

KAlSiO₄-based Potassium Aluminosilicates for Alkali Corrosive Environments

N. Brachhold, Chr. G. Aneziris

Alkali corrosion of refractory materials is a problem in high temperature aggregates. The problem has increased strongly during the last years due to secondary fuels used as energy carriers. This study presents potential new materials for alkali corrosive conditions. It investigated the synthesis of potassium aluminosilicates of the nominal composition of KAlSiO₄. Two synthesizing procedures were applied: a pure thermal treatment at 1200 °C and a combined synthesizing procedure consisting of a hydrothermal treatment at 200 °C followed by a sintering step at 1200 °C. Furthermore, the study concentrated on the use of K₂CO₃ as K₂O source and compared the results to previous studies based on KOH as K₂O source. The results showed that the use of K₂CO₃ yielded the intended target phase, too. The reaction products based on K₂CO₃ had a phase composition similar to thermally synthesized KOH-based material and were alkali corrosion resistant.

1 Introduction

Alkali components are a usual impurity in raw materials and energy carriers like coal or liquid fuels. The use of these substances in high temperature processes introduces the alkali components in the aggregates [1, 2]. The corrosive effect of alkali components on the lining of high temperature furnaces has long been known for example in the steel making industry or the cement industry [1, 3]. In recent years, more and more so called secondary fuels, such as waste, tyres and biomass have been used to replace conventional fuels. However, these secondary fuels have a higher alkali content compared to conventional energy carriers leading to massive corrosion problems in the refractory lining of high temperature furnaces [4, 5].

Aluminosilicate based refractory material such as alumina, fireclay, mullite and silica, are widely used in the lining of high temperature furnaces especially as heat insulation layer [6, 7]. The corrosion of these materials due to alkali components consists of

two possible effects [8, 9]: Firstly, the degradation of refractory material is caused by the fluxing effect of alkalis which results in general in the formation of low viscosity melts. The second possible corrosion mechanism is due to chemical reactions yielding alkali aluminosilicates like feldspars (KAlSi₃O₈, NaAlSi₃O₈) or feldspathoids such as leucite (KAlSi₂O₆), kaliophilite/kalsilite (KAlSiO₄) or carnegieite/nepheline (NaAlSiO₄). These reaction products have usually lower densities compared to the original material which leads to spalling effects. The actually dominating corrosion mechanism depends on the local temperature and the local alkali corrosion in the furnace. Nevertheless, both corrosion mechanisms cause a destruction of the lining material which determines the service life of the high temperature furnace [8, 9].

The analysis of phase diagram data shows that some of the observed corrosion products have very high melting points [10]. For example the melting point of KAlSiO₄ (kaliophilite/kaliophilite) is known to be at approxi-

mately 1750 °C. Because these phases form in the alkali rich atmosphere at high temperatures in the industrial furnaces they seem to be stable under these highly corrosive conditions. Therefore, alkali aluminosilicate-based materials are an interesting approach for new alkali resistant materials if a synthesizing procedure could be established. In the field of ceramics various techniques are available to produce powders, granular materials or solid bodies [11, 12]. In the processing of oxidic refractory materials a thermal treatment is typically involved. This can be either a calcination step in the powder processing or a sintering step involving reaction and densification or a melting of the raw material to form the intended target phases. Furthermore, a hydrothermal treatment can be included in the synthesizing procedure of a certain material [12]. The application of elevated temperature and pressure and the presence of water enable different reaction routes in comparison to a purely thermal treatment. Additionally, materials of high porosity can be produced by such a processing step which is very useful for heat insulation applications [13]. Furthermore, the hydrothermal technology is able to contribute to sustainability and

Nora Brachhold, Christos G. Aneziris
Institute of Ceramics, Glass and
Construction Materials
TU Bergakademie Freiberg
09599 Freiberg
Germany

Corresponding author: Nora Brachhold
E-mail: nora.brachhold@ikgb.tu-freiberg.de

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Tab. 1 Oxidic composition of the target compound KAlSiO₄

Target Compound	Oxide Content [mass-%]		
	SiO ₂	Al ₂ O ₃	K ₂ O
KAlSiO ₄	37,97	32,28	29,75

Tab. 2 Chemical composition of kaolin A and B

Kaolin		Oxide Content [mass-%]							
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	L.o.I.
A	Salzmünde	54,0	31,0	0,7	0,3	0,6	0,4	1,3	11,4
B	BZ	54,2	32,5	0,38	0,16	0,18	0,25	0,28	11,8

Tab. 3 Raw materials and synthesizing procedure for each mixture

Mixture No.	Synthesizing Procedure	Kaolin	K ₂ O Source
1	Thermal	A	KOH
2	Combined	B	KOH
3	Combined	B	K ₂ CO ₃

energy saving [13]. The technology itself is characterized by high-energy efficiency. In combination with a thermal treatment lower maximum temperatures are often possible to achieve synthesizing results comparable to a pure heat treatment. A decrease in the maximum process temperature results usually in a lower energy consumption, which is generally preferred.

Previous studies investigated if the synthesis of alkali aluminosilicates is possible starting from kaolin as main Al₂O₃ and SiO₂ source and KOH solution as K₂O source [14, 15]. Two synthesizing procedures were studied: a purely thermal treatment and a combined process consisting of a hydrothermal step followed by a thermal treatment. They showed that multi-phase reaction products containing ternary alkali aluminosilicates were formed and were alkali corrosion resistant for some synthesizing parameters. Especially, materials based on the stoichiometry KAlSiO₄ showed promising results concerning the alkali corrosion resistance. This study compares the application of K₂CO₃ as alternative K₂O source to the previous KOH based results. Due to the highly caustic character of KOH solution it is important for a potential production process of these materials to investigate alternative raw materials to ensure a safe process chain.

2 Materials and methods

The intended target phases in this study had the chemical composition corresponding to

the stoichiometry of KAlSiO₄. Tab. 1 shows the oxidic composition of KAlSiO₄. According to the previous studies [14, 15] two types of kaolin were used as main Al₂O₃ and SiO₂ source (Kaolin A: Type Salzmünde from *Ton- und Kaolinwerke Salzmünde GmbH/DE* and Kaolin B: Type BZ from *AKW Amberger Kaolinwerke Hirschau/DE*). Tab. 2 presents the chemical composition of the used kaolin materials. As further Al₂O₃ source Al(OH)₃ was necessary to realize the intended target composition (*Thor Minerals/USA*). KOH and K₂CO₃ as K₂O sources were supplied by *Brenntag AG/DE* and *Degussa/DE* respectively. Their composition was specified as technical quality according to the suppliers. The K₂O sources were introduced in the mixtures as aqueous solutions, which were generated right before the experiment. These solutions consisted of 50 mass-% of the K₂O source and 50 mass-% of distilled water.

Tab. 3 reports the raw materials and the synthesizing procedure for each mixture in this study. The raw materials were thoroughly mixed according to the oxide relation presented in Tab. 1. Further distilled water was added to generate slurry for maximum homogenization. For the combined synthesizing procedure this slurry was directly hydrothermally treated at 200 °C for 24 h in an autoclave with a volume of 50 l (*Heckmann/DE*). The resulting material was dried at 110 °C for 48 h and crushed to particles smaller than 0,5 mm using pestle and mortar. For the second synthesizing

procedure via the thermal treatment the resulting slurry after the mixing step was dried at 110 °C for 48 h and ground to powder using a swing mill.

The resulting granular material of both synthesizing procedures was pressed uniaxially to cylinders (weight approx. 25 g, diameter approx. 50 mm, height approx. 10 mm) at a pressure of 50 MPa (press ES 270, *Rucks/DE*). Finally, for both synthesizing procedures the sintering step took place at 1200 °C for 3 h in an electric chamber furnace (*Nabertherm/DE*).

The phase composition of the synthesized material was analysed qualitatively by powder diffractometry (MPD 3040/60, *PANalytical*, Almelo/NL) with CuKα radiation scanning 2θ angular region from 5–90°. Phase identification was done using X'Pert Highscore Plus analysis software (*PANalytical/NL*). Some trends of quantitative phase formation were deduced by analysing the peak height of the main phases. For this analysis a characteristic strong peak was chosen for each main phase, which was not overlapped by peaks of other phases.

Alkali corrosion resistance of the synthesized material was tested using a test method already presented in the literature [14–16]. It simulates the alkali attack with the help of a salt mixture (K₂SO₄:K₂CO₃:KCl = 1:1:1 by weight). The material to be tested was ground to powder by a swing mill to a grain size below 0,5 mm. The salt mixture was added to the sample in the ratio 30:70 by weight and homogenized in a tumbling mixer. The resulting material was pressed to cylinders (weight approx. 20 g, diameter approx. 50 mm, height approx. 7 mm) at a pressure of 50 MPa (press ES 270, *Rucks*). These samples were sintered in an electric chamber furnace at 1100 °C for 5 h (*Nabertherm/DE*). The temperature parameters were chosen to simulate the conditions in heat insulation materials in an industrial furnace under high alkali load. After the test the diameter change of the corroded samples was registered. An expansion is attributed to the formation of corrosion phases with lower densities compared to the original material. Shrinkage is considered to be caused by liquid phase sintering. A maximum diameter change of 2 % is acceptable because of alkali corrosion, which is in accordance to refractory specifications

[17]. In the corrosion test two samples were investigated for each mixture.

3 Results and discussion

The results of the phase analysis of the three investigated mixtures are summarized in Fig. 1. All mixtures resulted in multi-phase reaction products and modifications of the stoichiometry KAlSiO_4 occurred as main phases. However, the actual phase composition was different between mixtures 1, 2 and 3 in spite of the same nominal composition of the overall sample which corresponded to the stoichiometry of KAlSiO_4 .

The phase composition of mixture 1 consisted of orthorhombic KAlSiO_4 as main phase [14]. Additionally, small amounts of leucite (KAlSi_2O_6), a feldspathoid richer in SiO_2 than KAlSiO_4 , were detected. The occurrence of the orthorhombic modification of KAlSiO_4 as main phase after a thermal treatment at 1200 °C was in good agreement with the literature. *Dimitrijevic et al.* realized similar results starting from zeolites as raw materials to investigate potassium aluminosilicates with the stoichiometry KAlSiO_4 [18].

Mixture 2 showed a different phase composition compared to mixture 1. One of the main phases was a hexagonal modification of KAlSiO_4 whose diffraction pattern was strongly similar to natural kaliophilite [15]. Orthorhombic KAlSiO_4 was detected as second main phase. This result was remarkable because the sintering step of mixture 2 followed the same parameters as the thermal treatment of mixture 1. The differences in the phase composition were attributed to the different kaolin raw material and the hydrothermal treatment within the combined synthesizing procedure. Furthermore, traces of quartz were detected which were considered to originate from the kaolin used as raw material.

The analysis of mixture 3 yielded a phase composition consisting of orthorhombic KAlSiO_4 and leucite as main phases. This showed that the synthesis of potassium aluminosilicates was possible when K_2CO_3 was used as K_2O source. The phase composition resembled the results of mixture 1 whose phase analysis identified these two phases, too. Tab. 4 summarizes the heights of a characteristic peak of the main phases for mixtures 1 and 3. It reports that the quantitative

relation between orthorhombic KAlSiO_4 and leucite was very different between these two mixtures. Mixture 1 consisted mainly of orthorhombic KAlSiO_4 showed by the high peak height in Tab. 4. It contained only small amounts of leucite. In contrary to mixture 1, mixture 3 showed approximately half the peak height for orthorhombic KAlSiO_4 and an approximately nine times higher peak height for the characteristic leucite peak. These values show that mixture 3 consisted of two main phases because the quantitative relation between orthorhombic KAlSiO_4 and leucite was in mixture 3 much closer to 1 than in mixture 1. This similarity between the qualitative phase composition of mixture 1 and 3 will be investigated in further studies. Furthermore, quartz was detected as secondary phase in mixture 3 similar to mixture 2, which was again attributed to the kaolin used as raw material. However, the peak heights of the quartz peaks of mixtures 2 and 3 in Fig. 1 differed strongly. The higher peak for mixture 3 showed that more quartz was present in the synthesized material. This indicated that the reaction rate in mixture 3 was probably lower than in mixture 2 although both mixtures were prepared with the same kaolin. In general, the aqueous solution of KOH (mixture 2) is more reactive than the aqueous solution of K_2CO_3 (mixture 3), which would explain the higher reduction of quartz in the synthesized material of mixture 2.

The synthesized material of the three mixtures was tested on alkali corrosion using the test described above. Fig. 2 reports the optical results and Tab. 5 the observed diameter changes. The results of the diameter change showed that only mixtures 1 and 3 passed the test and were alkali corrosion resistant. The samples of mixture 2 shrank strongly during the corrosion test and a concave deformation of the bottom surface of the sample was observed. Therefore, this material was not alkali corrosion resistant.

Tab. 4 Peak heights of the main phases in mixtures 1 and 3

Mixture No.	Peak Height [cts]	
	Orthorhombic KAlSiO_4	Leucite
1	10 928	385
3	5123	3194

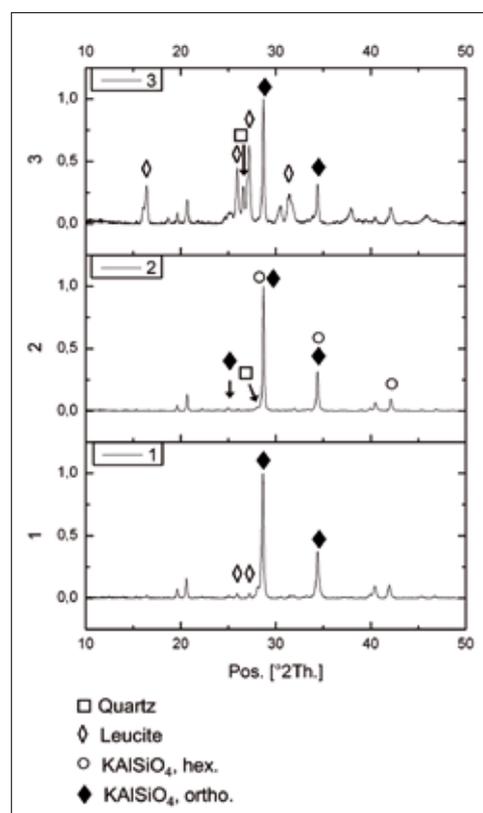


Fig. 1 XRD analysis of the synthesized materials (KAlSiO_4 , hex. = hexagonal modification of KAlSiO_4 ; KAlSiO_4 , ortho. = orthorhombic modification of KAlSiO_4)

The differences in the corrosion resistance were attributed to the differences in the phase composition of the synthesized materials. Mixture 2, which was not alkali corrosion resistant differed in its phase composition strongly from the other materials because it contained hexagonal KAlSiO_4 as main phase. Compared to orthorhombic KAlSiO_4 or leucite which formed in the other mixtures, hexagonal KAlSiO_4 is only stable at lower temperatures. Temperatures of 1100 °C and above cause a transformation to orthorhombic phases [18]. Therefore, it was considered for the present investigation that mixtures 1 and 3 showed alkali corrosion resistance due to the formation of orthorhombic KAlSiO_4 and leucite immediately during the synthesizing process. The alkali corrosion resistance was

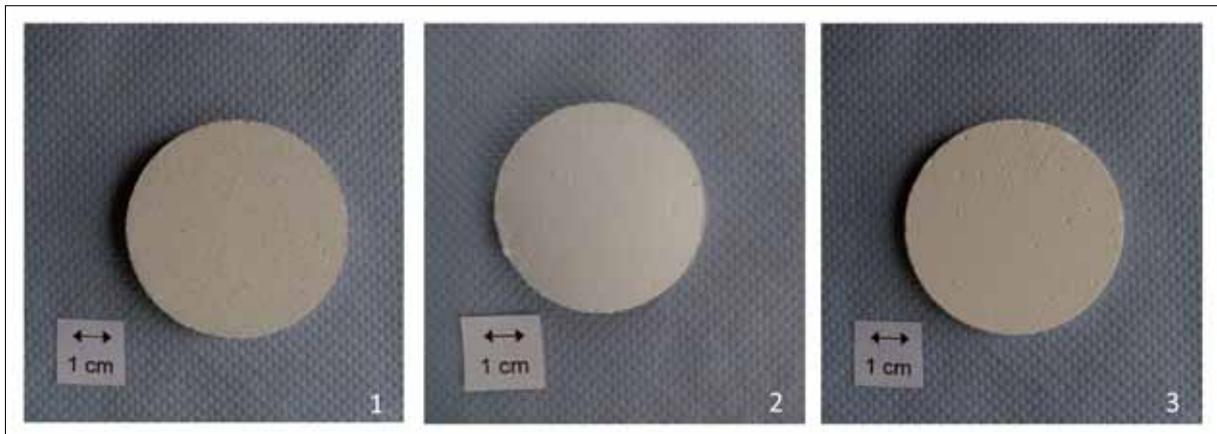


Fig. 2 Sample of each mixture after the corrosion test

Tab. 5 Results of the corrosion test

Mixture No.	Change of Diameter [%]	
1	1,1	1,0
2	-5,4	-7,9
3	1,7	1,6

attributed to the existence of these phases and their stability at higher temperatures.

4 Conclusion

This study reports the synthesis of potassium aluminosilicates of the nominal composition of KAlSiO_4 as potential material for high temperature applications with alkali corrosive atmosphere. This study concentrated on synthesized materials using K_2CO_3 as K_2O source applying a combined synthesizing procedure (hydrothermal treatment with subsequent sintering step). It compared the results to previous studies based on KOH as K_2O source. The results showed that the intended target phases with the stoichiometry KAlSiO_4 were formed. Similarly to the KOH based materials multi-phase reaction products were formed. The material was alkali corrosion resistant. The phase composition and the corrosion behaviour were similar to thermally synthesized KOH -based material. Further investigations will be undertaken to fully understand the influence of the different K_2O sources on the synthesizing and corrosion results.

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