

THE IN-SITU SPINEL FORMATION IN A MAGNESIA ALUMINA CASTABLE AND THE EFFECT OF SELECTED ADDITIVES ON THE PROPERTIES OF THE CASTABLE

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Keywords: spinel, phase formation, castable, sintering, additive

ABSTRACT

Four additives (a sodium polyphosphate, microsilica, titania and zirconia) were tested in a magnesia alumina castable to investigate their influence on the spinel formation at high temperatures. The impact of the additives is studied with respect to both the amount of spinel formed in the burned castable and the microstructure established by the spinelization.

Dilatometric measurements conducted on the castables allowed to determine the onset temperature of the spinel formation, which was indicated by a strong increase of the linear thermal expansion. For phosphate-containing samples, the expansion associated with the spinelization occurred already ~100 °C below the temperature at which the corresponding expansion was observed for the additive-free reference sample.

Furthermore, by a heat-treatment of the castables at 1200 °C or 1500 °C, the phosphate-containing samples developed notably higher amounts of spinel than the reference sample. The phosphate addition in these samples also results in a remarkably larger increase of the sample volume during the heat treatment and comparatively lower mechanical strengths of the burned samples. The SiO₂, TiO₂, or ZrO₂ additions influenced the physical properties of the castable in a substantially smaller degree than the addition

of sodium phosphate, and they also exerted a smaller effect on the spinelization in the castable than the latter one.

1. INTRODUCTION

By heating powder mixtures of corundum (Al₂O₃) and periclase (MgO), the precursor material starts to develop spinel (MgAl₂O₄) at a temperature of ~1100 °C. The formation temperature of spinel depends, however, on the applied load and the chemical composition of the precursor material. Sintering agents added in refractory castables can help to lower the formation temperature of phases crystallizing at high temperatures and to improve densification of the refractory material during the burning process [1-3]. Through additions of CaCO₃, SiO₂ and TiO₂, for example, the density of spinel-forming castables can be increased considerably [4]. Furthermore, the presence of additives might act on the chemical composition of the spinel or influence the size and shape of its grains. For additions of MgCl₂, LiF, AlCl₃, MnO₂ and ZrO₂, Mohan et al. showed that spinel grains develop a different morphology depending on the additive additions [5, 6]. This circumstance is economically interesting as the average crystal shape of spinel is a parameter which controls the service life of castables employed as lining material in steel ladles [7].

Another additive which strongly influences the spinelization is ZnO. In alumina-based castables, the ZnO addition promotes a formation of a Zn-containing spinel (ZnAl_2O_4) allowing the spinelization to start at a lower temperature than the spinel formation of the Mg-containing analog (MgAl_2O_4) [8].

As spinel-forming refractory castables are widely produced from water-containing thixotropic masses, the green bodies used as precursor material in our investigations were likewise casted from a hydrous mass. Masses containing one of four additives (sodium polyphosphate, microsilica, titania or zirconia) were produced to probe the influence of the additives on the spinelization.

Originally, the addition of the sodium phosphate aimed to optimize the flowability of the thixotropic mass. The phosphate addition in the magnesia alumina castable was, however, found to be associated with an increase of the amount of spinel in the burned product. This observation is contrasted by findings obtained for phosphate-bonded spinel-containing alumina castables possessing a low magnesia content, indicating a destabilization of the spinel phase through a presence of phosphates at high temperatures [9].

Considering the densities of corundum ($\sim 3.99 \text{ g/cm}^3$), periclase ($\sim 3.56 \text{ g/cm}^3$) and spinel ($\sim 3.58 \text{ g/cm}^3$), the spinel formation is expected to lead to a theoretical volume increase of $\sim 8\%$. Practically, the resulting volume increase of spinel-forming castables is, however, significantly larger because of grain size effects of the phases involved in the spinel formation increasing the pore size volume in the castable. Especially the grain size effect of periclase can be responsible for a volume change which is even much larger than the theoretical volume increase caused by the spinelization alone [10].

2. MATERIALS AND METHODS

Several batches of dry mixtures with a chemical composition close to spinel were produced by combining magnesia and alumina raw materials and small amounts of additives (Tab. 1).

Tab. 1: Relative amounts of raw materials combined to dry mixtures, values in wt%.

	magnesium oxide	aluminum oxide	sodium phosphate	microsilica	titanium oxide	zirconium oxide
X	28	72	-	-	-	-
½P	28	71.5	0.5	-	-	-
1P	28	71	1	-	-	-
1M	28	71	-	1	-	-
1T	28	71	-	-	1	-
1Z	28	71	-	-	-	1

The tested additives were a sodium polyphosphate, microsilica, titania and calcia-stabilized zirconia. The alumina in the dry mixtures was composed of equal amounts of tabular alumina and reactive alumina (Tab. 2) balancing the water demand and the flowability of the thixotropic masses, which were produced from the different dry mixtures by the addition of 10 wt% water.

Each thixotropic mass was used to cast three test cylinders (two of which were burned at 1200 °C and 1500 °C, respectively, and the remaining one was used for a dilatometric measurement). As the hydration of the dry mixtures resulted in a formation of a geopolymer, no additional binder was needed to establish a sufficiently high green strength of the castables.

Tab. 2: Chemical composition (typical) and average grain size of different raw materials.

reactive alumina	99.7% Al ₂ O ₃ , 0.3% others	2.5 μm
tabular alumina	99.5% Al ₂ O ₃ , 0.5% others	2.0 μm
magnesium oxide	97.2% MgO, 2.1% CaO, 0.25% SiO ₂ , 0.25% Fe ₂ O ₃ , 0.3% others	15 μm
microsilica	98.0% SiO ₂ , 0.5% K ₂ O, 0.5% CaO, 0.3% MgO, 0.3% Al ₂ O ₃ , 0.4% others	
titanium oxide	80-90% TiO ₂ , SiO ₂ <9%, Fe ₂ O ₃ <2%, Al ₂ O ₃ <3%	<10 μm
zirconium oxide	ZrO ₂ > 95.0%	~30 μm
sodium phosphate, water-soluble	~30% Na ₂ O, ~70% P ₂ O ₅	

Before burning, the samples were dried for 24 h at room temperature and at 110 °C, respectively. Burning of the samples was accomplished in a high-temperature furnace using a heating rate of 5 °C/min to increase the furnace temperature either to 1200 °C or 1500 °C and holding these temperatures for 5 h.

To check the mass and volume changes of the cylinders caused by the heat-treatments, the weights and proportions of the samples were measured before and after burning. The cold crushing strengths (CCS) of the burned samples were determined using a standard testing machine of Form+Test.

Pieces of each sample were investigated by scanning electron microscopy (SEM), and ground powder samples were used for powder X-ray diffraction (XRD) measurements. The XRD patterns were recorded for a scattering angle 2θ ranging from 5 to 70 deg employing a PANalytical X'Pert³ diffractometer equipped with a Cu K_α X-ray tube. The measured data

were evaluated in qualitative and semi-quantitative phase analyses using the computer program Highscore and entries of the Crystallography Open Database (COD) [11]. Strong peaks in the powder diffractograms were identified as intensity contributions of the phases corundum, β-alumina (NaAl₁₁O₁₇), periclase and spinel (Fig. 1, Tab. 3).

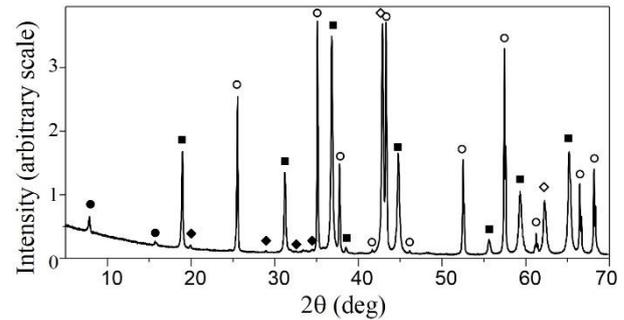


Fig. 1: XRD pattern of sample X after burning at 1200 °C. Symbols mark peaks of phases identified by data base entries in the COD (Tab. 3).

Tab. 3: Selected phases and identification numbers of data base entries in the COD. Symbols refer to peak labelling in Fig. 1.

phase	ID	
spinel	9003481	■
corundum	9008081	○
β-alumina	9011270	●
periclase	5000225	◇
grossite	9007446	◆
enstatite	9001601	-
olivine	9001096	-
perovskite	9006172	-
β-alumina (type 2)	4344192	-
brownmillerite	9003351	-
zirconia	2300612	-
tungsten carbide	2100645	-

For the samples burned at 1200 °C, additional small peaks in the measured diffraction patterns were found to match with patterns of enstatite, grossite and olivine. In the diffraction patterns measured on the TiO₂- and ZrO₂-containing samples, respectively, some additional peaks indicated the presence of perovskite and zirconia after burning.

After the heat-treatment at 1500 °C, some samples showed in their XRD patterns different small peaks which were identified as reflections of brownmillerite and a MgO-rich β -alumina phase. Furthermore, some patterns contained characteristic broad peaks indicating a sample contamination with small amounts of tungsten carbide, the grinding set material in the vibratory disk mill.

SEM investigations were carried out on the samples by using a Hitachi TM3000 microscope. An energy dispersive X-ray spectroscopy (EDX) detector implemented in the microscope allowed to map element distributions of selected chemical elements.

To measure the linear expansion of test cylinders as a response to the heating, dilatometric measurements were conducted employing a RUL850 instrument from Netzsch. For these measurements, the sample was loaded with 0.02 N/mm² and heated with a rate of 10 °C/min to a temperature of 1700 °C.

3. RESULTS AND DISCUSSION

In the dilatometric measurement conducted on sample X, which contained none of the four tested additives (Tab. 1), the thermal expansion starts to deviate from an initial linear slope of the curve at a temperature of ~1100 °C. The deviation can be interpreted as an additional expansion of the sample caused by the onset of the spinel formation. The maximal expansion of sample X is reached at a temperature of ~1450 °C at which the height of the cylinder is ~5 % larger than at the start of the measurement. Higher temperatures result in a shrinking of the

sample due to a progress in sintering. Dilatometric plots measured for the samples ½P and 1P (whose dry mixtures contained 0.5 and 1.0 wt% sodium polyphosphate, respectively) show already a drift from linearity at a temperature of ~1000 °C. The maximal length changes of these samples are ~9 % and ~11 % (Fig. 2).

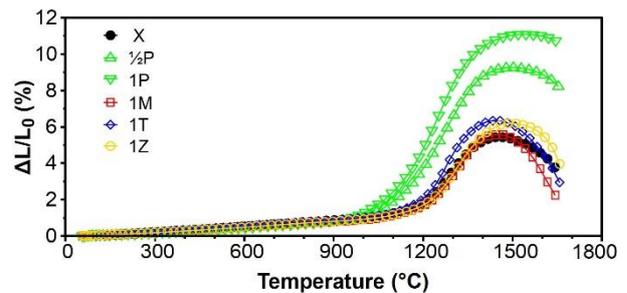


Fig. 2: Linear expansion of samples heated in dilatometric experiments. Samples are denominated accordingly to Tab. 1.

While the curves of samples ½P and 1P differ remarkably from the curve of sample X, the curves measured for samples containing the other additives (samples 1M, 1T and 1Z) strongly resemble the trend of the expansion of sample X.

For the samples 1T and 1Z, however, the maximal expansion is found to be larger than the maximal expansion of sample X (Fig. 2). Furthermore, the curve of sample 1T increases with a steeper slope from the initial linearity than the curve of sample X. For the ZrO₂-containing sample, the maximal length change is observed at a higher temperature compared to the curve of sample X, pointing to a later onset of the sintering process of the sample.

In agreement with the dilatometric measurements, the volume changes of the test cylinders resulting from a heat-treatment at 1200 °C and 1500 °C, respectively, confirm a particularly large expansion for samples containing sodium polyphosphate (Tabs. 4 and 5). Interestingly, these samples show in parallel a higher weight loss than the other samples pointing to a volatilization of parts of

the polyphosphate during the heat-treatment. A volatilization of phosphates was also observed during a heating of phosphate-bonded magnesia castables [12].

Tab. 4: Mass and volume changes caused by burning samples at 1200 °C. Cold crushing strengths determined after heat treatment.

	Δm [%]	ΔV [%]	CCS [MPa]
X	-0.9	15.2	15.2
½P	-1.6	23.5	8.9
1P	-2.0	31.0	5.1
1M	-0.7	12.5	26.6
1T	-0.9	19.8	11.1
1Z	-0.7	16.5	15.5

Tab. 5: Mass and volume changes caused by burning samples at 1500 °C. Cold crushing strengths determined after heat treatment.

	Δm [%]	ΔV [%]	CCS [MPa]
X	-0.9	19.6	54.8
½P	-1.7	38.9	21.6
1P	-1.6	54.2	10.2
1M	-0.9	20.2	25.3
1T	-0.9	23.6	74.1
1Z	-0.7	21.7	49.2

The values of the cold crushing strength (CCS) determined for the samples burned at 1200 °C range between 5 to 27 MPa and the CCS of samples burned at 1500 °C between 10 to 74 MPa (Tabs. 4 and 5). As a result of the extraordinary ballooning of the samples ½P and 1P, the CCS drastically decreases. After burning at 1500 °C, the CCS value of sample 1T (74.1 MPa) is significantly larger than the one of sample X (54.8 MPa) or any of the other samples. The strong CCS increase through the TiO₂ addition agrees well with

findings of other authors who reported an improvement of the mechanical strength of magnesia alumina castables and magnesia ceramics for small TiO₂ additions [13, 14]. The addition of TiO₂ in these products enhances the formation of a liquid phase during the burning process leading to an improved grain sinterability in the material [4, 13, 14].

In some further tests, whose results are mentioned here just in brevity, the corrosion and thermal shock resistance of the samples X, ½P and 1T were examined. For this purpose, three crucibles and three test cylinders with a composition according to sample X, ½P and 1T were produced and pre-heated at 1000 °C and 1500 °C, respectively. A corrosion cup test showed that the crucible containing the phosphate is less slag resistant than the crucibles of samples X and 1T, which showed a similar slag resistance.

Both the addition of phosphate and titania resulted in a decrease of the thermal shock resistance of cylinders pre-burned at 1500°C. This is attributed to a higher porosity in the case of the phosphate-containing sample and a facilitated crack propagation along glass-rich areas in the titania-containing sample.

A comparison of the physical properties of the investigated castables with the ones of refractories installed as lining material is problematic because all raw materials used to produce the investigated castables were fine-grained powders (Tab. 2). Spinel-forming castables used as lining material in steel plants, in contrast, often contain a large quantity of coarse-grained aggregates, not participating in the spinel formation. During burning, they form therefore a lower amount of spinel and consequently experience a smaller volume increase than the castables investigated in this work.

To consider, however, the specifications of a spinel-forming castable, which is in practical use as a lining material, its properties should be outlined here in few words. After burning

at 1500 °C, the refractory material consists of ~60 wt% corundum and ~40 wt% spinel. The CCS of the burned castable is 120 MPa (± 20 MPa). During heating, the castable experience a linear thermal expansion $\Delta l/l$ of 2.1 % (± 0.5 %).

The phase compositions of the burned castables produced for this work are given in the tables 6 and 7.

Tab. 6: Phase composition of samples burned at 1200 °C, values in wt%.

	spinel	corundum	β -alumina	periclase	grossite	enstatite	others
X	40.5	38.5	1.0	18.6	0.6	0.7	-
$\frac{1}{2}$ P	57.6	26.6	2.0	13.7	-	-	0.1
1P	65.7	22.3	1.6	10.1	-	-	0.3
1M	43.0	36.2	0.8	17.8	0.2	0.4	1.7*
1T	47.9	33.6	2.2	15.7	0.2	-	0.4
1Z	44.5	33.9	0.9	19.6	0.7	-	0.4

* sample 1M: 1.6% olivine

Tab. 7: Phase composition of samples burned at 1500 °C, values in wt%.

	spinel	corundum	β -alumina	β -alumina (type 2)	periclase	others
X	92.2	1.4	0.5	0.6	4.4	0.8
$\frac{1}{2}$ P	97.2	0.2	1.0	-	0.5	0.9
1P	96.4	0.3	2.8	-	0.3	0.2
1M	94.4	0.4	0.6	-	1.0	1.6*
1T	94.9	0.4	0.9	0.5	2.0	1.3
1Z	95.2	0.3	0.5	0.5	2.6	0.9

* sample 1M: 0.9 % olivine

As can be concluded from the tables 6 and 7, higher amounts of spinel formed in the additive-containing castables than in the reference samples. For the samples burned at 1200 °C, the amount of spinel was estimated to range between 40 to 66 wt% (Tab. 6). The highest amounts of spinel and the lowest amounts of corundum and periclase were determined for samples $\frac{1}{2}$ P and 1P (Tab. 6) evidencing the sodium polyphosphate to possess a large effect on the turnover rate of the spinelization reaction. Samples burned at 1200 °C contained β -alumina in phase amounts of 1-2 wt%. The amounts of enstatite (MgSiO_3), grossite and impurities (like e.g. tungsten carbide) were determined to be smaller than 1 wt%, respectively. In the sample 1M (in whose dry mixture 1 wt% microsilica was added) olivine formed in a phase amount of 1.6 wt%.

In analogy to the castables burned at 1200 °C, also samples heat-treated at 1500 °C developed higher amounts of spinel if the precursor contained the phosphate (Tab. 7). However, since the amount of spinel exceeds in every sample 90 wt%, differences in the phase compositions are less pronounced for samples burned at 1500 °C.

Moreover, a burning at the higher temperature seems to lower the amount of β -alumina in samples with same starting compositions. An exception is sample 1P for which a β -alumina content of 2.8 wt% was determined after burning at 1500 °C. The stabilization of the β -alumina phase in this sample might be induced by the presence of sodium ions originating from the addition of the additive. Some of the samples with a low sodium content formed during burning at 1500 °C another β -alumina phase (β -alumina type 2, Tab.7) which contains beside sodium also magnesium atoms in its crystal structure.

By scanning electron microscopy (SEM), it was found that the morphology of the periclase grains is particularly susceptible to the additive additions. In the following, some

morphological peculiarities of the periclase grains are described. For the sake of consistency, the considerations are restricted to the samples burned at 1500 °C (Fig. 3).

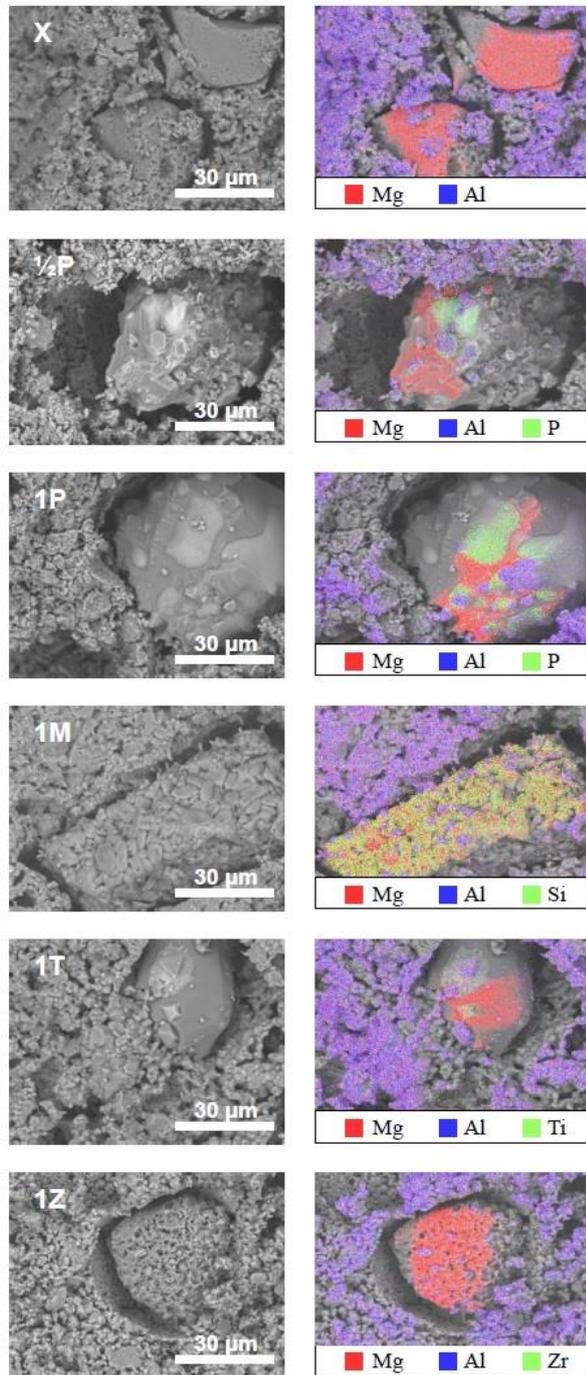


Fig. 3: SEM images of samples burned at 1500 °C. Colored images on the right side visualize atomic distributions mapped for selected chemical elements.

As can be seen in the micrograph of sample X, the burned castable still contains some fine-grained periclase showing no signs of a transformation into spinel.

Because of a large specific surface area and an angular grain boundary, one would expect, however, these grains to be quite reactive [1]. That the periclase grains sustained the heat-treatment instead unreacted seems to be the result of a lack of contact to the surrounding material.

The addition of sintering aids, in contrast, leads to a more aggressive attack of the periclase grains with residues often covered by alteration products. In the burned samples 1/2P and 1P, for example, many periclase grains show rounded surfaces covered with remains of a phosphate-rich melt (Fig. 3). Moreover, the two samples exhibit numerous small cavities with diameters of ~30 µm which could have accommodated periclase grains in the early stages of the burning process. As magnesium phosphate melts at a temperature of ~1200 °C, phosphate-rich melts should be able to dissolve parts of the periclase at higher temperatures.

In the burned sample 1M, the periclase grains are covered by layers of silicate crystals which are few micrometers in size. As the silicate layers prevent the interior of the grains to react with alumina to spinel, the formation of the layers might also be responsible for the lower spinel amount found for sample 1M in comparison to the other samples containing sintering aids (Tabs. 6 and 7). The square-edged appearance of the periclase grains in sample 1M let assume that the covering in a silicate layer allows some grains to preserve their original grain shape.

In sample 1T, the periclase grains are well-rounded and show partly titanium-rich areas from which spinel grains evolved (image 1T in Fig 3). Apparently, the TiO₂ addition led to a formation of a liquid phase which eroded the periclase grains and which facilitated the spinel formation. This assumption agrees well

with findings of reference [13] showing that a TiO₂ addition in magnesia alumina castables increases the amount of liquid phase forming on heating. For small TiO₂ additions, the increased amount of liquid seems to improve densification of the castable and to enhance its mechanical strength [13, 14].

Similarly, ZrO₂ particles might serve as a nucleus for the spinel growth as cavities in the surface of periclase grains from which spinel was grown possess a higher Zr concentration than other areas on the surface. However, a large portion of the zirconium oxide in sample 1Z persisted the burning process unreacted as well-defined grains with diameters of > 30 μm.

4. CONCLUSIONS

The spinel formation in refractory castables can be promoted by additions of small amounts of sodium polyphosphate, SiO₂-, TiO₂- or ZrO₂-containing additives. By burning castables at 1200 °C or 1500 °C, higher amounts of spinel formed in samples containing these additives than in additive-free reference samples.

Among the four tested additives, sodium polyphosphate proved to exert the largest effect on the amount of formed spinel. Through additions of 0.5 and 1 wt% sodium polyphosphate, respectively, spinel already formed ~100 °C below the temperature at which the spinel formation starts in the reference sample. During the burning process, castables containing additions of sodium polyphosphate were subject to significantly larger volume expansions and larger weight losses than reference samples. The extraordinarily large swelling of the phosphate-containing samples on heating is attributed to a volatilization of parts of the phosphate.

Samples containing additions of microsilica were found to develop silicate phases during the burning process. The silicates covered the

surface of periclase grains hampering the interior to participate in the spinel formation.

An addition of 1 wt% of the TiO₂-containing additive resulted in a lowering of the formation temperature of spinel by ~20 °C compared to the reference sample. Furthermore, the TiO₂-containing additive was found to clearly increase the material strength of the sample after burning at 1500 °C.

The addition of the ZrO₂-containing additive was associated with an increase of the thermal stability of the castable. The ZrO₂ addition seems to exert a positive influence on the spinel formation at a temperature of ~1200 °C and above. This effect is presumably caused by fine ZrO₂ particles, a few micrometers in size, serving as nuclei for the spinel formation.

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