

Functional Spinel-Binder Based Additives for Improved MgO–C Performance in Ladle Applications



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Carbon bonded magnesia and magnesia-alumina bricks are used in the side walls and bottom of steel ladles for more than 30 years. They have to withstand aggressive steel/slag systems in the range of 1600–1750 °C and also provide an excellent thermal shock performance. During service or pre-sintering, alumina is able to react with magnesia to form spinel. In order to improve thermomechanical and chemical performance MA-spinel raw materials alumina-rich spinel and highly reactive spinel binder/clinker have been introduced in the composition. The impact of spinel or spinel forming phases on physical and thermomechanical properties as well as corrosion resistance has been found to depend on the grain size, chemistry, and amount of added raw materials. In order to implicate and reflect the influence of spinel formation on material properties the carbonization temperature has to be above common 1000 °C. Two different pre-reacted coarse- and fine-grained MA-spinel raw materials were added to common MgO–C with 3 mass-% C (after carbonization) and carbonized at 1000 °C and 1400 °C respectively. Thus, improved MgO–MgAl₂O₄–C samples with pre-reacted and in situ formed spinel for application in steel ladles were produced. Material properties like cold crushing strength (CCS) and thermal shock resistance, microstructure, and phase composition have been analysed.

1 Introduction

MgO–C is first choice refractory material for the slag line of steel ladles as it exhibits excellent slag penetration resistance due to non-wetting property of carbon with slag, thermal shock resistance, high thermal conductivity, low thermal expansion and high toughness [1]. Poor oxidation resistance as well as low strength at high temperatures are limiting service life of MgO–C refractories. In addition, higher wear due to increased severity in operating conditions reduces service life as well. Hence, steel producers seek refractories with enhanced thermomechanical properties which e.g. led

to the development of spinel-containing or spinel-forming carbon-containing refractories of type Al₂O₃–MgAl₂O₄–C [2]. Compared to conventional high alumina and doloma refractories, Al₂O₃–MgAl₂O₄–C bricks show better performance in steel ladle [3]. Another type of spinel- and carbon-containing refractories are MgO–MgAl₂O₄–C bricks. The properties of MgO–MgAl₂O₄–C refractories can be influenced by the manufacturing process and the material composition (spinel and carbon content). Choi and Jun produced MgO–C–MgAl₂O₄ by adding thermite reaction products of MgO and Al to MgO–C. Compared to MgO–C and MgO–C–Al, these refractories showed a

higher corrosion resistance against CaO/SiO₂ slag (ratio 3:3) [4]. Also ultra-low-carbon-containing MgO–MgAl₂O₄–C bricks with a carbon content <1 % showed good properties by means of oxidation resistance, HMOR, volume stability and slag resistance and were used in slag line of 200 t converter obtaining average service life of 75 heats [5]. Ganesh et al. have shown that the addition of 20 mass-% MgAl₂O₄ prepared by reaction of a stoichiometric mixture of Al(OH)₃ with particle size of 85 µm and caustic MgO with particle size of approx 5 µm improves the slag erosion resistance of MgO–C by 48 % [6]. In addition, nano-sized MgAl₂O₄ spinel, prepared by citrate-nitrate gel method, incorporated into matrix of

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Tab. 1 Sample composition

Raw Material [mass-%]	MgO-C	CMA_Z	CMA_K	MA_F	MA_G
MgO	97,8	92,8	92,8	92,8	92,8
CMA 72 cement	–	5,0	–	–	–
CMA 72 clinker	–	–	5,0	–	–
AR78 –90 µm	–	–	–	5,0	–
AR78 1–2 mm	–	–	–	–	5,0
Graphite	1,1	1,1	1,1	1,1	1,1
Carbon black	1,1	1,1	1,1	1,1	1,1
Powder resin	1,5	1,5	1,5	1,5	1,5
Liquid resin	1,5	1,5	1,5	1,5	1,5
Hardener	0,3	0,3	0,3	0,3	0,3

Tab. 2 Mineral composition of AR78 and CMA 72

Phase [mass-%]	AR78 –90 µm	CMA 72 Cement
CaO·Al ₂ O ₃ (CA)	–	18–22
CaO·2Al ₂ O ₃ (CA ₂)	–	8–12
MgAl ₂ O ₄ (MA)	100	68–72
Ca ₂ Al[AlSiO ₇] (C ₂ AS)	–	<1

MgO–C refractory showed better properties than MgO–C refractory and commercially available micron-sized spinel-added MgO–C [7]. The addition of 0,5 and 1 mass-% respectively nano-spinel improved the corrosion, oxidation, and thermal spalling resistance due to the effective protection of graphite from being decarburized, as nano-spinel modifies the pore size distribution and hence restricting the flow of oxygen and slag into the matrix.

Additionally, the chemistry of the spinel raw material influences the properties of MgO–C refractories. Wu et al. have shown that CaAl₄O₇–MgAl₂O₄ is beneficial to improve the thermal shock resistance of MgO–C brick with 4 % carbon, whereby the appropriate addition of these compound has been found to be 6 mass-% [8].

As the grain size and chemical composition of the spinel raw material has been found to be essential for improving the properties of MgO–Al₂O₃–C refractories, the aim of this paper is to show the potential of the addition of two different common spinel raw materials with coarse and fine grain size to affect the thermomechanical properties, the microstructure, and phase composition of MgO–C. Furthermore, the influence of carbonization temperature has been investigated.

2 Experimental

As reference material MgO with varied fractions up to 4 mm particle size and 2,2 mass-% carbon was prepared. Graphite and carbon black were used in equal parts as carbon source. Fine grained spinel cement CMA 72 ($d_{50} = 18 \mu\text{m}$), coarse CMA 72 clinker (Kerneos SA/FR), alumina-rich spinel AR78 with fraction –90 µm (fine), and 1–3 mm (coarse) (Almatis GmbH/DE) were added as magnesium aluminate spinel raw material respectively. Both coarse AR78 and CMA 72 clinker were sieved to a maximum grain size of 2 mm in order to replace parts of the MgO 1–2 mm fraction. Also the finest MgO fraction was replaced by fine AR78 as well as by CMA 72 cement. Next to MgO and magnesium aluminate spinel raw materials 1,5 mass-% liquid and 1,5 mass-% powder resin as well as 0,3 mass-% of hexamethylenetetramine hardener were added. Tab. 1 displays the composition of the five formulations. The mineralogical compositions of AR78 and CMA 72 are given in Tab. 2 [9]. In first step all coarse MgO fractions and spinel raw materials were mixed for 3 min. Afterwards the liquid resin was added followed by a 2 min second mixing step. Finally, fine-grained MgO, fine spinel raw material, hardener, graphite, carbon black, and powder resin were added and mixed for another 5 min.

After mixing bar shaped sample bodies (25 mm × 25 mm × 150 mm) and cylinders with 50 mm height and a diameter of 50 mm were pressed using a uniaxial press (RUCKS engine building GmbH/DE) with an applied pressure of 120 MPa. After pressing, the samples were thermally treated (hardening) in a three steps schedule with a maximum temperature of 180 °C. The carbonization of the sample bodies has been taken place in a steel box filled with petrol coke for 5 h in order to provide a reducing atmosphere. In order to evaluate in situ spinel formation, 1000 °C and 1400 °C have been chosen as carbonization temperatures respectively. After carbonization the samples consist of a residual carbon content of 3 % composed of graphite, carbon black, and carbon yield of the resin binder. Cold crushing strength (CCS) of the cylindrical samples have been determined with a 4000 kN servohydraulic universal testing machine (Toni Technik, Berlin/DE) after pressing, hardening, and carbonization. In order to investigate the resistance against thermal shock, bar-shaped samples were quenched 5-times from 950 °C with pressurized air of 1 bar for 5 min according to EN 993-11. During heating to 950 °C, the samples were embedded in petrol coke. The bending strength before and after thermal shock have been measured with a 200 kN servohydraulic universal testing machine with a support distance of 125 mm and 0,15 N/mm²·s traverse speed according to EN 993-6. The open porosity was measured at broken bits of the samples after bending strength test by Archimedes principle according to EN 993-1 using toluol as intrusion medium. Pore size distribution has been determined by mercury intrusion method. In addition, phase identification of milled powders with a maximum grain size of 63 µm based on the bars of the five compositions was performed by X-ray diffraction analysis (XRD) using a PHILIPS diffractometer with CuK_α radiation. The milling of the bars was carried out using a vibration grinding mill.

3 Results and discussion

3.1 Phase composition – XRD

The phases, which will be formed during carbonization, will have an impact on material properties and are expected to be

different by using spinel-binder CMA 72 compared to alumina-rich spinel AR78. CMA 72 with CA-phases is able to interact with MgO in a different way compared to AR78 with slight alumina-excess. The spinel portion of CMA 72 will not interact with the other constituents of the sample body during carbonization, as it exists almost stoichiometric. In contrast, the CA-phases containing in CMA 72 (CA and CA₂) have the potential to form additional magnesium aluminate spinel by reaction of Al₂O₃ of the CA-phases with MgO, if the carbonization temperature is high enough. Compared to CMA 72, AR78 may take MgO in its spinel-structure and form additional spinel, even at lower temperature. Tab. 3 gives an overview of all main phases as well as detectable traces of MgO–C and MgO–C with CMA 72- and AR78-addition after carbonization at 1000 °C and 1400 °C respectively. MgO–C reference sample is composed of MgO and carbon. Additionally, trace phases (e.g. Ca₃Mg(SiO₄)₂) are detectable, which are composed of impurities of MgO. As expected, there are no differences in phase composition after carbonizing at 1000 °C compared to 1400 °C. After carbonization at 1000 °C, samples MA_F and MA_G consist of MgO, MgAl₂O₄, and C. Ca₃Mg(SiO₄)₂ can be detected as trace phase. By comparing the peak positions of the main spinel peak at 31,3 °2θ, some differences can be detected. The spinel peak of sample MA_F with fine AR78 can be found at the same position like the raw material AR78 –90 μm (31,35 °2θ) with same high and width. In contrast, the spinel peak of sample MA-G with coarse AR78 can be found at position 31,45 °2θ in the diffractogram, with a peak

Tab. 3 Main phases and detectable traces after carbonization at 1000 °C and 1400 °C

Sample	Carbonization Temperature			
	1000 °C		1400 °C	
	Main Phase	Traces	Main Phase	Traces
MgO-C	MgO, C	Ca ₃ Mg(SiO ₄) ₂	MgO, C	Ca ₃ Mg(SiO ₄) ₂
CMA_Z	MgO, MgAl ₂ O ₄ , C	CaAl ₂ O ₄	MgO, MgAl ₂ O ₄ , C	–
CMA_K	MgO, MgAl ₂ O ₄ , C	CaAl ₂ O ₄	MgO, MgAl ₂ O ₄ , C	–
MA_F	MgO, MgAl ₂ O ₄ , C	Ca ₃ Mg(SiO ₄) ₂	MgO, MgAl ₂ O ₄ , C	Ca ₃ Mg(SiO ₄) ₂
MA_G	MgO, MgAl ₂ O ₄ , C	Ca ₃ Mg(SiO ₄) ₂	MgO, MgAl ₂ O ₄ , C	Ca ₃ Mg(SiO ₄) ₂

being nearly two times higher compared to MA-F (Fig. 1 a). This indicates an interaction of coarse AR78 with MgO by means of taking some MgO in the structure. After carbonization at 1400 °C, no differences can be detected in sample MgO–C. In contrast, sample MA_F shows a slightly higher spinel content, whereas sample MA_G shows less spinel. However, this can be explained by measuring inaccuracy. By comparing the XRD-analysis of samples containing AR78 with samples containing CMA 72 after carbonization at 1000 °C, only marginal differences in the spinel peaks can be detected. The peak of spinel containing in CMA-samples can be found at 31,5 °2θ in the diffractogram. In samples CMA_Z and CMA_K, next to MgO, C, and MgAl₂O₄ as main phases, additional CA-phases (e.g. CaAl₂O₄) can be detected. With respect to carbonization temperature of 1000 °C, this result does not surprise as spinel formation starts taking place at temperatures in range of 1400 °C under normal conditions and without any promoting agents. Hence, Al₂O₃ containing in CA-phases of CMA 72 does not react with MgO during carbonization of the samples. This is also proven by

presence of CaAl₂O₄ in the samples. This implies that after carbonization at 1000 °C no additional in situ-spinel formation will influence the microstructure of MgO–MgAl₂O₄–C. Hence the addition of AR78 and CMA 72 to MgO–C will have much more influences on chemistry relating properties like corrosion and oxidation resistance than on microstructure relating properties like strength and thermal shock resistance after carbonization at 1000 °C. After carbonization at 1400 °C, CaAl₂O₄-phase cannot be detected anymore, which indicates that an additional spinel formation has been taking place. However, the additional spinel formation is only marginal. Overall, sample MA-F has the highest spinel peak after carbonization at 1400 °C, followed by sample CMA_K, CMA_Z (all 31,3 °2θ), and MA_G (31,45 °2θ) (Fig. 1 b). Of course, it is not possible to deduce the total spinel content based only on information given by XRD-diffractogram.

3.2 Cold crushing strength

Fig. 2 displays the average cold crushing strength values (CCS) after pressing, hardening, and carbonization at 1000 °C and

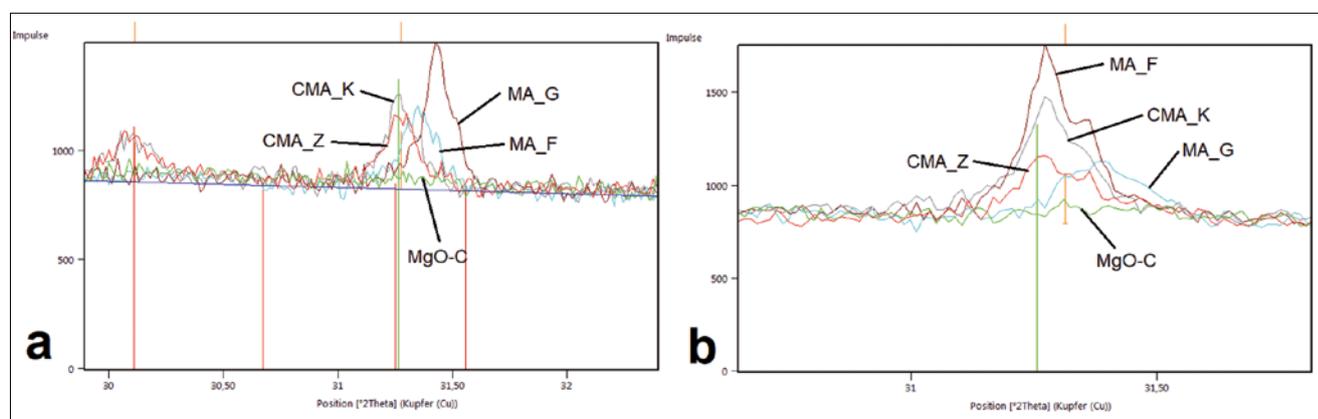


Fig. 1 a–b Change of MgAl₂O₄ peak position in sample MA_F, MA_G, CMA_Z, and CMA_K after carbonization at: 1000 °C (a), and 1400 °C (b) (extraction of diffractogram)

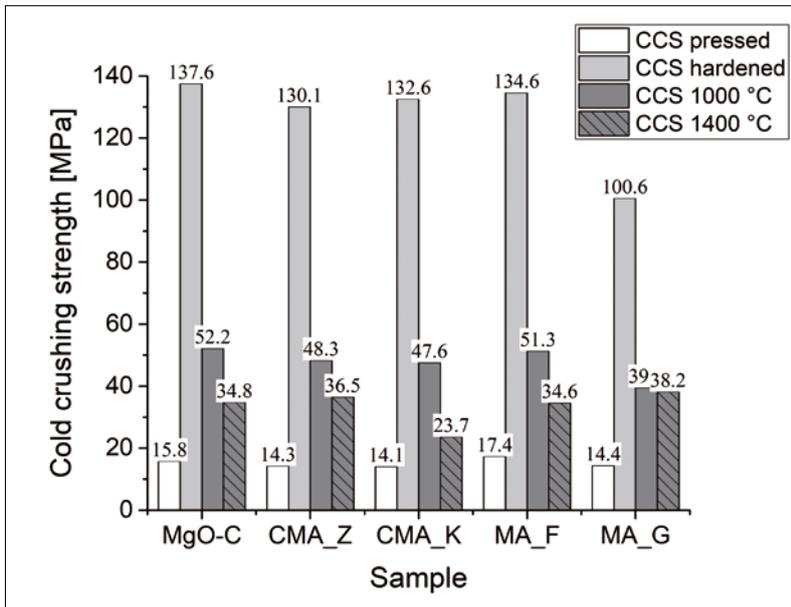


Fig. 2 Cold crushing strength after pressing, hardening and carbonization at 1000 °C and 1400 °C

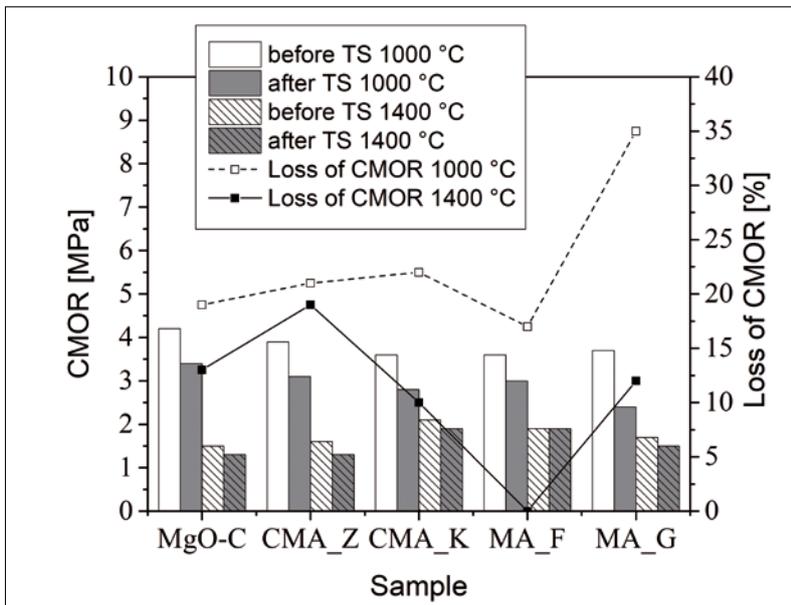


Fig. 3 CMOR before and after thermal shock in dependence on carbonization temperature

1400 °C respectively. As it is well known, carbon-bonded MgO–MgAl₂O₄–C refractories have their highest strength after the hardening process. After carbonization at 1000 °C, sample MgO–C shows the highest strength of all samples of about 52 MPa. The addition of 5 mass-% spinel-rich cement and clinker (samples CMA_Z and CMA_K) does not have a significant effect on the mechanical property. In contrast spinel raw material with alumina-excess (AR78) has a marked impact on the me-

chanical property. It depends on the grain size of added AR78, as the CCS of MgO–C with 5 mass-% of fine AR78 (sample MA_F) is nearly in the range of pure MgO–C. The addition of coarse AR78 (sample MA_G) results in a CCS which is about 25 % lower compared to MgO–C (39,5 MPa). As sample MA_G shows this quite lower CCS even after hardening, the different CCS values can be explained by a different grain size distribution compared to the other formulations due to the replacing of MgO 1–2 mm

fraction by coarse AR78. It has been found that an increase of carbonization temperature from 1000 °C to 1400 °C results in lower compressive strength values. After carbonization at 1400 °C sample MA-G with coarse AR78 shows the highest compressive strength of all samples with value of 38,2 MPa. Also sample CMA_Z shows a slightly higher CCS (36,5 MPa) compared to MgO–C. Reference sample MgO–C and sample MA_F are in the same level of CCS in range of 34,6–34,8 MPa. In contrast, sample CMA_K with CMA 72 clinker shows a significant lower CCS (23,7 MPa). Based on the results shown in Fig. 2, spinel raw materials can be added to MgO–C without having a critical effect on the cold crushing strength, if the materials were subject to carbonization at 1000 °C. In contrast, after carbonization at 1400 °C, three different effects on compressive strength were observed: increase of CCS (addition of coarse-grained AR78 or fine-grained CMA 72), no significant change on CCS (addition of fine-grained AR78), and decrease of CCS (addition of coarse-grained CMA 72).

3.3 Thermal shock resistance

Next to strength, thermal shock resistance is one of the crucial material properties of refractories. Lining materials of converters and steel ladles are rated by the number of passed batches or heats until a relining is necessary. Overall, the service life of the lining is being defined by the number of passed batches. There are three dominating wear mechanisms: mechanical wear, thermal shock due to free cooling of the ladle during the steel casting, and corrosion by steel and slag. Consequently, a high thermal shock resistance of a refractory will result in higher service life. Pure MgO is known to provide a poor thermal shock resistance. The addition of carbon intensely increases the thermal shock resistance in carbon-bonded and carbon-containing MgO–C compounds due to its low thermal expansion and high thermal conductivity. Furthermore, magnesium aluminate spinel or reactants (e.g. Al₂O₃) which form spinel in situ during thermal treatment is another well-known way to increase the thermal shock resistance of MgO and is expected to be prospective in MgO–C as well. Both the in situ formation of MA spinel which accompanies with a volume increase and the varying thermal

expansion of MgO and MgAl₂O₄ causes the formation of microcracks relieving stresses caused by thermal cycling. Fig. 3 displays the 3-point-bending strength (CMOR) of MgO with coarse and fine MA-spinel before and after thermal shock in dependence on the carbonization temperature. Beside the total CMOR values the percentage loss of CMOR is a good indicator of thermal shock resistance of a material. After carbonization at 1000 °C, the CMOR of the five compositions before thermal shock differs only in a small range and confirms the results of CCS determination. As expected, thermal shock will reduce the bending strength. Furthermore, after the thermal shock test more decisive differences are visible. Again, MgO–C exhibits the highest CMOR after thermal shock followed by sample CMA_Z. Hence, by taking the CMOR values into account, it can be stated that the addition of spinel to MgO–C reduces the CMOR after five quenches. Furthermore, addition of coarse spinel results in the lowest determined CMOR value after thermal shock, as sample MA_G with coarse AR78 shows the lowest CMOR of all samples (2,4 MPa). Compared to CCS value, the percentage loss of CMOR is a much more significant parameter. It describes how a refractory will behave against internal stresses caused by thermal differences without just taking the strength into account. With respect to percentage loss of CMOR, the thermal shock resistance of MgO–C can be improved by adding fine spinel with alumina-excess (sample MA-F). In contrast, fine and coarse CMA 72 have no significant influences on the thermal shock resistance. These results can be explained by the generation of microcracks due to differences between the thermal expansion of MgO and MgAl₂O₄. This effect is expected to be much more present with fine spinel powder in the microstructure compared to coarse spinel particles.

After carbonization at 1400 °C, a total different thermal shock behaviour can be detected. On the one hand, the CMOR after carbonization at 1400 °C is much lower compared to carbonization at 1000 °C, which is in accordance with the results of compressive strength. On the other hand, MgO–C exhibits the lowest CMOR after thermal shock and sample CMA_K as well as sample MA_F show the highest CMOR after thermal shock. The CMOR after five

Tab. 4 Open porosity (OP) and d_{50} -pore diameter after carbonization at 1000 °C and 1400 °C

	Sample	MgO–C	CMA_Z	CMA_K	MA_F	MA_G
1000 °C	OP [%]	13,0	15,3	13,5	14,6	14,5
	d_{50} [µm]	3,6	3,3	2,0	3,3	2,4
1400 °C	OP [%]	16,2	16,4	16,5	15,8	14,5
	d_{50} [µm]	7,3	4,6	3,7	7,9	3,7

quenches of sample MA_G and CMA_Z are nearly in same level. Taking the loss of CMOR after thermal shock into account, a different result is detectable. Especially sample MA_F with fine AR78 show no loss of bending strength due to thermal cycling. According to XRD-analysis, it has been found that sample MA_F seems to contain the highest amount of spinel. However, the differences in spinel portion are too marginal to be an explanation for the detected differences in thermal shock resistance of all samples. In contrast to sample MA_F with fine AR78, the addition of fine CMA 72 results in the highest loss of CMOR. The loss of CMOR of sample MA_G and CMA_K with coarse spinel raw material addition is nearly in the same level like those of MgO–C reference material. This is a remarkable effect, because even if the loss of CMOR is in same manner, especially the residual stress of sample CMA_K is much higher than MgO–C reference material.

3.4 Open porosity and pore size distribution

Tab. 4 displays open porosity (OP) as well as d_{50} pore diameter of the samples after carbonization at 1000 °C and 1400 °C respectively. Furthermore, the pore size distribution as result of mercury intrusion method can be found in Fig. 4. After carbonization at 1000 °C, sample MgO–C shows the lowest open porosity of 13 %, but exhibits the highest median pore diameter (d_{50}). The addition of spinel raw material results in increase of open porosity, whereas sample CMA_K (coarse CMA 72 clinker) shows only a slightly higher open porosity of 13,5 % compared to MgO–C reference material. Overall, the median pore diameter of all samples is in a narrow range of 2,0 (sample CMA_K) to 3,6 µm (sample MgO–C). Hence, even if the addition of spinel to MgO–C increases the open porosity, the median pore size is found to be slightly

decreased by spinel addition. The critical pore size to prevent infiltration by steel is known to be approx 30 µm. In this range, the curves of all samples are very close together (Fig. 4 a). However, the critical pore size of slag infiltration can be much lower depending on slag chemistry. Especially between 8–4 µm as well as 3 µm and below 1 µm, there are remarkable differences in pore size distribution, which may influence the slag infiltration resistance. Sample CMA_K has the highest portion of pores in this pore size classes. Compared to a carbonization temperature of 1000 °C, carbonization at 1400 °C will result in a remarkable higher open porosity as well as median pore diameters. Reference sample MgO–C as well as the samples containing CMA 72 are in the same high level of porosity, whereas the samples with AR78 exhibit lower open porosity. Sample MA_G (coarse AR78) shows the lowest OP of all samples (14,5 %). Regarding the median pore diameter sample MgO–C and MA_F have the highest d_{50} of 7,3 and 7,9 µm respectively. In contrast, sample CMA_K and MA_G (both with addition of coarse spinel) are in a low level (3,7 µm), which is comparable with the median pore size values of the samples after carbonization at 1000 °C. The pore size distribution of all samples differs compared to carbonization temperature of 1000 °C and shows a characteristic plateau between 7–4 µm (Fig. 4 b).

Below pore diameter of 30 µm, there are greater differences between each sample. All materials with spinel addition show a higher amount of small pores compared to MgO–C reference material, whereat sample MA_G contains the highest amount of pores with diameter below 30 µm. The same applies for even lower pore diameters, which implies that sample MA_G as well as sample CMA_K may show less steel and slag infiltration.

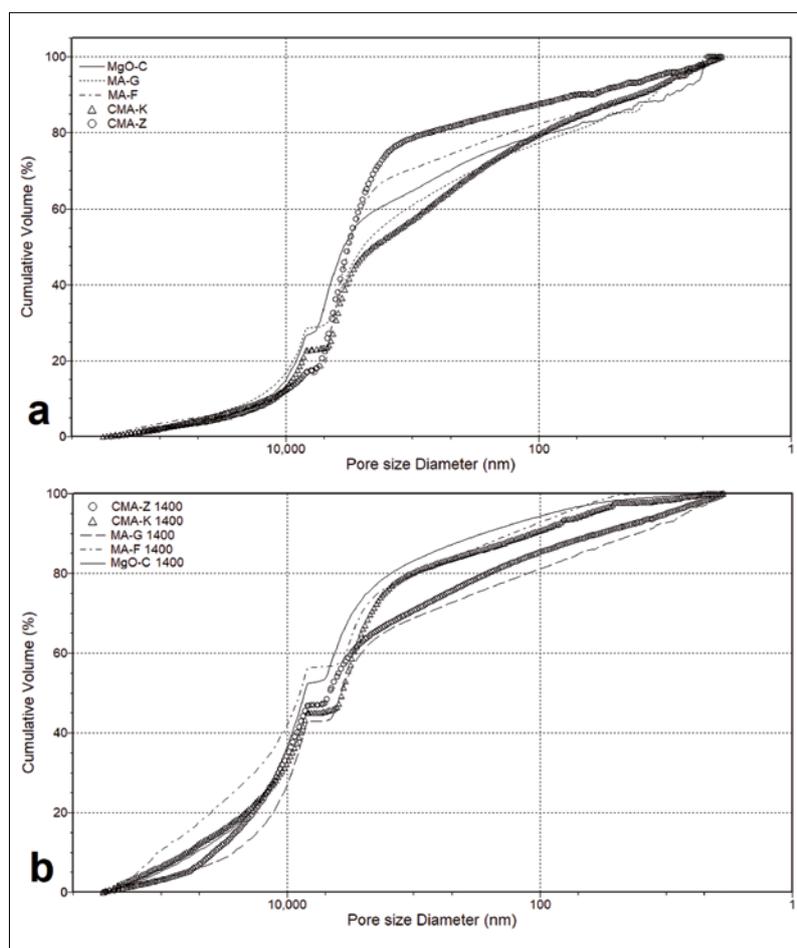


Fig. 4 a–b Pore size distribution after carbonization at: 1000 °C (a), and 1400 °C (b)

3.5 Microstructure

The microstructure of sample MgO–C is composed of coarse and medium sized MgO-fractions embedded in a matrix composed of fine MgO and graphite/carbon. Beside MgO particles and carbon typical CaO- and SiO₂-containing impurities can be detected). The spinel containing samples have a microstructure which show several crack-containing coarse grains composed of both MgO and MgAl₂O₄. However, compared to sample MgO–C, no distinguishing differences like additional microcracks can be detected. Furthermore, there are no specific differences in microstructure after carbonization at 1000 °C compared to 1400 °C. The condition of the microstructure of the different samples confirms the findings made by XRD-analysis. No particular changes like microcracks in microstructure of MgO–C can be detected. According to EDS-mapping, spinel is distributed homogeneously in the matrix. Furthermore, any interaction of spinel raw material with MgO

is too marginal to change the microstructure remarkably.

4 Conclusions

Material properties like thermal shock resistance, as well as corrosion resistance of MgO–C are influenced by addition of Al₂O₃ or MgAl₂O₄. Improvement of thermal shock and corrosion resistance of MgO–C-rich ladle linings is important to increase the service life. Hence, the aim of this study was to clarify the effect of the addition of 5 mass-% of two common MA-spinel raw materials and carbonization temperature on the properties of MgO–C with carbon-content of 3 %. After carbonization, changes in phase composition are only marginal but shifts in position and height of spinel peak are obvious. No specific new in situ spinel formation can be detected but CA-phases origin from CMA 72 raw material are not present anymore after carbonization at 1400 °C. However, interaction of MgO and free CA-phases of the cement/clinker are

not detectable with aid of XRD-method. After carbonization at 1000 °C, the addition of spinel-rich cement and clinker has only marginal influence on thermal shock resistance. Compared to 1000 °C, carbonization at 1400 °C reduces compressive and bending strength, and increases open porosity and median pore diameter. Loss of CMOR after thermal shock of sample MA_G, CMA_K, and MgO–C reference material is in same manor. However, sample CMA_K provides higher residual strength and exhibits higher portion of small pores below 30 μm, which is expected to provide great advantage for corrosion resistance which will be investigated in the future.

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