



# Preparation of $\beta$ -sialon Bonded $\text{Al}_2\text{O}_3$ -Refractories in Different Atmospheres

S. PICHLBAUER<sup>1\*</sup>, H. HARMUTH<sup>1</sup>, Z. LENČEŠ<sup>2</sup>, P. ŠAJGALÍK<sup>2</sup>, V. PETRUŠKOVÁ<sup>2</sup>

<sup>1</sup> University of Leoben, Department Mineral Resources and Petroleum Engineering, Chair of Ceramics, Leoben, Austria

<sup>2</sup> Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovak Republic  
e-mail: Sabine.Pichlbauer@unileoben.ac.at

## Abstract

Six test series of sialon bonded  $\text{Al}_2\text{O}_3$ -refractories with the same composition have been sintered at different temperatures and in different atmospheres. A reasonable phase composition was ascertained. For the sintering, two different electrically heated furnaces were used, one heated with graphite heating elements (furnace G) and one with  $\text{MoSi}_2$  heating elements (furnace M). The samples were sintered in nitrogen atmosphere at temperatures from 1400 to 1650°C. The oxygen partial pressure in furnace M was partly defined by the use of a carbon bed and partly by the use of  $\text{N}_2/\text{CO}$  gas. The results show that  $\beta$ -sialon cannot be prepared at a sintering temperature of 1400°C. At 1550°C and 1650°C different atmospheres lead to the formation of different phases in the matrix. These phases are  $\beta$ -sialon, X-sialon, mullite, glassy phase, Si, SiC and carbon besides the main component  $\text{Al}_2\text{O}_3$ . The occurrence of silicon shows that the control of the atmosphere is also very important to assure a complete nitration, which is necessary for  $\beta$ -sialon formation.

**Keywords:**  $\text{Al}_2\text{O}_3$ -refractories,  $\beta$ -sialon, X-sialon, Sintering conditions, Sintering atmosphere, Phase composition

## KORUNDOWE MATERIAŁY OGNIOTRWAŁE WIAZANE $\beta$ -SIALONEM WYTWARZANE W RÓŻNYCH ATMOSFERACH

Sześć serii korundowych materiałów ogniotrwałych o takim samym składzie, wiązanych sialonem, wytworzono w różnych temperaturach i atmosferach. Ustalono uzasadniony skład fazowy. Dwa różne piece elektryczne wykorzystano do spiekania, jeden ogrzewany grafitymowym elementem grzejnym (piec G) i drugi ogrzewany elementem  $\text{MoSi}_2$  (piec M). Próbki spieczono w atmosferze azotu w temperaturze od 1400 do 1650°C. Ciśnienie parcjale tlenu w piecu M było częściowo zdefiniowane poprzez użycie zasypki węglowej, a częściowo poprzez użycie gazu  $\text{N}_2/\text{CO}$ . Wyniki pokazują, że  $\beta$ -sialonu nie można wytworzyć w temperaturze spiekania wynoszącej 1400°C. W 1550°C i 1650°C różne atmosfery prowadzą do powstania różnych faz w osnowie. Oprócz głównego składnika  $\text{Al}_2\text{O}_3$  tymi fazami są  $\beta$ -sialon, X-sialon, mullit, faza szklista, Si, SiC i węgiel. Występowanie krzemu pokazuje, że kontrola atmosfery jest również bardzo ważna, aby zapewnić całkowite azotowanie, które jest konieczne do utworzenia  $\beta$ -sialonu.

**Słowa kluczowe:** materiały ogniotrwałe korundowe,  $\beta$ -sialon, X-sialon, warunki spiekania, atmosfera spiekania, skład fazowy

## 1. Introduction

Oxide and non-oxide composite refractories get more and more interesting because of the high requirements on refractory materials, e.g., for the production of high quality steel. A very interesting material is  $\beta$ -sialon because of its good thermal shock resistance, caused by a low coefficient of thermal expansion, its high strength and its good corrosion resistance. It combines the good properties of silicon nitride and aluminium oxide [1]. Sialon is structurally related to  $\beta$ - $\text{Si}_3\text{N}_4$  and has the chemical formula  $\text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}$  with  $0 \leq z \leq 4.2$  [2-4]. It can be prepared by reactive sintering of a mixture of  $\text{Si}_3\text{N}_4$ , AlN and  $\text{Al}_2\text{O}_3$  powders [5, 6]. If sialon is used as a bonding phase in an  $\text{Al}_2\text{O}_3$  refractory, it can be produced in a similar manner by in situ reaction. Instead of expensive  $\text{Si}_3\text{N}_4$ , silicon can be applied as a starting material. It has to be nitrated during the sintering process. The atmosphere during the sintering process plays an important

role for nitration of silicon and to get the desired  $\beta$ -sialon bonding phase. Depending on the atmosphere, different phases occur in the product. In the present study,  $\beta$ -sialon- $\text{Al}_2\text{O}_3$  refractories are produced in different atmospheres to investigate which phases are formed in the sintered product under different conditions.

## 2. Experimental

Firstly an optimum grain size distribution was determined according to the Dinger-Funk equation [7, 8]. Tabular alumina with a grain size of 0-3 mm and two different kinds of fine  $\text{Al}_2\text{O}_3$  powders (tabular alumina and calcined alumina) were used as main components. Powders of metallic Si, AlN,  $\text{Si}_3\text{N}_4$  and very fine  $\text{Al}_2\text{O}_3$  were used as precursors for the  $\beta$ -sialon bonding phase. The composition was calculated to achieve  $z = 2$ . Six test series T1 to T6 were produced with identical composition (Table 1). The binder was either isopropanol or

Table 1. Composition and sintering conditions. G – graphite heating elements, M – MoSi<sub>2</sub> heating elements.

[wt%]	T1	T2	T3	T4	T5	T6
Al <sub>2</sub> O <sub>3</sub> 0-3 mm	80.3	80.3	80.3	80.3	80.3	80.3
Al <sub>2</sub> O <sub>3</sub> fine	8.8	8.8	8.8	8.8	8.8	8.8
Precursor for β-sialon	10.9	10.9	10.9	10.9	10.9	10.9
Phosphoric acid	x		x	x	x	x
Isopropanol		x	x			
Mixing method	1	1	2	2	3	3
Max. Temp. (°C)	1400	1650	1650	1650	1650	1550
Furnace	G	G	M	M	M	M
Measures for pO <sub>2</sub> control				Embedded in coke		N <sub>2</sub> /CO gas

phosphoric acid. Two trials were carried out under the condition of T1 to get more information about the used binders, the first one with phosphoric acid and the second one with isopropanol.

The components were mixed in three different ways. For method 1 first both the fine and the coarse fraction were mixed separately for 30 minutes on a roller homogenizer. Then a proper amount of binder and the fine components were added to the coarse fraction and were mixed with a laboratory mixer. In case of method 2, the raw materials were mixed in a compulsory mixer. All the components were added one after another. For method 3 the fine components were mixed separately. Then all the components were mixed together in a compulsory mixer. The different mixing methods should show if there is an influence of the premixing of the fine components on the properties of the sintered samples. After mixing cylindrical specimens with the size of  $h = d = 50$  mm were uniaxially pressed with 140 MPa. For each test series four samples were pressed.

The samples have been sintered in two different electrically heated furnaces. For the first two series a furnace with graphite heating elements (furnace G) was applied. The samples were situated in a graphite crucible on a Si<sub>3</sub>N<sub>4</sub>-BN powder bed and fired in a static nitrogen atmosphere. T1 was sintered with a three-step heating regime. The maximum temperature was 1400°C and held for six hours. The samples of T2 were sintered with a four-step heating regime, after six hours holding time at 1400°C there was an additional dwell for two hours at the maximum temperature of 1650°C. T3 to T6 were sintered in a gas tight furnace with MoSi<sub>2</sub> heating elements (furnace M) in flowing nitrogen atmosphere. The samples of T3 were sintered without any additional measures, T4 and T5 were embedded in carbon with a particle size < 20 mm and T6 was sintered in a N<sub>2</sub>/CO gas with 10 % of CO. The heating regime for T3 to T5 was the same as for the samples T2. The samples T6 were sintered at a maximum temperature of 1550°C.

The weight and size of the samples were measured before and after sintering to quantify shrinkage or volume expansion. Bulk density (BD), apparent porosity (AP), cold crushing strength (CCS) and Young's modulus of the sintered

samples have been measured. The phase composition was determined by X-ray diffraction (XRD) and energy dispersive X-ray microanalysis (EDX). Furthermore the XRD results were used to determine the unit cell parameters  $a$  and  $c$  of β-sialon. The  $z$ -value of the β-sialon bonding phase was then calculated from the following equations [6]:

$$a = 7.603 + 0.0296 \cdot z_a \text{ [Å]} \quad (1)$$

$$c = 2.907 + 0.0255 \cdot z_c \text{ [Å]} \quad (2)$$

The  $z$ -value was determined as the average of  $z_a$  and  $z_c$ . The microstructure of the samples was investigated by reflected light microscopy and scanning electron microscopy (SEM).

### 3. Results and discussion

#### 3.1. Influence of binder and temperature

The results for the T1 samples showed that the phosphoric acid pollutes furnace G, therefore for the other experiments carried out in furnace G isopropanol was used as binder. However, the results also showed that samples with phosphoric acid exhibit higher strength and bulk density and a lower porosity (Table 2).

Table 2. Properties of T1.

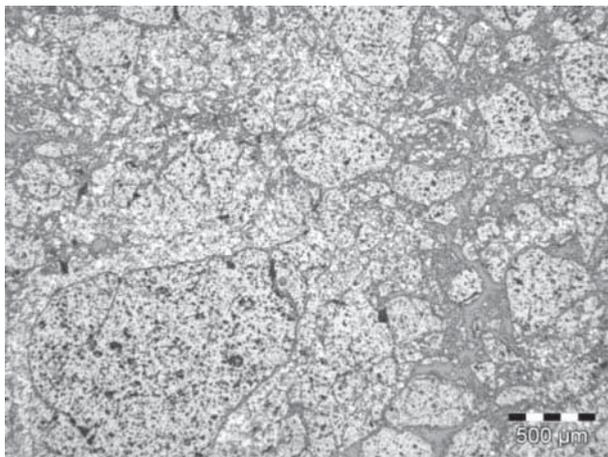
	T1	
Binder	Phosphoric acid	Isopropanol
BD [g/cm <sup>3</sup> ]	2.96	2.93
AP [%]	19.35	20.97
Young's Modulus [GPa]	27.07	20.05
CCS [MPa]	145.17	106.06
ΔV/V <sub>0</sub> [%]	0.28	1.40

For this reason for all the samples sintered in furnace M phosphoric acid was used as binder.

The XRD analysis of the samples T1 showed hardly any β-sialon and still a high amount of Si<sub>3</sub>N<sub>4</sub>. The maximum temperature of 1400°C was too low to produce a β-sialon bonding phase. XRD analysis of T2 showed that after sintering at 1650°C β-sialon as the only phase besides the main component Al<sub>2</sub>O<sub>3</sub>. The  $z$ -value of β-sialon was calculated from Eq. (1) and (2) as  $z = 2.3$ . The microstructure of T2 is shown in Fig. 1. The bonding phase is very dense. However the sample is not completely homogeneous. Fig. 1a shows that the bonding phase is not evenly distributed in the whole sample which results in a lower CCS of 68.36 MPa. However, in Fig. 1b the good bonding between β-sialon and Al<sub>2</sub>O<sub>3</sub> is illustrated.

#### 3.2. Influence of the furnace

The XRD and EDX analysis of T3 showed that it was not possible to produce a pure β-sialon bonding phase in furnace M. The oxygen partial pressure during the sintering process was too high. At the surface of the samples an oxidized layer which contains mullite and glassy phase was produced during sintering. The layer has a thickness of approximately



a)

b)

Fig. 1. Microstructure of T2: a) overview, b) detail. The formation of  $\beta$ -sialon was accompanied by shrinkage of the samples  $\Delta V/V_0 = -2.32\%$  (Table 3).

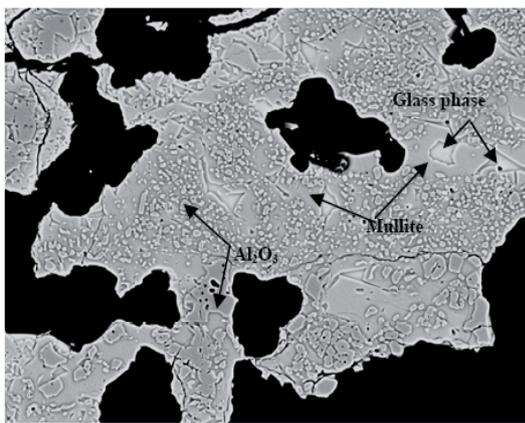
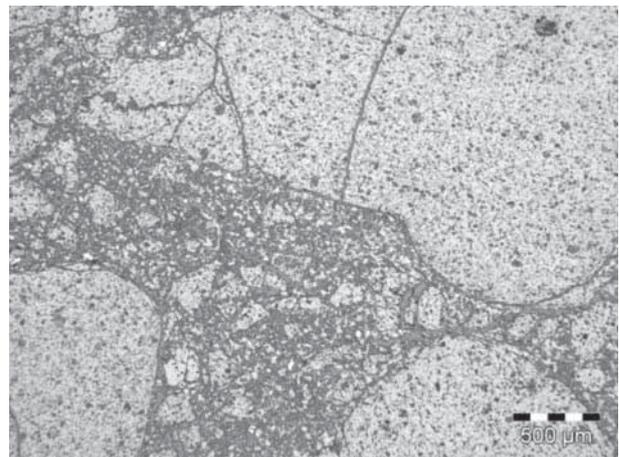


Fig. 2. SEM image of oxidized layer of T3.

one millimetre. The bonding phase in the sample contains two sialon phases,  $\beta$ -sialon and X-sialon. The appearance of X-sialon also suggests a too high oxygen partial pressure to produce a pure  $\beta$ -sialon bond. The bonding between  $\text{Al}_2\text{O}_3$  and the sialon phases is incomplete. In Fig. 2, the surface of the sample with mullite and glassy phase is illustrated.

Fig. 3a shows that there is no continuous bonding phase. In Fig. 3b, the two sialon phases which occur in the bulk of the samples are pictured.



a)

b)

Fig. 3. Microstructure of T3: a) overview, b) detail.

During the sintering, a volume expansion of  $\Delta V/V_0 = 2.26\%$  occurs. The properties of the samples are summarized in Table 3.

### 3.3. Influence of the atmosphere in furnace M

The T4 and T5 samples, with a direct contact to the carbon breeze, have a greenish colour. XRD and EDX analysis confirmed the formation of SiC which causes this colour especially at the surface of the samples. In the bulk hardly any SiC could be detected. Furthermore, reflected light microscopy showed the occurrence of a small amount of carbon at the surface of the samples (Fig. 4). The thickness of the SiC and carbon containing layer is approximately three to four millimetres.

The occurrence of these phases might be the reason for crack formation at the surface of the samples due to volume expansion. The main phases in the matrix were again  $\beta$ -sialon and X-sialon despite the use of carbon as reducing agent. However, the content of the sialon phases was lower compared to the samples of T3. The results indicate that there is a high gradient of atmosphere from very reducing at the surface of the sample to oxidizing atmosphere in the centre. The more direct contact of carbon with the surface hinders the formation of  $\beta$ -sialon. Instead of  $\beta$ -sialon, SiC and a small amount of carbon can be found in this area. Approximately three millimetres from the surface,  $\beta$ -sialon

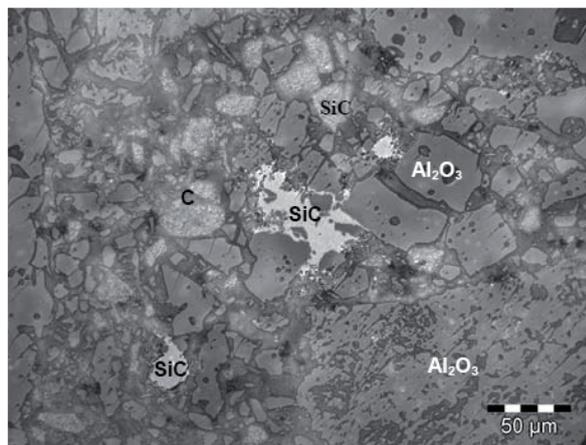


Fig. 4. Microstructure of SiC containing area of the samples of T4 and T5.

starts to form and appears together with SiC. In few areas only,  $\beta$ -sialon can be found. The structure is similar to that of T2. On the other hand, it seems that in the centre of the samples the oxygen partial pressure was too high to form a single  $\beta$ -sialon bonding phase. The bonding phase therefore consists of  $\beta$ -sialon and X-sialon. The results show that covering the samples in carbon cannot provide a proper oxygen partial pressure to produce a pure  $\beta$ -sialon bonding phase for  $\text{Al}_2\text{O}_3$  refractories.

To avoid the formation of SiC at the surface of the samples but nevertheless get a lower oxygen partial pressure in furnace M than with pure nitrogen, the samples of T6 were sintered in  $\text{N}_2/\text{CO}$  gas mixture. However, the results showed that under this condition the oxygen partial pressure still was too high and the formation of pure  $\beta$ -sialon was not possible. During the sintering, a dense layer is formed on the surface of the samples. The layer contains mullite and glassy phase, comparable to the layer of T3. The atmosphere was not reducing enough. Beside the formation of glassy phase and mullite,

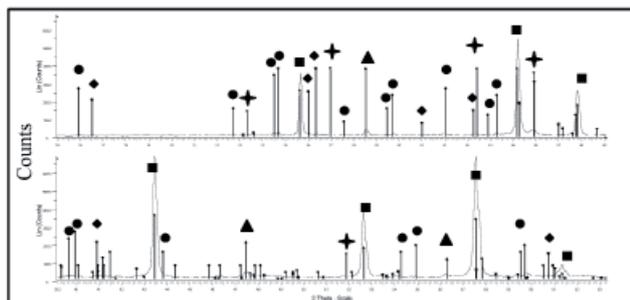


Fig. 5. XRD of T5: ■ –  $\text{Al}_2\text{O}_3$ , ● – X-sialon, + –  $\beta$ -sialon, ◆ – mullite, ▲ – Si.

Table 3. Properties of the samples sintered in furnace M compared to T2.

	T2	T3	T4	T5	T6
BD [ $\text{g}/\text{cm}^3$ ]	2.98	2.93	2.90	2.88	2.97
AP [%]	18.73	20.05	21.90	22.19	17.98
Young's Modulus [GPa]	9.16	13.94	19.29	18.39	17.61
CCS [MPa]	68.36	57.72	88.37	93.47	91.40
$\Delta V/V_0$ [%]	-2.32	2.26	0.54	0.48	0.92

another problem occurred. The formation of the dense layer on the surface impeded the nitration of silicon in the centre of the samples and a high amount of silicon still can be found there. Beside the silicon, X-sialon and a very small amount of  $\beta$ -sialon can be found in the centre of the samples (Fig. 5).

Table 3 shows the mechanical and physical properties of the samples sintered in furnace M. For comparison the properties of samples T2 sintered in furnace G are also shown in there. Important information is the volume change of the samples during the sintering process. Only T2 with a pure  $\beta$ -sialon bonding phase shows shrinkage. In all the other test series volume expansion took place.

### 3.4. Influence of the mixing

The premixing of the fine powder has no significant influence on the properties of the samples. T5 with premixed fine powder shows a higher CCS but also a higher porosity and a lower bulk density compared to T4. The Young's modulus is low for all test series. The inhomogeneity of T2 may be due to the mixing method. The energy input of a roller homogenizer and a laboratory mixer is lower than that of a compulsory mixer. The mixing with a compulsory mixer may help to get a more homogenous mixture of the raw materials and thus an evenly distributed bonding phase in the sintered samples.

## 4. Conclusions

The results show that the temperature plays an important role for the preparation of  $\beta$ -sialon bonded  $\text{Al}_2\text{O}_3$  refractories. After sintering at  $1400^\circ\text{C}$ , the precursors of  $\beta$ -sialon still can be found in the samples. At  $1650^\circ\text{C}$ , a continuous bonding phase containing only  $\beta$ -sialon can be produced. However, it is important to control the atmosphere. The production of pure  $\beta$ -sialon is possible in a furnace with graphite heating elements. In a gas tight furnace with  $\text{MoSi}_2$  heating elements, it is difficult to produce a pure  $\beta$ -sialon bonding phase for  $\text{Al}_2\text{O}_3$  refractories. The oxygen partial pressure is too high. The bonding phase consists of two sialon phases,  $\beta$ -sialon and X-sialon. The surface of the samples gets oxidized and mullite and glassy phase form. If carbon is used to cover the samples and generate a lower oxygen partial pressure, SiC is formed. From this it follows that the atmosphere was too reducing. However, X-sialon still could be found in the centre. This suggests that there is a gradient concerning the atmosphere which is not appropriate to produce a pure  $\beta$ -sialon bonding. If the samples are sintered in a  $\text{N}_2/\text{CO}$  gas, the atmosphere is not reducing enough. Again glassy phase and mullite are formed on the surface of the samples. Additionally the dense layer impeded the nitration of silicon in the centre of the samples. Thus a high amount of silicon still can be found. The mechanical and the physical properties are influenced by the phase composition in the sintered sample. Additionally the binder which is used influences the properties. Shrinkage of the samples occurs if a pure  $\beta$ -sialon bonding phase is formed. The premixing of the fine powder does not have a significant effect on the properties. The mixer however has an influence on the homogeneity of the mixture and thus on the properties of the samples. It is difficult to achieve a suitable atmosphere in an electrically heated furnace with  $\text{MoSi}_2$

heating elements to produce a pure  $\beta$ -sialon bonding phase. Therefore suitable measures are necessary to control the  $p\text{O}_2$  partial pressure. Additional experiments will focus on this.

## Acknowledgements

This research was performed with the financial support of the Austrian Research Promotion Agency (FFG) (project no. 814277) and RHI AG.

## References

- [1] Yang J.F., Beppu Y., Zhang G.J., Ohji T., Kanzaki S.: „Synthesis and properties of porous single-phase  $\beta$ -sialon ceramics”, *J. Am. Ceram. Soc.*, (2002), 1879-1881.
- [2] Jack K.H.: Review: „Sialons and related nitrogen ceramics”, *J. Mater. Sci.*, (1976), 1138-1158.
- [3] Riley F.L.: „Silicon nitride and related materials”, *J. Am. Ceram. Soc.*, (2000), 245-265.
- [4] Ekström T., Nygren M.: „Sialon ceramics”, *J. Am. Ceram. Soc.*, (1992), 259-276.
- [5] Křest'án J., Pritula O., Smorčok L., Šajgalik P., Lenčeš Z., Wannberg A., Monteverde F.: „Corrosion of  $\beta$ -sialon based ceramics by molten steel”, *J. Eur. Ceram. Soc.*, (2007), 2137-2143.
- [6] Zheng J., Forslund B.: „Carbothermal preparation of  $\beta$ -SiAlON powder at elevated nitrogen pressures”, *J. Eur. Ceram. Soc.*, (1999), 175-185.
- [7] Dinger D.R., Funk J.E.: „Particle packing II”, *Interceram*, 41, (1992), 176-179.
- [8] Dinger D.R., Funk J.E.: „Particle packing IV”, *Interceram*, 42, (1993), 150-152.




---

*Received 6 April 2010; accepted 12 May 2010*