INFLUENCE OF $MgAl_2O_4$-SPINEL ADDITIONS ON THE PHOSPHATE BONDING IN Al_2O_3-REFRACTORIES

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ABSTRACT

Phosphates are used in high-temperature materials as bonding agents to increase the (early-)strength and resistances towards corrosive media. Although the initialization of phosphate bonds has been explained in scientific literature, especially the cross-linking behavior of phosphate species during firing as well as their interaction and compatibility with other ceramic components are still not clearly understood and insufficiently investigated. This research concerns how the addition of $MgAl_2O_4$ to an alumina-rich refractory changes its bonding mechanism and, consequently, affects key performance characteristics of the ceramic. The approach is based on a comprehensive analysis which gives insight into structural changes of the bonding phase and, ultimately, allows structure-property-correlations to be drawn. Results demonstrate that the addition of $MgAl_2O_4$-spinel (1) leads to the formation of Magnesium hydrogen phosphates during initialization, (2) influences the cross-linking of the Aluminium phosphate bonding network (less polymerization) and (3) results in Mg-containing high-temperature ortho phosphates, which significantly reduce the bonding capacity and high temperature properties of the refractory.

INTRODUCTION

Alumina-rich ceramics are used in high-temperature applications because of their excellent thermal properties. When adding Aluminium-Magnesium spinel ($MgAl_2O_4$, hereinafter referred to as "spinel") to Al_2O_3, chemical and physical high-temperature properties of the product can be specialized and improved. These especially include increasing the corrosion resistance and reducing slag infiltration, as well as improving the thermomechanical properties such as thermal shock resistance and hot flexural strength.[1,2]

In general, Magnesium and Aluminium cations within the spinel structure are able to exchange lattice positions. The so-called degree of inversion depends on temperature.[3,4] By in-situ neutron scattering experiments, an increase in the inversion (order-disorder transition), in which the disorder within the spinel structure increases significantly (as well as the ion mobility), has been evinced for temperatures of $T > 600°C$. This conversion changes the material properties of the spinel: For example, the material resistance to chemical reactions with sulfur oxides (SO_x) is decreased.[5]

Physicochemical properties of high-temperature ceramics may also be enhanced by inorganic phosphates as chemical binders. Adding phosphate binders can improve strengths of ceramics even at low temperatures, usually have a permanent effect up to their sintering temperatures and can at the same time improve the high-temperature properties of the ceramic at application temperatures.[6-9] The mode of action of phosphate binders, e.g. $Al(H_2PO_4)_3$ or alternative phosphate binders with Mg, Ca or Zr as cation, in alumina-rich refractories has been examined in detail by structural analyses of phase developments in the binding phase.[10,11] A combination of structural analysis methods using solid-state NMR spectroscopy and X-ray diffractometry (XRD) is suitable for identifying phosphate

components actively involved in bonding formation.[10-13] Phosphate bonding mechanisms are generally composed of two different reaction schemes (Fig. 1): Initialization is based on neutralization / acid-base reactions, which are caused by dissociation processes during water addition to the formulation. Here, phosphoric acid phases react with ceramic oxides to form branched phosphate structures after thermal treatment. Especially amorphous Aluminium phosphates, which build up an interlocked, three-dimensional binding network, have an active binding effect. The degree of branching within the binding network is continuously increased by condensation when the temperature rises, whereby the connectivity of the phosphate structures can be described using the $Q^n(mM)$ nomenclature (n = # of P-O-P cross-links at a P; m = # of counter cations M as next-nearest neighbors).[10,11] In addition to this formation of binding-active phosphate structures, phosphate conversions also occur without reacting with ceramic components (Fig. 1). These phosphate-phosphate conversions are based on the fundamental nature of a phosphate to polymerize with increasing temperature. These mostly crystalline structures only could be assigned minor binding effects.[11]

Structural investigations of the binding mechanisms exposed that the ceramic composition (and the cations involved) significantly influences the reaction behavior of the phosphate components.[10,11] So far, however, no studies are available that describe or clarify the influence of spinel additives on the phase development or the binding effect of phosphate-bonded Al_2O_3-ceramics during curing, cross-linking process and with regard to high-temperature phase formation based on structural analysis.

MATERIALS AND METHODS

An alumina-rich fine ceramic with grain sizes of x < 0.06 mm bonded with crystalline Aluminium phosphate ($Al(H_2PO_4)_3$, AP, Budenheim) was investigated. The P_2O_5 content of the mass was set at 9.5 wt.-% (Table I). The spinel content of the samples varied from 0 wt.-% to 48 wt.-%. This corresponded to an MgO content of approx. 5.5 wt.-% for ASAP and approx. 11.0 wt.-% for A2SAP. These ceramic bodies represented the fine fraction and bonding phase of a coarse alumina refractory with a fine-to-coarse-grain ratio of 31.5/68.5 and a corresponding P_2O_5 content of 3 wt.-% based on the total ceramic mass.
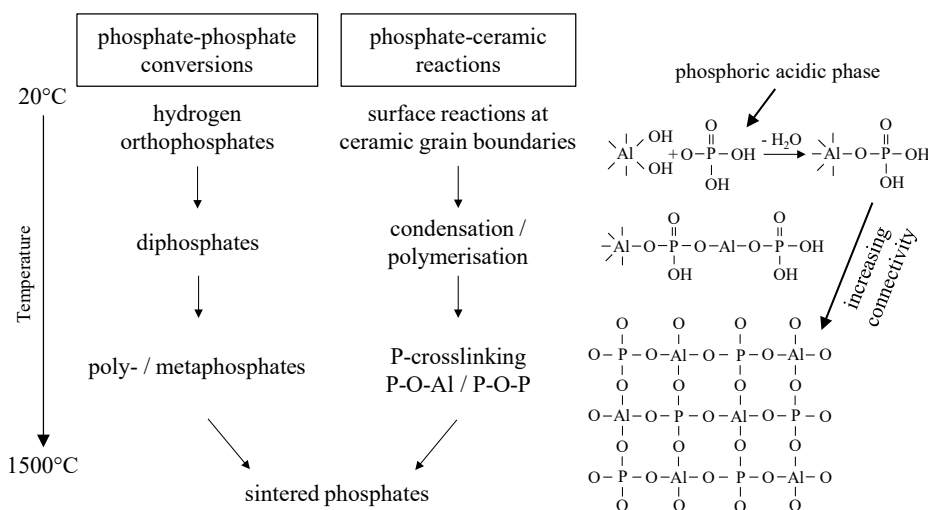

Fig. 1. Phase evaluation of phosphate-bonded alumina-rich refractories

Table I. Sample compositions and names

Composition [wt.-%]	Spinel AR78 (Almatis)	Reactive Alumina (Almatis)	Calcined Alumina (Silkem)	AP (Budenheim)
AAP	0.00	36.87	47.77	15.36
ASAP	24.06	26.39	34.19	15.36
A2SAP	48.12	15.91	20.61	15.36

The raw materials were homogenized manually, 6-8 wt.-% water was added, mixed again and shaped. The samples were left at room temperature for t = 24 hours and then dried at T = 110°C for 24 hours. The samples then were treated for t = 5 hours at T_{end} = 200/300/600/1000/1500°C and, after free cooling, were finely pulverized manually.

To investigate high-temperature reactions (T ≥ 1000°C), comparative systems with the same composition and sample preparation but bonded with different inorganic phosphate additives were also investigated (CP1: $Ca(H_2PO_4)_2$, Budenheim; CP2: $CaHPO_4$, ThermoFisher Scientific; MP1: $Mg(H_2PO_4)_2$, Budenheim; MP2: $MgHPO_4 \cdot 3H_2O$, ThermoFisher Scientific). The respective sample designations indicate the phosphate binder used (e.g. ASCP1). A reference sample not bonded with phosphate is called AS.

Solid-state magic angle spinning NMR investigations (MAS-NMR) were carried out on a Jeol 500 MHz spectrometer ECZR (B_0 = 11.75 T; two-channel probe head; 3.2 mm rotors) with a resonance frequency of v_r (^{31}P) = 202.5 MHz. Proton-decoupled ^{31}P single pulse measurements were carried out under MAS conditions with 512-1024 scans per measurement and relaxation delays of 20s ≤ t_r ≤ 120s. NMR spectra are given in standardized intensity.

X-ray diffraction analyses were carried out on a Bruker X-ray diffractometer D8 Discovery (Lynx-Eye-XT-E linear detector; Ni filter; divergence and Soller-slits; Cu-K$_\alpha$ radiation source: voltage 40 kV; current intensity 30 mA; Bragg-Brentano geometry 300 mm goniometer radius; angular range 5° ≤ 2θ ≤ 70°; step size 0.02°; time/step 0.3s; sample rotation 15°/min). The diffractograms are given in standardized intensity.

Differential scanning calorimetry (DSC) and differential thermogravimetric analysis (DTG) were carried out on a Netzsch STA 449 C Jupiter. Fine-grained samples (m = 80 mg) were tested in Al_2O_3 sample crucibles in a protective argon atmosphere at a flow rate of v_F = 100 ml/min and additionally v_s = 50 ml / min purging gas with a heating rate of v_H = 10 K/min at 30°C ≤ T ≤ 1500°C.

RESULTS
Bonding phase evaluation in dependence of spinel additions

^{31}P solid-state MAS-NMR analyses of AAP, ASAP and A2SAP after temperature treatments at 20°C ≤ T ≤ 1500°C are demonstrated in Fig. 2. At room temperature, AAP (Fig. 2a) shows main peaks at 1.3 ppm and -13.2 ppm, which can be assigned to $Al_2(H_2PO_4)_3(H_2O)_6(PO_4)$, and two secondary peaks at approx. -5 ppm and -18 ppm for $Al(H_2PO_4)(HPO_4)(H_2O)$ as crystalline Aluminium hydrogen orthophosphates. The assignment is based on XRD measurements not documented here. The spectrum also shows a broad background between 5 ppm and -25 ppm, which indicates amorphous Aluminium phosphate compounds Q^0(mAl).[10] After drying at T = 110°C, the peaks for $Al(H_2PO_4)(HPO_4)(H_2O)$ increase significantly in intensity. From T = 200°C, the widths of the signals generally increase and overlap. This indicates a high amount of amorphous, unstructured phosphate species. Furthermore, the signals shift to negative ppm-values, which indicates increased phosphate polymerization. Between 200°C ≤ T ≤ 600°C, signals more negative than -30 ppm are to be assigned to Q^2 structures, signals at -12 ppm, -15 ppm and -19 ppm as Q^1. At T = 600°C predominantly Q^2 structures were existing. Signals between -25 ppm and -30 ppm can be assigned to $AlPO_4$ (Q^0). At T ≥ 1000°C, $AlPO_4$ is predominantly present. The half width at half maximum of the
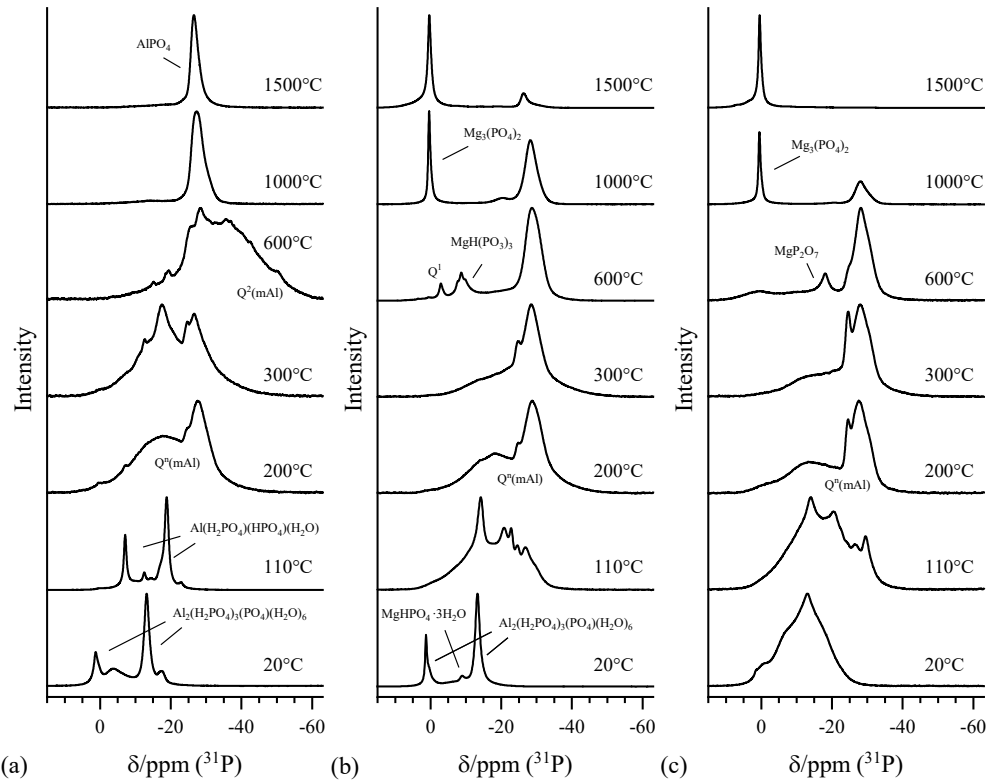
Fig. 2. ^{31}P MAS NMR spectra of (a) AAP (b) ASAP (c) A2SAP after thermal treatment at 20°C ≤ T ≤ 1500°C

AlPO$_4$ structure is decreased after T = 1500°C (FWHM = 550 Hz).

With ASAP (Fig. 2b), comparable to AAP, Al$_2$(H$_2$PO$_4$)(H$_2$O)$_6$(PO$_4$) is formed at room temperature. In addition, a small peak at -8.3 ppm can be seen for MgHPO$_4$·3H$_2$O. The spectrum at T = 110°C significantly shows fewer crystalline structures than with AAP. At T = 200°C, Q^0(mAl) is the main phase. Compared to AAP, the intensity of polymerized Q^1 and Q^2 structures is significantly decreased. At T = 600°C a peak with two shoulders develops at -8.7 ppm, which can be assigned to MgH(PO$_3$)$_3$ by comparison with XRD measurements (Fig. 3). At T ≥ 1000°C a new phase formation of Mg$_3$(PO$_4$)$_2$ is detected with a peak at 0.4 ppm, correlating with a decrease in AlPO$_4$ (Fig. 3). The peak at

-20 ppm can be interpreted as a Q^0(2Al, 2Mg) structure.

A2SAP (Fig. 2c) shows broad overlapping signals at room temperature, which, analogous to AAP and ASAP, can be assigned to Al$_2$(H$_2$PO$_4$)$_3$(H$_2$O)$_6$(PO$_4$), Al(H$_2$PO$_4$)(HPO$_4$)(H$_2$O) and MgHPO$_4$·3H$_2$O. Overall, the crystallinity is greatly decreased and MgHPO$_4$·3H$_2$O is represented more intensively here than with ASAP. The signals at T = 110°C are comparable to ASAP. The crystallinity is lower and AlPO$_4$ is more intense. At T = 200°C and T = 300°C, the intensity of the signals between -33 ppm and -45 ppm for Q^2 structures are significantly decreased compared to AAP and ASAP. In addition, more intense signals can be detected at -1 ppm and -10 ppm, which indicate amorphous Q^0(Mg) compounds.[11] At T = 600°C, MgP$_2$O$_7$ is present at -18 ppm and Mg$_3$(PO$_4$)$_2$ at 0.5 ppm. With a further increase in temperature, Mg$_3$(PO$_4$)$_2$ evolves to the main phase with decomposition of AlPO$_4$.
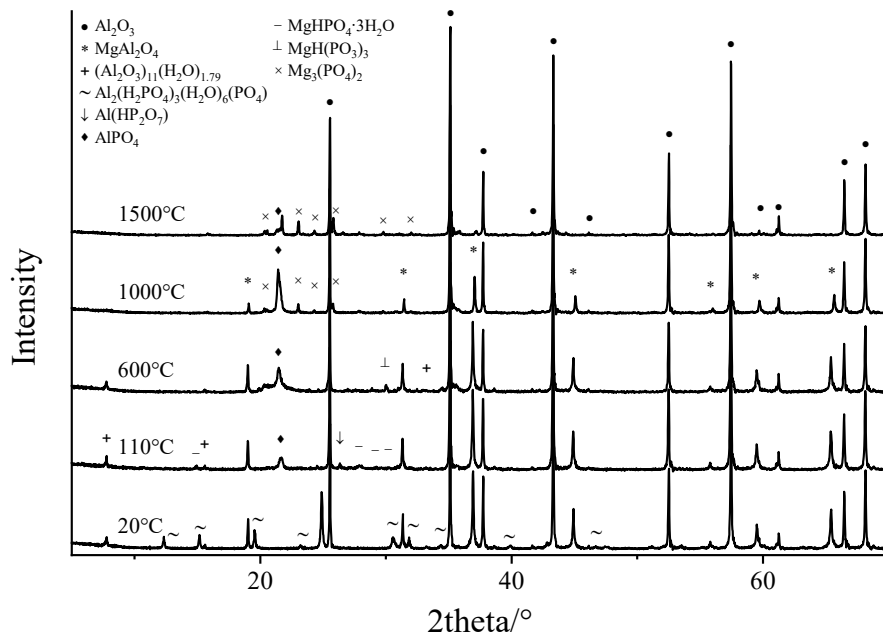
Fig. 3. XRD of ASAP after thermal treatment

High temperature phosphate phases when using alternative phosphate binders

Fig. 2 and 3 have already clarified that at T ≥ 600°C and in the presence of spinel, Magnesium phosphates may evolve. To further characterize phase developments and the thermal behavior of the phosphate phases, simultaneous thermal analysis (DSC and DTG) of refractories bonded with phosphates (Mg, Ca and Zr) has been carried out (Fig. 4). The thermal behavior of the samples can be described as follows:

(1) Preferable condensation at T < 300, water loss and endothermic intense events

(2) Structural changes in the phosphate phase (polymerization, modification changes, recrystallization), endo- and exothermic events over a wide T range up to T < 1000°C

(3) at T > 1100°C: endothermic rise for sintering, in addition narrow endothermic peaks for melting processes
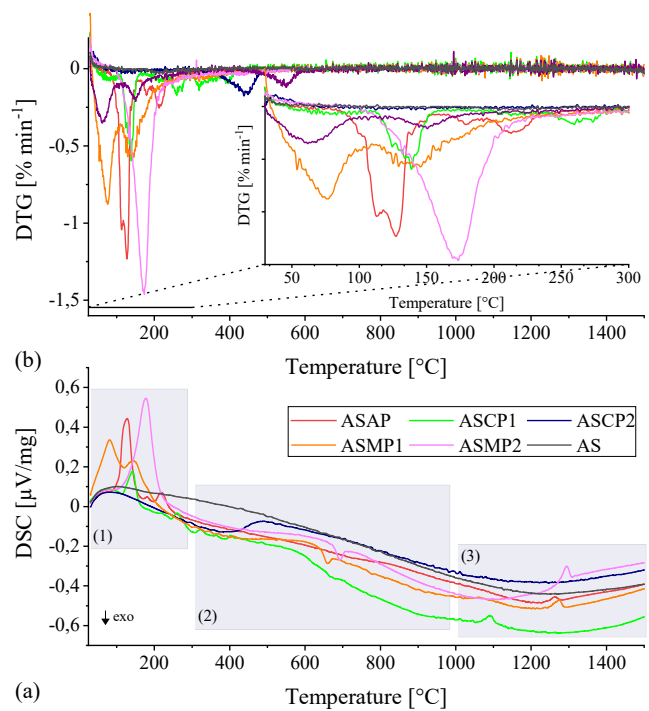

Fig. 4. Simultaneous thermal analysis of phosphate bonded Al_2O_3-$MgAl_2O_4$ refractories

To further investigate the high-temperature phosphate phase formation using different phosphate binders, ^{31}P MAS NMR investigations have been carried out (Fig. 5).

The binding phases after high temperature treatment of T = 1000°C and T =

1500°C differ depending on the phosphate binder used. Without Magnesium being present in the mix, $AlPO_4$ is the stable phosphate phase. It is to be noted that the crystallinity of $AlPO_4$ increases with temperature. If Magnesium is present, a sharp peak can be seen besides $AlPO_4$ at 0.3 ppm for crystalline mode of $Mg_3(PO_4)_2$. In addition, there are broader signals at 3 ppm and 7 ppm, which indicate the integration of Aluminium in the $Mg_3(PO_4)_2$ structure. When using Calcium phosphates, peaks at -2 ppm, 3.4 ppm, 5.3 ppm and 7.6 ppm can be correlated to the Calcium-Magnesium orthophosphates $Ca_7Mg_2(PO_4)_6$ and $Ca_4Mg_5(PO_4)_6$, whose formation is confirmed by XRD analyses. ASMP1 and ASMP2 show narrow peaks for $Mg_3(PO_4)_2$, signalizing high crystallinity. With increased temperature, $AlPO_4$ intensity decreases in favor of Magnesium phosphate formation, respectively. When using water soluble phosphate binders (like AP, CP1 and MP1), generally more $AlPO_4$ is formed than if water insoluble phosphates are added. [10,11,12]
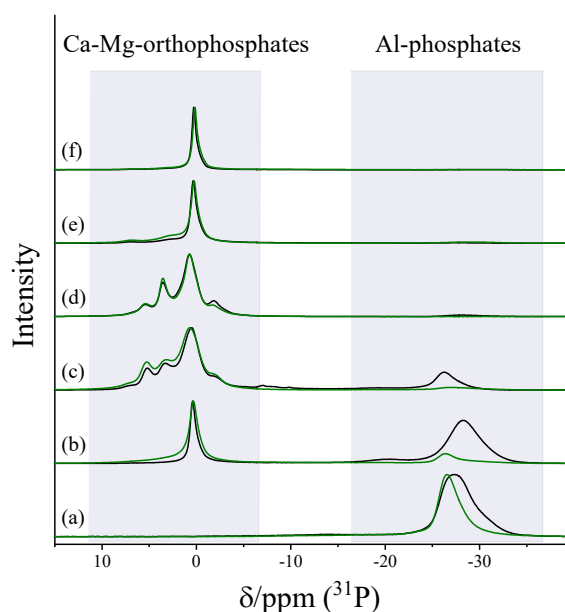

Fig. 5. ^{31}P MAS NMR spectra of phosphate-bonded refractories after temperature treatment of T = 1000°C (black line) und T = 1500°C (green): (a) AAP (b) ASAP (c) ASCP1 (d) ASCP2 (e) ASMP1 (f) ASMP2

DISCUSSION
Influence of spinel additions on the phosphate phase development

Research results show that the phosphate bond occurs already at room temperature as a result of neutralization reactions of phosphoric acid compounds with hydroxylated oxides on ceramic surfaces. Subsequently, a bonding-promoting network of Aluminium phosphates develops through cross-linking of the phosphates by polymerization and condensation reactions. If Magnesium is present in the composition, the phosphate-oxide acid-base reaction is more distinct, since MgO is more basic than Al_2O_3. An increased formation of $MgHPO_4·3H_2O$ is observable with increasing Magnesium concentration. $MgHPO_4·3H_2O$ reacts with increasing temperature to form amorphous $Q^0(mMg)$ as well as $Mg_2P_2O_7$ and $MgH(PO_3)_3$. The degree of cross-linking, hence, the binding effect of $Q^0(mMg)$ and polymerized Magnesium phosphates is to be assessed as low compared to $Q^0(mAl)$.[12] The increased reactivity, and consequently the increased reaction heat due to the addition of $MgAl_2O_4$, also results in the formation of $AlPO_4$ even at low temperatures (T < 110°C) and, hence, a decrease in binding capacity (crystalline < amorphous). Furthermore, the degree of polymerization via P-O-P at 200°C ≤ T ≤ 600°C is also strongly influenced by the spinel additives. The higher the spinel content within the ceramic composition, the lower the tendency of the phosphate species to polymerize via P-O-P (Q^2), which may also lead to a decrease in bonding capacity. In addition, at T > 600°C spinel reacts with Aluminium phosphates to form $Mg_3(PO_4)_2$ with high crystallinity. This results in a partial break of the Aluminium phosphate network and, hence, again loss in bonding capacity. This can be explained by the causal link of rapid spinel inversion at T > 600°C leading to high mobility of Magnesium and the decreased resistance of the material against P_2O_5. Also,

the formation of Magnesium phosphates is thermodynamically preferred. In sum, spinel additives have a decisive (negative) influence on the overall phase formation of the phosphate bond.

High-temperature phase formation

Investigations of the high-temperature phase compositions revealed that when a phosphate binder is used in the presence of $MgAl_2O_4$, magnesium phosphates are steadily developed. Regardless of the counter cations of the phosphates used here, the phosphate is able to incorporate within the spinel structure and to react with Magnesium. With increasing temperature, Magnesium replaces Aluminium to form crystalline $Mg_3(PO_4)_2$. Using Calcium phosphates leads to the formation of Mg-Ca-mixed orthophosphates besides $Mg_3(PO_4)_2$. Spatial proximity of the phosphate species to the spinel is decisive to form Magnesium phosphates, thus, prerequisite is a homogeneous distribution of the binder in the matrix.

Especially when used in high-temperature applications, the melting behaviors of phosphates must be assessed, as these have an impact on the refractory's properties such as infiltration tendency and maximum working temperature. When using spinel, $Mg_3(PO_4)_2$ and mixed Al-Mg-Ca-orthophosphates are formed ($1150°C \leq m_p \leq 1550°C$), which show lower melting temperatures compared to $AlPO_4$ ($m_p = 1800°C$) as seen by thermal analyses. Lower melting points of the phosphates correspond with high Magnesium content incorporated in the phosphate structures. However, the structures identified here (T = 1500°C, after cooling) do not show high amounts of glass phase forming melts. This suggests that melt phases recrystallize again as orthophosphate when cooled to room temperature. To further investigate the melting behavior of phosphate binders, in-situ measurement methods, for example HT-XRD or HT-Raman, are necessary to be applied.

CONCLUSION

The phase development of phosphate-bonded alumina-rich ceramics were investigated by combining solid-state MAS-NMR, XRD and thermal analyses. General conclusions about the reaction behavior of phosphate phases depending on the addition of spinel can be drawn. It has been demonstrated that spinel additives decisively influence the mode of action of the phosphatic binders during curing, in the temperature-induced reaction process and at high temperatures of up to T = 1500°C. Spinel addition leads to:

- Higher reactivity within the ceramic resulting in rapid formation of $AlPO_4$, reducing the quality of the cross-linking, hence loss in bonding capacity
- Formation of Magnesium phosphates with minor contribution to bonding
- Less phosphate polymerization via P-O-P linkages (less Q^2)
- Reaction of phosphates with Magnesium of the spinel at $T \geq 600°C$ to form $Mg_3(PO_4)_2$ and other crystalline mixed orthophosphates by partial breakage of the Aluminium phosphate bonding network

Direct structure-property correlation indicate that Magnesium spinel additions decrease the ability to form strength-increasing phosphate bonding phases. It is to be highlighted, that, in some applications, phosphates and spinel may not be compatible and that an incorrect use within refractory formulations may lead to significant loss in performance. The influence on the tendency to infiltration and corrosion of the ceramics to slags and alkalines will be evaluated in follow-up investigations.

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