Novel method for fabrication of sialon corundum composite ceramics by air atmosphere sintering

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A novel approach was developed for synthesizing sialon in an air atmosphere, and then used to obtain O'-sialon bonded corundum composite ceramics (O'-sccc) by a sintering reaction process in an air atmosphere. The morphology, microstructure, and properties of the O'-sccc were investigated. The process of forming sialon by air atmosphere sintering is discussed. It was found that a novel configuration, using fused white alumina, alumina powder, and ferro silicon nitride powder, allowed the synthesis of sialon without a controlled nitrogen atmosphere furnace.

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1. Introduction

Sialons were discovered in the early 1970 s. Sialon is a generic name for compounds or solid solutions made up of the elements Si–Al–O–N.^{1)–3)} Sialon has various compositions and structures, but the most thoroughly studied are β -, α -, O'- and X-sialon.^{4)–15)} It has been reported that β -sialon can be prepared by synthesis from natural alumino-silicate minerals, such as clay and pyrophyllite,¹⁶⁾ alumino-silicate gels,¹⁷⁾ or zeolites (with or without polyacrylonitrile)^{18),19)} by carbothermal reduction and nitridation processes, such as a self-propagating high-temperature synthesis (SHS) in flowing N₂ gas.²⁰⁾ Sialon ceramics are typically produced via high-temperature liquid phase sintering of either a powdered mixture of Si₃N₄–AlN–M_xO_y, where M is a metal, such as Li, Mg, Ca, Y, or a rare earth element, or Si₃N₄–AlN–Al₂O₃.^{21)–23)} The atmosphere during the sintering process plays an important role, and N₂ gas at a pressure of around 10⁶ Pa has become the predominant sintering condition for Si₃N₄ ceramics in industry.²⁴⁾ Many papers have discussed the stability of Si₃N₄ and Si–O–N systems at high temperature in terms of thermodynamics.^{25)–29)} At the present state of knowledge of the synthesis of sialon, one has to conclude that it is necessary to employ a nitrogen flow in the furnace, and that sintering Si₃N₄ and Al₂O₃ in an air atmosphere furnace does not lead to the synthesis of sialon.

It was the purpose of this investigation to apply a solid-gas reaction for sintering in an air furnace of an Si₃N₄ + Al₂O₃ powder of appropriate composition for preparing corundum composite refractories with a sialon matrix.

2. Experimental

Sialon corundum composites were prepared from a high quality white fused alumina (from Almatiss), with low K₂O and Na₂O content, characterized by a close to zero porosity and a density of 3.90 g/cm³. Reactive alumina CTC-50 (Almatiss d₅₀ = 1.0–2.0 μ m) and tabular alumina T60 (Almatiss 0–0.045 mm) were used. Nitrosil 20 (Ferro Silicon Nitride obtained from ferrosilicon 75), supplied by Pechiney Electrometallurgie, was used as a Si₃N₄-bearing raw material. These raw materials were used to create

Table 1. Raw materials used in producing the O'-sialon bonded corundum composite ceramics

	d (μ m)	SCCC-1 (%)	SCCC-2 (%)	SCCC-3 (%)
Electrocorundum	1000–3200	43	43	43
	500–1000	18	18	18
	32–500	8	13	9
T-60		5	3	3
CTC-50		13	12	11
Nitrosil 20		13	11	16

the sialon matrix at high temperature. In addition, white fused electrocorundum, ranging in particle size from 32 to 3200 μ m, was added to the mixture. The grain size distribution was determined, according to the methods described by Dinger and Funk,³⁰⁾ for a grain distribution coefficient n equal to 0.37 CPFT (cumulative percent finer than) distribution. Raw materials were combined in the proportions by mass described in **Table 1**.

The mixtures were homogenized using an Eirich mixer, and specimens were formed as cylinders with a diameter of 50 mm and a comparable height, or as bricks 63 mm $\times$ 114 mm $\times$ 230 mm. The compaction pressure of 85 MPa was used. The synthesis was carried out with a one-step heat treatment procedure. Green refractory composites were heated up to 1173, 1473, or 1773 K, without nitrogen flow, with a constant heating rate of 10°C min^{–1}, heated at a constant temperature for 1 h, and then cooled within the furnace Nabertherm HT16/18.

The microstructure of the polished fracture surface of the sialon corundum composite was examined using a scanning electron microscope (SEM), the ultra high definition NOVA NANO SEM 200. Qualitative and quantitative elemental analysis with energy dispersive X-ray spectroscopy (EDS) was also carried out. The phase composition of the final product was examined by XRD equipment (PANalytical X'Pert Pro MPD) using Cu-K α radiation. The specimens were scanned over an angular range of 10° < 2 θ < 90°. IR studies in the range 4000–400 cm^{–1} were carried out using a Fourier BIO-RAD FT60V spectrometer. The samples were prepared as KBr pellets. The bulk density and apparent porosity of the sialon-corundum composites were

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determined according to PN-EN 993-1:1998 (methods of test for dense shaped refractory products). The cold crushing strength of the sialon-corundum composites was determined according to PN-EN 993-5:2001 (methods of test for dense shaped refractory products - Part 5: Determination of cold crushing strength).

3. Results

3.1 Microscopy studies

A photograph of the surface and cross-section morphology of a brick after firing at 1773 K for 1 h in an air atmosphere is shown in Fig. 1. It can be seen that cracks, bubbles, and pits exist on the glaze surface. The cross-section sample shows the typical macrostructure of sccc.

When Si_3N_4 is sintered in an air furnace, there are two different sources of oxygen: one is the oxygen in the powder bed (there exists some SiO_2 phase on the Si_3N_4 , about 1.5 mass % oxygen) and another the atmosphere in the kiln, composed of 80% N_2 gas and 20% O_2 gas ($p_{\text{O}_2} = 2 \times 10^4 \text{ Pa}$). The important fact is that at a pressure of $p_{\text{O}_2} = 2 \times 10^4 \text{ Pa}$ ($N_2 = 8 \times 10^4 \text{ Pa}$), silicon nitride changes to SiO_2 by passive oxidation as shown in reaction (1). The passive oxidation of Si_3N_4 ceramics is mainly influenced by the protective layer formed at the surface by the oxidation process, and the ability of this layer to prevent oxygen from diffusing into the material. A surface layer of pure SiO_2 causes a very low rate of oxygen diffusion into the material³²⁾

Reaction (2) occurs when p_{O_2} decreases to below 10^2 Pa , active oxidation takes place

The main reaction leading to mass loss of the specimen during sintering is reaction (3).²⁴⁾

Reactions (4) and (5) take place in the insulating layer

(a) oxygen transfers from the interface by diffusion through the boundary layer between the gas phase and the solid phase to the surface;

(b) after oxygen physisorption, chemisorption and surface penetration, as well as oxygen diffusion through the oxide product layer, oxygen reacts with Si_3N_4 to produce $\text{SiO}(g)$, $\text{Si}(l)$, $\text{Si}(g)$, $\text{SiO}_2(l)$ - the insulating layer is formed which became

impermeable.

Reaction (6) takes place in the bulk ceramic

(c) nitrogen transfer from the bulk of the gas flow to the surface occurs;

(d) the insulating layer stops nitrogen transfer from the surface to the interface.

The macrostructure [Fig. 2(a)] and SEM images of samples near top (insulating) layer [Fig. 2(b)], the transition zone [Fig. 2(c)], and the bulk of the sialon corundum ceramic [Fig. 2(d)] are shown. As can be seen, it comprises two distinguishable parts - the high O_2 surface (insulating layer) and the low O_2 part located inside the bulk ceramic.

Figure 2(b) shows that the microstructure consists of Al_2O_3 grains (points 4 and 5) dispersed in the silicate phases. The glass silicate matrix layer, which was produced by the chemical reaction between Al_2O_3 , Si_3N_4 , O_2 , and FeSi_2 , contains bright iron oxide dendrites and small, gray mullite crystals. The average chemical composition of phases found in the insulating layer is listed.

The transition zone is clearly distinguished [Fig. 2(c)]. The contrast on backscattered electron micrographs depends mainly on the mean atomic number: pores appear black, Al_2O_3 grains appear deep gray, whereas the sialon phase appears gray, the silicate phases appear light gray, whilst iron appears white.

The details of the phases in the bulk region are well illustrated in the SEM image [Fig. 2(d)]. EDS was conducted at six points. Al_2O_3 aggregate grains (point 6) are well-bonded by the somewhat porous matrix of sialon (points 1, 2, and 3). The microstructure is not pore-free, and has iron accessory phases (points 4 and 5).

To characterize the concentration gradients of the elements Fe, Si, Al, O, and N in the sialon matrix region, EDS line-scan analysis (in atom %) was carried out from the locations marked in Fig. 3(a); the outcome is shown in Fig. 3(b). The signal intensity of N throughout the matrix is higher than the initial line scanning on the Al_2O_3 grains, and the line maintains a relatively high intensity in the matrix and gives a strong intensity when it comes into contact with the Si_3N_4 grains. Results show the existence of a dispersed iron phase (the random distribution of elements along the line).

3.2 Infrared spectroscopy

The IR spectra of sialon have been discussed.³³⁾ In general, the sialon powders differ from each other considerably and also, naturally, from the IR-spectra of silicon nitride and aluminium oxide.

During our IR investigation of the sialon corundum composite, we obtained a spectrum of a matrix before and after sintering in an air atmosphere. This sample showed obvious changes in the IR spectra before and after heating, with increased absorption in the regions near 650 and 900 cm^{-1} (Fig. 4). In the range 930 – 1050 cm^{-1} , the spectrum of O'-sialon most closely resembles that of silicon nitride; absorption can be associated with Si–N vibrations.^{34),35)} Bands in the area of 650 – 900 cm^{-1} appear due to the replacement of Al–O and Si–N bonds with Al–N bonds. Al–N stretching occurs in the 700 – 760 cm^{-1} region. The IR spectrum at 400 – 650 cm^{-1} is a typical spectrum of α - Al_2O_3 . Characteristic features common to all spectra of α - Al_2O_3 are the occurrence of two strong bands near 600 and 650 cm^{-1} ; they were assigned to Al–O stretching vibrations of AlO_6 groups.³⁶⁾ After heating,

Fig. 1. Macrostructure of bricks; surface and cross-section.

Fig. 2. a) overview of the macrostructure, b) SEM micrographs of insulating layer, c) SEM micrographs of transition zone, d) SEM micrographs of bulk ceramic.

substantial weakening and broadening of the absorption bands of $\alpha\text{-Al}_2\text{O}_3$ were noted. This testifies to increasing disorder and the destruction of the lattice. Taking into account the data of X-ray phase analysis, the most probable cause of this change must be formation of sialon.

3.3 X-ray diffraction

The X-ray powder diffraction pattern of the matrix of sialon after sintering at 1173 K is shown in **Fig. 5(a)**. Besides the characteristic peaks of Al_2O_3 , weak diffraction peaks are observed on samples [Fig. 5(b)]. Polycrystalline phases of the samples at 1173, 1473, and 1773 K (**Fig. 6**) found by XRD are also summarized in **Table 2**.

According to this data, the samples formed at 1173 and 1473 K showed hardly any O'-sialon and still had a high amount of silicon nitride. Si_3N_4 under ambient conditions does not melt, but

it decomposes into its elements at about 2120 K³⁷⁾ [Eqs. (7), and (8)]; iron enhances the decomposition, which can start at 973 K in its presence.³⁸⁾

The decomposition of Si_3N_4 at a lower temperature than 2120 K is confirmed by our work. When using the powder bed technique and air sintering, it is hard to say what is the role of reactions in the gas phase, the effect of nitrogen pressure, or the path of reactions involving atomic nitrogen on the O'-sialon formation process. O'-sialon could be obtained at 1173 K, but the quantity of O'-sialon is low. In the temperature region of 1173 to 1473 K, the content of O'-sialon is almost constant and SiO_2 was detected. Furthermore an $\alpha \rightarrow \beta\text{-Si}_3\text{N}_4$ transformation has been observed. N_2 gas is very unreactive, and true gaseous reactions

Fig. 3. a) SEM image and line-scan profiles of sample and b) their corresponding atom profile.

Fig. 4. IR-spectra of samples: a) matrix before heating, b) matrix after heating.

seem unlikely, but it has been reported^{39),40)} that gas phase reactions can lead to β - Si_3N_4 . The activation energy separating the two phases, α - and β - Si_3N_4 , is large. The transformation $\alpha \rightarrow \beta$ - Si_3N_4 is reconstructive,⁴¹⁾ involving the breaking and remaking of strong Si-N bonds.

Fig. 5. a) XRD patterns matrix of sialon at 1173 K and b) magnification of XRD spectra.

Fig. 6. a) XRD patterns matrix of sialon at 1773 K and b) magnification of XRD spectra.

Table 2. Phase composition of the sialon-corundum composite ceramic

Sample	Crystalline phases
1173 K	Al_2O_3 , α - Si_3N_4 , Si, β - Si_3N_4 , $\text{Si}_{1.84}\text{Al}_{0.16}\text{O}_{1.16}\text{N}_{1.84}$, SiO_2 , Fe_2O_3
1473 K	Al_2O_3 , α - Si_3N_4 , SiO_2 , β - Si_3N_4 , Si, $\text{Si}_{1.84}\text{Al}_{0.16}\text{O}_{1.16}\text{N}_{1.84}$, Fe_2O_3
1773 K	Al_2O_3 , $\text{Si}_{1.62}\text{Al}_{0.38}\text{O}_{1.38}\text{N}_{1.62}$, β - Si_3N_4 , SiO_2 , Fe_2O_3

XRD analysis showed that, after sintering at 1773 K (Fig. 6), O'-sialon becomes the second phase, besides the main component Al_2O_3 . For samples heated at 1173–1773 K, it was shown that the O'-sialon was synthesized from silicon nitride, aluminium powder, and corundum by nitridation reaction inside the samples, and that the O'-sialon bonded corundum composite ceramics were prepared by a pressureless sintering process using air atmosphere sintering.

3.4 Characteristics of sialon corundum composite ceramics

Following the results of the microscopy studies, IR spectroscopy, and XRD, we can create a 3D drawing of the bulk region,⁴²⁾ which is presented as Fig. 7 (it can be seen as a sialon matrix with hollow areas where corundum grains can be found).

Fig. 7. 3D Drawing of sialon matrix in the bulk region.

Table 3. Properties of sialon corundum composite ceramics

bulk density [g/cm ³]		apparent porosity [vol %]		cold crushing strength [MPa]	
sccc-1	literature	sccc-1	literature	sccc-1	literature
3.3	3.12	8.0	14.5	140	100

On the basis of the above, and Fig. 7, we can say that the improvement in the properties of the sccc could be attributed to increasing density, or the quality and quantity of the O'-sialon in the matrix. The key physical properties of our sialon corundum composite ceramic, and a comparison with literature values,⁴³⁾ are given in **Table 3**. The results indicate that the open porosity level of sccc formed by sintering in air is lower than commercial sialon-bonded corundum ceramics. It is influenced by the oxidation processes, which at >1373 K close the pores with the help of an SiO₂ surface layer.³¹⁾ The comparison of our sccc with the commercial sialon-bonded corundum ceramics formed at the same sintering temperature showed an improvement in crushing strength.

4. Summary

A novel method of fabrication of O'-sialon corundum composite ceramics has been successfully developed. The solid/gas reaction due to the thermal decomposition of Si₃N₄, can be slowed down by embedding the solid in a powder of appropriate composition. The grain size distribution was found to play a significant role in inhibiting volatilization, reducing weight loss, and keeping the microstructure uniform. The accepted wisdom that sintering Si₃N₄ and Al₂O₃ in an air furnace cannot give rise to the formation of sialon has been shown to be untrue.

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