was heated up to 65 °C and then mixed together with the TiO_2-powder. This slurry brings the benefit of avoided dust accumulation of the expensive micro scaled TiO_2 and a very good allocation of TiO_2 in the binding-matrix.

The raw materials were mixed at room temperature in an *Eirich* intensive mixer following the standard commercial practice. The grain size distribution of the raw materials has been selected with respect to an optimal packing density according to the theory of *Dinger-Funk* (q = 0,4; d_{min} = 0,04 µm; d_{max} = 4000 µm) [8]. A mixture of liquid and powder Novolak resin (*Momentive Specialty Chemicals*/DE) was used as binder. Hardening agent was hexamethylenetetramine.

After mixing bar shaped samples (25 mm × 25 mm × 150 mm) were uniaxial pressed at 150 N/mm². The pressed samples were cured in a drying chamber at 200 °C for 2 h. Afterwards the samples were coked at 1000 °C for 5 h in a retort filled with petrol coke. The physical and mechanical properties were determined after firing at 1000 °C according to EN 933-1 open porosity (OP) and bulk density (BD) with toluene, EN 993-6 cold modulus of rupture (CMOR) and in dependence on DIN ENV 843-2, using equation 1, dynamic Young's modulus. The residual carbon content was determined by LECO carbon detector CS200.

$$E = 0{,}9 \cdot \left(\frac{l_{sample} \cdot 1000}{t_{ultrasonic}}\right)^2 \cdot \rho_{bulk} \qquad (1)$$

The microstructure was investigated with the aid of scanning electron microscope (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD).

3 Results

Fig. 1 shows, that TiO_2 improves the mechanical properties of the fired samples in the doloma carbon system. The CMOR shows a significant increase of 30 % with a TiO_2-content of 0,2 mass-%. Also Young's modulus shows the same characteristics.

With increasing TiO_2-content both, CMOR and Young's modulus, are slightly decreasing. The physical properties evolution correlates with the evolution of mechanical properties as to be seen in Tab. 2.

Furthermore, as to be seen in Fig. 2, the pore size distribution is decreasing to smaller pore sizes with increasing TiO_2 content and reaches the minimum pore sizes with a TiO_2 content of 0,4 mass-%. With increasing TiO_2

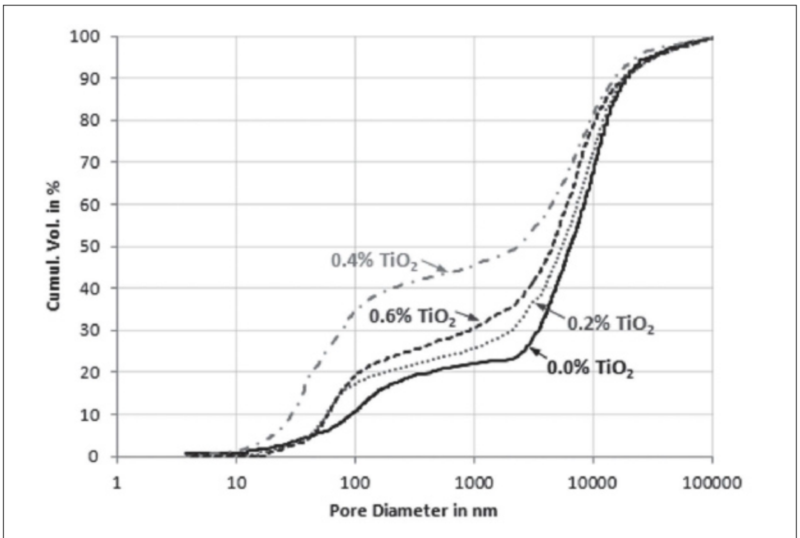

Fig. 2 Pore size distribution of TiO_2 containing doloma-C samples coked at 1000 °C

content, the pores are growing to larger sizes.

The addition of TiO_2 into the doloma carbon system led to the in-situ formation of $CaTiO_3$ in the matrix out of the reaction with CaO from the doloma according to equation 2.

$$CaO + TiO_2 \rightarrow CaTiO_3 \quad (2)$$

The formed $CaTiO_3$ is well distributed in the matrix and has formed directly on the doloma grain matrix interface as to be seen in Fig. 3. During firing process $CaTiO_3$ is formed and with the optimum amount of 0,2–0,4 mass-% TiO_2 the formed $CaTiO_3$-crystals reinforce the matrix. This joining between matrix and doloma grains leads to improved mechanical and physical properties. The problem is the growing mechanism of the $CaTiO_3$. $CaTiO_3$-crystals are formed out of a solid state reaction. The growing $CaTiO_3$-crystals need space. If the amount of TiO_2 is too high, the formed $CaTiO_3$-crystals are pressed in the matrix and due to the generated friction in this process, cracks are formed. So the primary beneficial influence of in-situ $CaTiO_3$-formation is changed into an unfavourable influence for the system.

After coking doloma carbon with TiO_2 addition at 1000 °C no residual TiO_2 can be found, as Fig. 4 shows. The main peaks can be identified as MgO from the doloma. As a result the complete initial TiO_2 has reacted with CaO to form $CaTiO_3$. Fig. 5 shows the model imagination of the microstructural influence of $CaTiO_3$ formation.

It was found that the residual carbon content after coking at 1000 °C is increasing

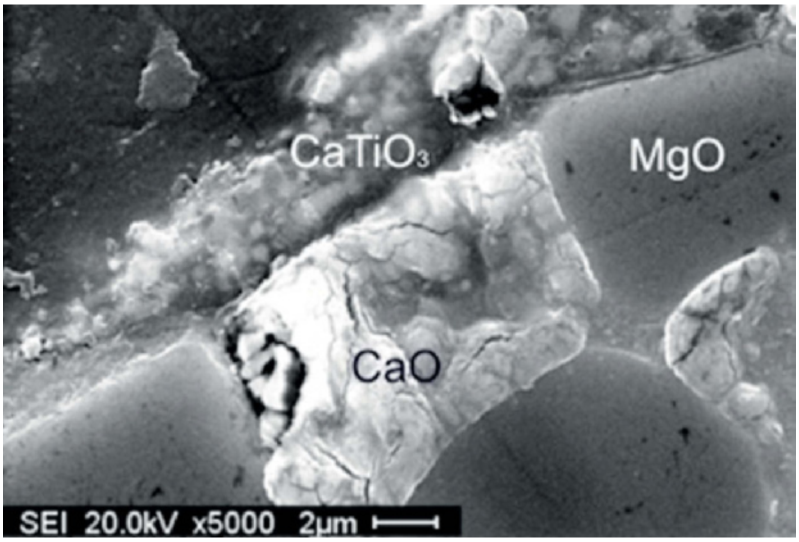

Fig. 3 $CaTiO_3$ formed on doloma grain

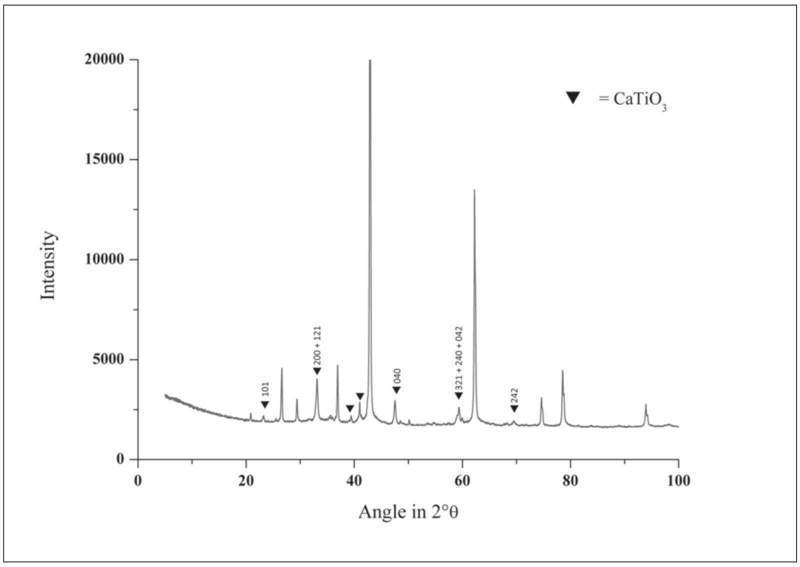

Fig. 4 XRD patterns of doloma carbon sample containing 0,6 mass-% TiO_2

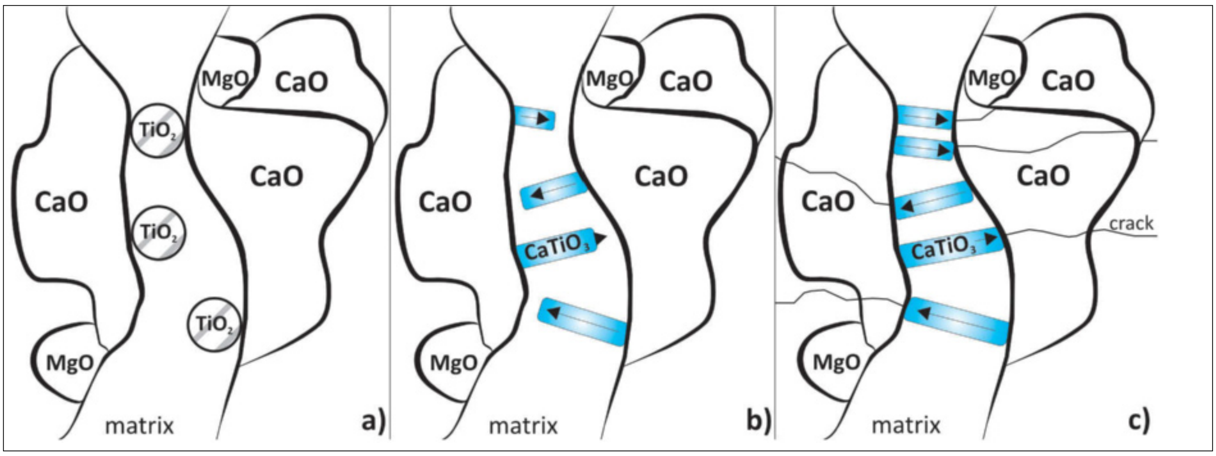

Fig. 5 Schematic draft of $CaTiO_3$ influence on the properties evolution in doloma carbon refractories: (a) situation before firing; (b) optimum amount of TiO_2 leads to formation of toothed $CaTiO_3$ crystals grown on doloma grains during firing; and (c) TiO_2 addition above optimum content leads to overexpansion and stresses in the microstructure due to a too strong $CaTiO_3$ growth (in a too high amount))

with increasing TiO_2 content as to be seen in Tab. 2. This behaviour can be explained by the mechanism that was described by *Yamaguchi, et al.* [6]. The stabilised carbon lattice structure in an early state of coking process is leading to a lower loss of carbon during the same. The calculated residual carbon of the initial binder in the reference system is 41,9 mass-%. The residual carbon content of the binder including 0,4 mass-% TiO_2 lays at 58,1 mass-%. This is a significant increase of the residual binder carbon content connected with reduced emissions. In consequence of this result it would be possible to reduce the binder content for approximately 1,0 mass-% to generate equal residual carbon content in the system.

Related to the production of carbon bonded doloma refractories this means a saving of approximately 10 kg resin per 1 t bricks. This is related with an environmental protective aspect and economic savings. It has to be kept in mind that the most expensive component of carbon bonded refractories is the resin.

4 Conclusion

The addition of TiO_2 into the doloma carbon system leads to improved physical and mechanical properties. First TiO_2 leads to a better matrix network linking of the resin binder due to a combined mechanism of adsorption of resin macro-molecules and stabilisation of the resite lattice. The very good distribution of in-situ formed $CaTiO_3$ and the fact that it has been formed on the doloma grains and has grown into the matrix leads to an interlocking mechanism between matrix and doloma grains. Improved mechanical and physical properties are achieved. With respect to the low amount of added TiO_2 of 0,2–0,4 mass-%, it seems an economical approach to improve the properties of doloma carbon bricks in use. Furthermore, the aim of increasing the residual carbon content of the resin binder was achieved. The mechanism of TiO_2 resin interaction is based on interaction between TiO_2 and adhered resin molecules or rather carbon lattice during coking (pyrolysis) process. The observed gain of residual carbon content of the binder resin is connected with reduced emissions. Furthermore, the introduced binder is used much more efficient. The higher carbon yield makes it possible to reduce the binder content of the doloma carbon refractory system or reduce the content of primary carbon (graphite and carbon black). Herewith, CO_2 emissions can be reduced as well as emissions from the binder during pyrolysis process. In this context it is very important to see the fact that the physical, mechanical and thermo-mechanical properties are not downgraded. Contrariwise, the properties are improved. Finally the positive effect for the environment and the positive economic effect are very important.

Acknowledgements

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