Preparation, characterisation and properties of Ca-alpha-sialon and Ca-alpha/beta-sialon composite materials

Citation for published version (APA):

DOI:
10.6100/IR536388

Document status and date:
Published: 01/01/2000

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Preparation, Characterisation and Properties of Ca-α-sialon and Ca-α/β-sialon composite materials

John van Rutten
Preparation, Characterisation and Properties of Ca-α-sialon and Ca-α/β-sialon composite materials

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. M. Rem, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 25 september 2000 om 16.00 uur

door

John Willebrordus Theodorus van Rutten

Geboren te Schiedam
Dit proefschrift is goedgekeurd door de promotoren:

prof.dr. R. Metselaar
en
prof.dr. S. Hampshire

Copromotor:

dr. H.T. Hintzen

Druk: Universiteitsdrukkerij, Technische Universiteit Eindhoven

CIP-DATA LIBRARY TECHNISCHE UNIVERSITEIT EINDHOVEN

Rutten, John W.T. van


NUGI 813
Trefwoorden: keramische materialen / keramische composietmaterialen; bereiding / sialon; carbothermische reductie / fasediagrammen
Subject headings: ceramic materials / ceramic composite materials; synthesis / sialon; carbothermal reduction / phasediagrams
CONTENT

1. INTRODUCTION........................................................................................................... 1
   1.1. Si₃N₄ and sialon materials ........................................................................... 1
   1.2. Choice of the Ca-α-sialon system ......................................................... 2
   1.3. Scope of this thesis .................................................................................. 3

2. LITERATURE REVIEW .................................................................................................... 5
   2.1 Structure and crystal chemistry of Si₃N₄ and Sialon materials ..................... 5
   2.2 Phase diagrams of α and β-sialon materials ........................................... 11
   2.3 The transformation of α to β-sialon and other phases and vice versa ........ 15
      2.3.1 Sm-α-sialon ...................................................................................... 16
      2.3.2 Y and rare earth-α-sialons .................................................................. 16
      2.3.3 Ca-α-sialon ...................................................................................... 17
   2.4 Preparation of sialon materials ................................................................... 17
   2.5 Properties of sialon materials .................................................................... 19
   2.6 Corrosion resistance of sialon materials .................................................. 23
   2.7 Potential and future prospects of sialon ceramics ..................................... 25

3. RELATION BETWEEN LATTICE PARAMETERS OF Ca-α-SIALON AND ITS
   COMPOSITION........................................................................................................... 31
   3.1 Introduction ................................................................................................. 31
   3.2 New model and determination of the model parameters ......................... 32
   3.3 Evaluation of the model parameters ......................................................... 33
   3.4 Interpretation of the model parameters .................................................... 35
   3.5 Application of the new model ................................................................. 37
   3.6 Conclusions ............................................................................................... 39

4. PHASE RELATIONS IN THE Ca-α/β-SIALON SYSTEM .......................................... 41
   4.1 Introduction ............................................................................................... 41
   4.2 Experimental Methods ............................................................................. 43
## Contents

### 4. Results and Discussion

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Starting Materials</td>
<td>43</td>
</tr>
<tr>
<td>4.2 Reaction sintering</td>
<td>43</td>
</tr>
<tr>
<td>4.3 Reaction hot pressing</td>
<td>45</td>
</tr>
<tr>
<td>4.4 Characterisation</td>
<td>45</td>
</tr>
</tbody>
</table>

### 5. Conclusion

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>52</td>
</tr>
<tr>
<td>5.2 Experimental Methods</td>
<td>56</td>
</tr>
<tr>
<td>5.3 Results and Discussion</td>
<td>57</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>61</td>
</tr>
</tbody>
</table>

### 6. CARBOOTHERMAL PREPARATION AND CHARACTERISATION OF Ca-α-SIALON

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>63</td>
</tr>
<tr>
<td>6.2 Experimental Methods</td>
<td>64</td>
</tr>
<tr>
<td>6.3 Characterisation</td>
<td>65</td>
</tr>
<tr>
<td>6.4 Results and Discussion</td>
<td>66</td>
</tr>
<tr>
<td>6.4.1 Synthesis of Ca-α-sialon</td>
<td>66</td>
</tr>
<tr>
<td>6.5 Conclusions</td>
<td>70</td>
</tr>
</tbody>
</table>

### 7. DENSIFICATION BEHAVIOUR OF Ca-α-SIALONS

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Introduction</td>
<td>75</td>
</tr>
<tr>
<td>7.2 Experimental Methods</td>
<td>76</td>
</tr>
<tr>
<td>7.2.1 Reaction hot-uniaxial-pressing and reaction sintering</td>
<td>76</td>
</tr>
<tr>
<td>7.2.2 Sintering of carbothermally prepared Ca-α-sialon powder</td>
<td>77</td>
</tr>
<tr>
<td>7.2.3 Dilatometry</td>
<td>78</td>
</tr>
<tr>
<td>7.2.4 Characterisation</td>
<td>78</td>
</tr>
<tr>
<td>7.3 Results and Discussion</td>
<td>78</td>
</tr>
<tr>
<td>7.3.1 Phase Composition</td>
<td>78</td>
</tr>
<tr>
<td>7.3.2 Densification mechanism</td>
<td>79</td>
</tr>
<tr>
<td>7.4 Conclusions</td>
<td>82</td>
</tr>
</tbody>
</table>

### 8. INFLUENCE OF THE αβ-RATIO ON THE PROPERTIES OF Ca-αβ-SIALON CERAMICS

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Introduction</td>
<td>85</td>
</tr>
<tr>
<td>8.2 Experimental Methods</td>
<td>86</td>
</tr>
<tr>
<td>8.2.1 Preparation</td>
<td>86</td>
</tr>
<tr>
<td>8.2.2 Characterisation</td>
<td>87</td>
</tr>
<tr>
<td>8.2.3 Hardness</td>
<td>87</td>
</tr>
<tr>
<td>8.2.4 Young's modulus</td>
<td>87</td>
</tr>
<tr>
<td>8.2.5 Fracture toughness</td>
<td>88</td>
</tr>
<tr>
<td>8.2.6 Thermal conductivity</td>
<td>88</td>
</tr>
<tr>
<td>8.3 Results and Discussion</td>
<td>89</td>
</tr>
<tr>
<td>8.3.1 Phase composition</td>
<td>89</td>
</tr>
<tr>
<td>8.3.2 Mechanical and thermal properties</td>
<td>90</td>
</tr>
<tr>
<td>8.4 Conclusions</td>
<td>93</td>
</tr>
</tbody>
</table>

### SUMMARY

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUMMARY</td>
<td>95</td>
</tr>
</tbody>
</table>

### DANKWOORD

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DANKWOORD</td>
<td>105</td>
</tr>
</tbody>
</table>

### LIST OF PUBLICATIONS AND PRESENTATIONS

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF PUBLICATIONS AND PRESENTATIONS</td>
<td>107</td>
</tr>
</tbody>
</table>

### CURRICULUM VITAE

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CURRICULUM VITAE</td>
<td>109</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction

1.1 Si₃N₄ and sialon materials

Silicon nitride and silicon nitride based materials are studied for already several decades. At the beginning of the seventies sialons were discovered [1]. These ceramics are based on silicon nitride where Si and N are partially replaced by O and Al resulting in β-sialon (general formula: Si₆₋₂AlₓOₓN₈₋₂ₓ). In 1978 Hampshire et al. [2] reported the discovery of a new class of these sialon materials, the so-called α-sialons. The general formula for an α-sialon is: Meₓ⁺ₘ⁻valSi₆₋₂(ₘ+n)Alₓ(m+n)Oₘ⁻ₙN₁₆₋ₙ where Me is a metal, val is the valency of the metal ion. The m and n-values are substitution coefficients. It was found that several metal ions can be incorporated in this silicon nitride structure. The metal ions can have a valency of 1 (Li, Na), 2 (Mg, Ca) and 3 (Y, lanthanides). Especially Y was investigated thoroughly as well as other lanthanides in contrast with the metal ions with a single and double valency [3,4,5,6]. Composite α/β materials give the possibility to make a combination of the advantages of both structures. These ceramics have very good properties like for example high hardness, high fracture toughness, high strength, good chemical resistance, high temperature and high wear resistance [7,8,9]. At high temperatures the strength is much higher compared to the commonly used super alloys. Sialon materials are being evaluated in a number of areas where materials have to operate at high stress and elevated temperatures. The advantages of sialon ceramics over silicon nitride ceramics are 1. Easier to prepare sialon materials; 2. Lower processing / sintering temperature; 3. Higher chemical resistance; 4. Higher oxidation resistance; 5. Higher thermal-shock resistance.

A few examples of current and potential applications for such materials are given below [9,10].

Engine components (diesel and petrol): Japanese companies are already marketing precombustion chambers and glow plugs for diesel engines manufactured in sialon ceramics. Field trials on diesel engine tappets were run to 70000 km with negligible wear. Silicon nitride turbochargers, fuel injector links and exhaust gas control valves are already introduced to automotive industry [9]. Car industry is very interested because using ceramics will lower
consumption of fuel. British and European engine manufacturers are currently testing components made from sialon and continue to have great interest in them.

Gas turbine engines: Sialon ceramics have mechanical properties at high temperature which, coupled with the possibility of turning them into a complex shape, makes them ideally suited to this application. The primary advantage is the marked fuel efficiency gain in turbines due to higher operation temperature. Potential applications include aerospace, land-based and automotive turbines. Sialon ceramics are being evaluated in long-term research programs for commercial automotive turbine engines. These ceramics have performed successfully in bearing trials.

Metal cutting: Sialon ceramics outperform cobalt-bonded tungsten carbide and alumina in cutting steel and super alloys. Sialon ceramics replaces or covers the hard alloys. Ceramics have low weight to volume ratios as an advantage over metals as well as a high operation temperature.

Welding: Small diameter gas shrouds with a wall thickness of less than 1 mm are used in automatic welding operations in the aerospace industry. Sialon ceramic shrouds perform many thousands of cycles where normal alumina shrouds cannot withstand the thermal shock. Various wear parts on resistance welding jigs have proved to be virtually indestructible. The properties required for this application are electrical insulation, thermal shock resistance, wear resistance, high strength, and resistance to molten metal spatter.

Wear parts and extrusion dies: The ability of sialon ceramic to operate in contact with metallic components with or without lubrication, and its ability to withstand high temperature and thermal shock, enables it to cope with a wide range of wear environments throughout manufacturing industry.

Another application is bottleneck capillaries [11] which are used in the production of highly integrated electronic devices. The main factor that slows down the application of sialon and silicon nitride ceramics is the high price of Si₃N₄ as starting material.

1.2 Choice of the Ca-α-sialon system
In this investigation the focus is on Ca-α-sialon and Ca-α/β-sialon composite materials. There are several arguments that justify the choice of the system mentioned above. At the start of this study it was known that the material exists, but further knowledge about phase formation, characterisation, sintering and properties was hardly available. Only little attention was paid to the stability area of the Ca-α-sialon materials. Properties of and phase studies on Y and lanthanide-sialon materials showed interesting results and there was no reason to assume that Ca-sialon would have less promising properties. A few investigations had been performed on Ca-sialon material, for example by Jack [12] and Mitomo et al. [13]. Only recently more attention has been paid to this material by groups at Monash University [14,15] and the University of Newcastle upon Tyne [16]. The advantage of Ca-α-sialon is the reduction of costs in starting materials and processing with the possibility of maintaining the qualities of α-sialon. This is even more so when the carbothermal reduction/nitridation of oxide starting materials proves to be possible. Therefore we have studied the phase relations, sintering and some mechanical and thermal properties of Ca-α-sialon ceramics. Moreover the application of the materials in higher (>1500°C) and middle range (1000-1500°C) temperatures is promising, since there are indications that the Ca-compound is stable in this region, in contrast to several of the rare earth sialons.

1.3 Scope of this thesis
One of the main purposes of this work is to investigate whether the carbothermal reduction / nitridation preparation route is not only suitable to synthesise β-sialon, but is also useable to prepare α-sialon material. Another main purpose is to study the phase relations and properties (not only mechanical) to see what potential dense Ca-α-sialon and Ca-α/β-sialon materials have when compared to the more expensive Y-sialon and lanthanide sialon materials. In order to do this the reaction sintering and hot pressing techniques are used to obtain dense materials and also enable to vary the composition in a simple way.

Chapter 2 presents a literature review concerning sialon materials in general, with the emphasis on the α-sialon materials. It deals with the discovery of sialon ceramics, the crystallographic structure of silicon nitride and sialon and the mechanical properties compared to e.g. other ceramic materials and super alloys. It also deals with the phase (behaviour) diagram to which Ca-α and Ca-α/β-sialon composite materials belong. The relation between the lattice parameters and the chemical composition is described in chapter 3 ("Relation between lattice parameters of Ca-α-sialon and its chemical composition"). A new model is derived and the application of the model is validated with some examples.

The work performed to reveal the phase (behaviour) diagram in which Ca-α-sialon materials are found is described in chapter 4 ("Phase relations in the Ca-α/β-sialon system"). It gives the stability area of single-phase Ca-α-sialon and the region of the Ca-α/β-sialon composite material in the system Si₃N₄ - Al₂O₃N - CaAl₂N. Especially the influence of temperature on the border between single-phase α and two-phase αβ area is also described in this chapter.

The phase formation of Ca-α-sialon by reaction sintering is dealt with in chapter 5 ("Phase formation of Ca-α-sialon by Reaction Sintering"). Here the formation mechanism is described and compared to results found in literature. Not only the Ca-α-sialon data but also the data reported for other α-sialon materials are compared to each other.

The preparation of Ca-α-sialon material by means of carbothermal reduction and nitridation of oxides is described in chapter 6 ("Carbothermal Preparation and Characterisation of Ca-α-sialon"). The composition of the material aimed at is Ca₀.₅Si₃N₄-etration of the model is validated with some examples.

The work performed to reveal the phase (behaviour) diagram in which Ca-α-sialon materials are found is described in chapter 4 ("Phase relations in the Ca-α/β-sialon system"). It gives the stability area of single-phase Ca-α-sialon and the region of the Ca-α/β-sialon composite material in the system Si₃N₄ - Al₂O₃N - CaAl₂N. Especially the influence of temperature on the border between single-phase α and two-phase αβ area is also described in this chapter.

The phase formation of Ca-α-sialon by reaction sintering is dealt with in chapter 5 ("Phase formation of Ca-α-sialon by Reaction Sintering"). Here the formation mechanism is described and compared to results found in literature. Not only the Ca-α-sialon data but also the data reported for other α-sialon materials are compared to each other.

The preparation of Ca-α-sialon material by means of carbothermal reduction and nitridation of oxides is described in chapter 6 ("Carbothermal Preparation and Characterisation of Ca-α-sialon"). The composition of the material aimed at is Ca₀.₅Si₃N₄-Al₂O₃N and was obtained as single-phase material. A proposal of the sequence of the different reactions that take place during the reduction and nitridation is given here. Chapter 7 ("Densification behaviour of Ca-α-sialons") describes the densification behaviour of Ca-α-sialon ceramics using three different methods. Reaction hot pressing, reaction sintering at low pressures (0.5 MPa) and sintering of carbothermally prepared powders were used to obtain dense ceramics. These methods were compared to each other and to results found in literature for other systems.

In chapter 8 ("Influence of the αβ-ratio on the properties of Ca-αβ-sialon ceramics") some properties of the materials are given. In this chapter the mechanical properties like hardness, toughness and the thermal conductivity in relation to the phase composition are dealt with. In the final chapter the discussion and conclusions are summarised.
Chapter 1

References

Chapter 2
Literature review

2.1 Structure and crystal chemistry of Si3N4 and Sialon materials
Silicon nitride can appear in more than one crystallographic form and it is therefore not surprising that the crystal structure of silicon nitride through the years has been a subject of extensive studies. The structure determination of the silicon nitride material by powder X-ray diffraction was performed accurately in 1957 when it was found that both $\alpha$ and $\beta$ silicon nitride have a hexagonal structure ($a = b \neq c, \alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$) [1]. The dimensions reported for $\alpha$-Si3N4 are $a = 0.7749-0.7757$ nm and $c = 0.5616-0.5622$ nm with the space group P31c [2]. For $\beta$-Si3N4, the lattice parameters are $a = 0.7605-0.7608$ nm and $c = 0.2907-0.2911$ nm with the space group P63/m [3]. Two authors reported that there is some evidence that the $\beta$-Si3N4 has a space group P63 [4,5]. Just recently a cubic spinel structure for Si3N4 was synthesised and reported and is called $\gamma$-Si3N4 [6]. The crystal structures in both $\alpha$ and $\beta$ consist of a three dimensional network of interconnected SiN4 tetrahedral units, the arrangement of these units, however, is different.

Figure 2.1. AB and CD Si-N layers in silicon nitride. The stacking sequence in the $\beta$-modification is ABAB... and for the $\alpha$-modification it is ABCD...[7].
In figure 2.1 AB and CD Si-N layers in silicon nitride are shown. The β-structure is obtained from an ABAB... stacking of these layers. In this structure there is a continuous set of channels parallel to the c direction (figure 2.2).

The α-structure can be obtained by an ABCD stacking of the planes. This is further explained in figure 2.3. The top layer, R (AB-layer), is removed from the bottom layer, S (AB-layer), turned (180°) and then moved back to the bottom layer forming an α-structure layer. Due to the glide plane connecting the AB layers to the CD layers, the channels are closed (see figure 2.4). Sialon materials are based on silicon nitride. Sialon is the acronym of the elements in the compound namely Si, Al, O and N. In the silicon nitride Si and N are partially replaced by Al and O. As well as for the most well known silicon nitride modifications (α and β), there are also the α and β crystallographic forms observed for the sialon materials.

**Figure 2.2.** Plot of the β- Si₃N₄ structure along the c-axis [8].

**Figure 2.3.** Relationship between the α and β structure of Si₃N₄. Four layers (ABAB = RS) of the β-structure (a) are split (AB) (b). The top layer, R (AB), is removed from the bottom layer, S (AB), turned (c) and moved back on the bottom layer (d) to compose four layers (ABCD) of the α-structure (see figure 2.4) [8].
The general formula for β-sialon is:

\[ \text{Si}_{6-\delta}\text{Al}_{\delta}\text{O}_{16-\delta}\text{N}_{16+\delta} \]  

(2.1)

where \( \delta \) is a substitution coefficient for Al and O in the silicon nitride lattice. The \( \delta \)-value varies in the range 0 - 4.2 [9]. The dimensions reported by Ekström and co-workers for β-sialon are \( a = \{0.76105(4) - 0.77155\} \) nm and \( c = \{0.29119(3) - 0.30069(4)\} \) nm for β-sialons with a \( \delta \)-value in the range of 0.25 - 4.00 [10]. The lattice parameters of the structure are related to the \( \delta \)-value. According to Ekström et al. [10] the linear equations for his samples are:

\[ a = 0.7603 + 0.00296 \delta \text{ (nm)} \]  

(2.2)

\[ c = 0.2907 + 0.00255 \delta \text{ (nm)} \]  

(2.3)

Two similar equations derived with the linear least squares fit taking data from literature into account as reported by Kokmeijer [11] are given below.

\[ a = 0.7599 + 0.00276 \delta \text{ (nm)} \]  

(2.4)

\[ c = 0.2904 + 0.00244 \delta \text{ (nm)} \]  

(2.5)

In equations 2.2 and 2.3 Ekström uses the \( a \) and \( c \) values of pure β-silicon nitride while in equations 2.4 and 2.5 the \( a_0 \) (0.7599 nm) and \( c_0 \) (0.2904 nm) are results from the fit Kokmeijer used resembling \( a \) and \( c \) of β-Si₃N₄. Besides β-sialon an α-sialon can be distinguished with the following general formula:

\[ \text{Me}_{m-3}\text{Si}_{12-n}\text{Al}_{m\alpha}\text{O}_{n\alpha}\text{N}_{16+n} \]  

(2.6)

where Me is Li, Na, Mg, Ca, Sr, Y or a lanthanide ion which stabilises the structure of the α-sialon. The valency of the metal ion is denoted as \( \alpha \). The \( m \) and \( n \) are substitution coefficients. For the general composition \( m(\text{Si-N}) \) is replaced by \( m(\text{Al-N}) \) and \( n(\text{Si-N}) \) is replaced by \( n(\text{Al-O}) \) [7]. The structure of α-sialon is based on the α-Si₃N₄ structure as shown above by partial replacement of Si⁴⁺ by Al³⁺ and N⁻³ by O²⁻. Because the Al and O concentration are different, additional Me-ion is incorporated for charge compensation.

The resulting two large interstitial sites (closed channels, fig. 2.4) per unit cell Si₁₂N₁₆ contain the stabilising cations to preserve the structure. The size of these sites (0.13 nm) [12] limits the solubility of these cations, it depends on the ionic radius (see figure 5) [13]. The early α-sialons were found with Li and Mg [14, 15]. Other stabilising cations were tried such as Na [16], Ca and Y. It is shown that most of the lanthanide’s are suitable for incorporation in the lattice. According to figure 2.5 La, Ce, Pr and Eu are exceptions because their ionic radii are too large to fit in the interstitial holes. However, recently it is reported that in combination with another cation some of these large cations can be incorporated in the lattice. If Ca is used as stabilising cation it is possible to incorporate a little Sr as well as La to obtain a Ca/Sr-α-sialon [17] or Ca/La-α-sialon [18]. Other examples of a mixed α-sialon is an Y/Ce-α-sialon.

Figure 2.4. Plot of the α-Si₃N₄ structure along the c-axis showing the hexagonal baseplane [8].
Later (1991) a revised model was reported by Redington et al. [23].

Relations between the cell parameters and the composition of α-sialon

A problem with this model is that the solubility limit. This was compared with 1.4 (Ca) by using m/val) for Li-α-sialon

In this model: (m, n) are introduced. The following equations are used in this model:

\[ a (nm) = 0.7706 + 0.00117 m + 0.00824 rad + 0.00555 x \] (2.9)

\[ c (nm) = 0.5587 + 0.018 m + 0.0097 rad - 0.0003 x \] (2.10)

This model seems to work quite well for the Nd and Yb stabilised α-sialon. However, the model is not universal for the complete solubility range and other stabilising cations. To overcome these problems, in this thesis (chapter 3) attention is paid to the relations between composition and lattice parameters of Ca-α-sialon (Ca2v3Si12,m3Alm3O6nN16-n).

\[ c = 0.5587 + 0.00259 m + 0.00774 rad + 0.00171 n \] (2.11)

However, this model is not satisfactory because with these equations compositions can be calculated that are not electrically neutral. This is due to the assumption that m is independent from x.

Similar to the model Ekström et al. proposed for the calculation of the z-values of β-sialon (eqs. 2.2 and 2.3), Shen et al. [24, 25] introduced a model for Nd and Yb stabilised α-sialon. This model is valid for compositions along the Si3N4-Ln2O3+NAlN line (Ln = Nd, Yb, m = 2n).

For Nd-α-sialon the equations are:

\[ a (nm) = 0.775 + 0.0156 x \] (2.12)

\[ c (nm) = 0.562 + 0.0162 x \] (2.13)

in the interval 0.3 ≤ x ≤ 0.5 (x = m/3). The increase in unit cell dimensions is split in two regions for Yb stabilised α-sialon and can be expressed as:

\[ a (nm) = 0.775 + 0.0139 x \] (2.14)

\[ c (nm) = 0.562 + 0.0153 x \] (2.15)

for the interval 0.3 ≤ x ≤ 0.67 and for the interval 0.67 ≤ x ≤ 1.0 the expressions are:

\[ a (nm) = 0.777 + 0.0109 x \] (2.16)

\[ c (nm) = 0.566 + 0.0076 x \] (2.17)

This model seems to work quite well for the Nd and Yb stabilised α-sialon. However, the model is not universal for the complete solubility range and other stabilising cations. To overcome these problems, in this thesis (chapter 3) attention is paid to the relations between composition and lattice parameters of Ca-α-sialon (Ca2v3Si12,m3Alm3O6nN16-n).

### 2.2 Phase diagrams of α and β-sialon materials

The majority of the research on sialons described in the literature is focused on the investigation of phases existing in the Si-Al-O-N system, the preparation and properties of β-sialon. The behaviour diagram of the Si3N4-AlN-SiO2-Al2O3 system is presented in figure 2.6, which shows the stability area (line) of β-sialon.
The phase relationships in the α-sialon systems are more complicated and can be described with a so-called Jänecke prism (figure 2.7). In the prism the base plane is the behaviour diagram shown in figure 2.6 with indicated in it the β-sialon line.

In figure 2.7 the α-sialon plane is marked. Most of the phase relationships are presented in phase diagrams, which can be represented as cross sections in the corresponding Jänecke prism.

For Ca-α-sialon only limited information is available. Some time ago Jack and co-workers [22] published tentative phase relationships in part of the \( \text{Si}_3\text{N}_4-4/3(\text{Al}_2\text{O}_3\text{N})-\text{Ca}_{15}\text{Al}_3\text{N}_4 \) system at 1700°C (figure 2.9). More recently Hewett et. al. [28] reported a phase diagram in the \( \text{Si}_3\text{N}_4-4/3(\text{Al}_2\text{O}_3\text{N})-\text{Ca}_{15}\text{Al}_3\text{N}_4 \) system (figure 2.10).
Both have the problem that there is uncertainty about the exact position of the boundaries for the $\alpha$ and $\alpha/\beta$-phase fields (no scale in figure). Later Wood et al. [29] gave an extension of the diagram shown in figure 2.10 to high $m$ and $n$-values (figure 2.11). In the former study the compositions had $m$ and $n$-values no greater than 3 and 3.5, respectively, while the latter reported results from compositions with larger $m$ and $n$-values.

In this thesis a most likely definition of the borders of the single-phase Ca-$\alpha$-sialon region is made. Especially the region where $m > 2n$ (i.e. oxygen poor) is focused on, while in literature the focus is on the oxygen rich area. Besides, the influence of the temperature on the single-phase area is studied (chapter 4).

Comparing the phase diagrams of Ca-$\alpha$-sialon with those of other $\alpha$-sialons like yttrium and samarium, it appears that the shape and the sialon phases found are very similar (figure 2.12). Phases with the AIN polytypoids are found in both the Sm and Y phase behaviour diagrams.

### 2.3 The transformation of $\alpha$ to $\beta$-sialon and other phases and vice versa

In the literature the transformation of $\alpha$ to $\beta$ in silicon nitride has been well investigated [31, 32], where the $\beta$-$\text{Si}_3\text{N}_4$ is the high temperature configuration. This transformation implies breaking and forming bonds. Due to the structural rearrangement that is required, the kinetics of the process are slow, and a solvent is often needed to enable the transformation to occur. The reverse transformation has hardly ever been observed. It is possible that the transition temperature is so low that kinetics barriers prevent the $\beta/\alpha$ transformation, especially considering the disruption necessary to go from one structure to the other. Only Clancy [33] mentioned this transformation. In literature indications are found that some of the $\alpha$-sialons are unstable in the temperature range 1200 - 1500°C and transform to $\beta$-sialon. The results differ for different cations and are discussed in the next sections. These phenomena are very important in high temperature applications such as engine turbines. When a transformation occurs during temperature variations, the material's mechanical and chemical properties also change.
2.3.1 Sm-α-sialon

Mandal and co-workers [34,35] observed that Sm-α/β-sialon composite materials, prepared by hot pressing (1775°C), show an α to β transformation after annealing the materials at 1000 - 1500°C. During this transformation the z-value of the β-sialon phase decreases and also a slight decrease in the α-sialon unit cell dimensions occurs as the heat treatment temperature increases. Other associated systematic differences occur with increasing temperature, namely the β-sialon grains become more needle-like, the amount of α-phase decreases and the amount of intergranular phase increases [34]. The transformation rate increases with increasing oxygen content i.e. for samples with a higher n-value. These observations are confirmed by Zhao et al. [36,37] and Falk et al. [38]. They show that in heat treatment experiments at 1450°C crystallisation of N-mellite (Sm₂Si₆Al₅O₁₈N₄O₄) as a stable grain boundary phase is the first process to occur, followed by the α to β transformation. The β-phase has a lower Gibbs energy than the α-composition at 1450°C and therefore the reduction of the Gibbs energy is a driving force for the α-β transformation [37]. It is thought that the β-phase nucleates on the already existing β-crystals. Shen et al. [39] report that samples with m = 0.9 - 1.83 are stable at temperatures > 1650°C, but decompose in two consecutive steps at lower temperature (1450°C). First the α-phase reacts with liquid to form an Al-containing Sm mellite phase plus α-phase with a lower m-value. Subsequently the new α-phase decomposes in mellite and β-sialon. The key point is that the liquid phase plays an active role in the transformation reaction [39]. The mellite phase forms rapidly upon cooling [39]. From the literature it may be concluded that the α to β transformation is reversible for the Sm-α-sialons.

2.3.2 Y and rare earth-α-sialons

As well as for the Sm-α/β-sialons the α-β transformation occurs in Nd, Dy, Y and Yb systems [35,38,40,41,42]. The α-sialon coexists with β-sialon and a liquid phase at 1750°C in Nd-, Dy-, and Yb doped systems but in case of Nd the α-sialon phase is not stable and decomposes at lower temperatures in the presence of liquid [41]. Below 1650°C the Nd-α-sialon phase tends to decompose to form the more stable β-sialon and mellite phase [24] depending on the amount of liquid phase. The Nd-mellite-phase is formed during the sintering of Nd-doped α-sialon and is dissolved at temperatures exceeding 1650°C, but it might be reformed very rapidly during the cooling process [24]. This shows that the cooling rate is very important for composition control. Mandal et al. [34] showed for Yb-α/β-sialons as well as other composites (Y, Dy, Sm) the changes in α to β ratios after heat treatment at different temperatures. However, Shen et al. [25] showed no α to β transformation in pure Yb-α-sialon. Instead of formation of β-phase after heat treatment Yb garnet/β-phase is formed unless the composition is near the border of the single-phase region. For Yb no transformation to β occurs at 1500°C when the α-sialon is produced from α-Si₃N₄ [43]. When β-Si₃N₄ is used as starting material, however, the transformation does take place. This indicates that the presence of β-nuclei promotes the transformation to β-phase. Ukyo et al. [40] finds a decreasing α/β ratio when Y-α/β-sialon (prepared by hot pressing 1850°C) is annealed for longer times (50 hrs) at the same temperature. They conclude that the α-sialon is metastable in the presence of

\[ \text{Y}_{2} \text{Si}_{2} \text{O}_{5} + 3 \text{H}_{2} \text{O} \rightarrow \text{Y}_{2} \text{Si}_{2} \text{O}_{5} \cdot 3 \text{H}_{2} \text{O} \] (2.18)

This reaction can be separated into two steps. First formation of mullite (3Al₂O₃·2SiO₂) due to loss of crystal water and modification of meta-kaolinite (2SiO₂·Al₂O₃·2H₂O) and carbon is described by the overall reaction:

\[ 3(2\text{SiO}_{2} \cdot \text{Al}_{2} \text{O}_{3} \cdot 2\text{H}_{2} \text{O}) + 15\text{C} + 5\text{N}_2 \rightarrow 2\text{Si}_3\text{Al}_5\text{O}_{14}\text{N}_4 + 15\text{CO} + 6\text{H}_2\text{O} \] (2.19)

Possible further reactions involve the formation of SiC as an intermediate product from the SiO₂ and finally β-sialon with a z-value of 3 from mullite and SiC.

\[ \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \] (2.20)

\[ 3\text{SiO}_2 \cdot 2\text{SiO}_2 + 4\text{SiC} + 3\text{C} + 5\text{N}_2 \rightarrow 2\text{Si}_3\text{Al}_5\text{O}_{14}\text{N}_4 + 7\text{CO} \] (2.21)
Recently it has been shown that the waste material fly ash (consisting of a mixture of mainly SiO₂ and Al₂O₃) can be used also as a starting material for the carbothermal preparation of β-sialon [56]. This carbothermal method is relatively inexpensive to prepare sialon powders. Carbothermal reduction and nitridation of oxides to prepare α-sialon is hardly reported. Mitomo et al. [57] described a method of carbothermal reduction and nitridation for the formation of Y-α-sialon and Ca-α-sialon. They used alkoxide-derived CaO-SiO₂-Al₂O₃ or Y₂O₃-SiO₂-Al₂O₃ mixtures fired at 1200-1450°C. In the first system, the formation of α-sialon was accelerated at 1450°C by the presence of a calcium-containing liquid phase. Additional heating at 1550°C for 1 hour in a second step formed single-phase Ca-α-sialon powder. In the yttrium system, a multi-phase powder was prepared at 1300-1450°C. The formation of α-sialon powder with a small amount of SiC was possible by heating at 1450°C for 16 hours and subsequently heating at 1600°C for 1 hour in a second step.

Other methods are the reaction sintering and reaction hot pressing methods to prepare α and β-sialon ceramics from nitride and oxide starting materials [58,59,60]. The method of reaction sintering can also be used to prepare powders, but the nitride starting materials are more expensive than those used in the method of carbothermal reduction and nitridation as mentioned above. Another disadvantage, more specifically for the hot pressing method is the limitation to simple shapes, which makes the method even less economical or simply impossible, because the required shapes cannot be produced in this way. The relatively high processing temperature, dependent on sintering additive, to prepare dense ceramics (high preparation and sintering temperatures during reaction sintering or hot pressing of starting from oxide/nitride materials) is a drawback for these routes. Besides, the required equipment is more expensive than the equipment necessary for sintering carbothermally prepared powders.

For sintering of β-sialon several sintering additives can be used. Effective sintering additives for Si₃N₄ in general can also be used for sintering β-sialon. In the research of Negita [61] a number of sintering additives for sintering Si₃N₄ was investigated. The research was based on the reactivity of metal oxide sintering aids with Si₃N₄, which are characterised by comparing the standard Gibbs energies for oxidation reactions of Si₃N₄ with those of metals and metal nitrides corresponding with the sintering additive. Materials that were successfully added as sintering aids were BeO, ZrO₂, Sc₂O₃, CeO₂, MgO and La₂O₃. Additives that are commonly used are Y₂O₃ and Al₂O₃ or a combination of both [62,63,64]. Actually a sialon is formed (instead of Si₃N₄). The possible formation of a relatively refractory intergranular phase (Y₃Al₅O₁₂) is one of the advantages of the use of these last sintering additives. Other oxide additives form a glassy phase that softens if the temperature is increased, resulting in worse mechanical properties at high temperatures. The formation and behaviour of a boundary phase can be the bottleneck for the mechanical properties. To improve the properties of the material at high temperatures the amount of these boundary phases should preferably be minimised. The use of nitride sintering additives is a possible solution. Ge et al. [65] showed in a review report several effective nitride sintering additives. The nitride additives (TN, AlN, ZrN, VN, NbN,YN, Mg₂N₃, TaN or HfN) significantly reduce the amount of glassy phase and raise its softening temperature. On the other hand it makes sintering more difficult, but dense ceramics can be obtained with gas pressure sintering or hot pressing. Another possibility can be found with the other sialon structure, the α-sialon structure. In theory it is possible to prepare a single-phase material without grain boundary phases by incorporation of the additives in the α-sialon matrix.

In case of the preparation of dense α-sialon ceramics the reaction sintering [27,66,67,68,69,70] and reaction hot pressing [70,71,72,73,74] methods are commonly used. In this thesis these methods were applied for preparation of Ca-α-sialon ceramics and compared with the sintering of carbothermally produced powders (chapter 7).

Nowadays the preparation, characterisation and properties of αβ-sialon materials are widely investigated. These composite materials combine the properties of both α-sialon and β-sialon [70,75,76]. If this can be controlled completely then a ‘tailor made’ ceramic material can be developed.

### 2.5 Properties of sialon materials

In table 2.1 properties of several commonly used ceramics besides the silicon nitride based materials are listed.

| Table 2.1. Some selected properties of some engineering ceramics. |
|----------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                      | ΔTₜe              | α                | λ                | σf              | Hv              | K1c              | E                |
| (K)                  | (K²)              | (W m⁻³ K⁻¹)     | (MPa)            | (GPa)           | (MPa m)         | (GPa) m)         | (GPa)            |
| Al₂O₃                | 200              | 5.4×10⁻⁶         | 30               | 450             | 19.3 (2N)       | 4.5             | 396 (2N)         |
| AlN                  | 250              | 2.5×10⁻⁶         | 200              | 340             | 12 (1N)         | 2.7             | 315 (1N)         |
| Al₂O₃                | 175              | 5.8×10⁻⁶         | 11               | 50-300          | 19 (2N)         | 2.4             | 330              |
| SiC                  | 250              | 4.0-7.4×10⁻⁶     | 45-150           | 400-500         | 25-33           | 4-12            | 410-440          |
| ZrO₂                 | 300              | 9-11×10⁻⁶        | 2.5              | 200-1300        | 12-15×4.5       | 10-12           | 138-191          |
| Si₃N₄                | >900             | 2.9-3.6×10⁻⁶     | 4-155            | 150-2000        | 16-22           | 3.4-8.2         | 300-330          |
| a-Sialon             | 900              | 3-5.5×10⁻⁶       | 7-25             | 350-960         | 14-20           | 2.5-10          | 227-240          |
| a-sialon₅            | 480              | 3.3-6×10⁻⁶       | 7-9              | 250-900         | 16-21           | 3.7-7           | 300              |

ΔTₜₑ = thermal shock resistance; α = thermal expansion coefficient (20°C); λ = thermal conductivity (20°C); σf = flexural strength; Hv = Vickers hardness; K₁c = fracture toughness; E = Young’s modulus.

1. references 74,75,77
2. references 77,78,79,80
3. reference 81
4. references 82 and 83
5. references 84 and 85
6. references 66,86,87,88,89
7. references 51, 86,91,92,93,94,95,96,97
8. references 16,91,97,98,99,100

The values presented in this table are an indication of the properties of these engineering ceramics and can be compared with Si₃N₄. The wide range of some values has a variety of causes. For the measurements and calculations several methods are used. For example the K₁c-values can be measured by indentation (absolute value not very reliable) and the single edged notched beam method (more reliable). The differences in materials (e.g. porosity, density or
preparation method) can cause a variation in the values of the properties as well. For silicon nitride data both hot pressed and reaction sintered materials are considered. The data in table 2.1 for α and β-sialon apply to a group of materials in general. β-Sialons with z-values ranging from 0 - 4 are considered, prepared in different ways (reaction sintering, carbothermal preparation or reaction hot pressing). The α-sialon data are for all compositions irrespective of the metal ion. This includes the most important stabilising cations (Ca, Mg, Y and rare earth elements). The α-sialons are prepared with several different methods (reaction sintering and hot pressing). There are only a few thermal conductivity data available for the sialon materials in the literature. Table 2.1 shows that the sialon materials have similar properties compared to silicon nitride ceramics. Except for the thermal shock resistance especially the α-sialons show a good resemblance. If the values of the properties given for silicon nitride in table 2.1 are compared to the values obtained for β-sialon materials the values proved to be similar also or a little lower. However, preparation of dense α-sialon ceramics is easier to achieve than dense Si₃N₄ materials without sintering additives that influence the properties of the material. Although the mechanical strength of α-sialon is somewhat lower, it has, as well as β-sialon, better oxidation and chemical resistance than silicon nitride.

![Figure 2.13](image)

**Figure 2.13.** Vickers hardness (98N) as a function of z-value for β-sialon, with (△) and without (●) 1% Y₂O₃ addition [10].

Besides, the stable α-phase makes it possible to prepare α/β composite materials. The hardness of sialon is in the same range as silicon nitride but it is much lower than that of SiC. Ekström [10] showed that the hardness and the fracture toughness of sialon materials prepared by reaction hot pressing decrease with increasing aluminium (z-value) content (figures 2.13 and 2.14). The fracture toughness of single-phase β-sialon decreases just a little. Addition of yttria causes an amorphous intergranular phase, changing the grain size and shape and gives a clear rise in the fracture toughness and a moderate decrease in hardness. The minimum at a z-value of ± 4 is at the border between single-phase and multi-phase material. Above this z-

![Figure 2.14](image)

**Figure 2.14.** Indentation fracture toughness (Kic) measured as a function of z-value for the β-sialon phase, with (△) and without (●) 1% Y₂O₃ addition [10].

Although the properties of β-sialon ceramics obtained with the carbothermal route (HV2 = 12.5 GPa, Kic = 5.4 MPam¹/² strength = 450 MPa [53]) are not as good as compared to the routes of reaction sintering and reaction hot pressing, it is still a very good material. The main advantage of the carbothermal preparation route is that it is a relatively inexpensive way of preparing β-sialon materials.

![Figure 2.15](image)

**Figure 2.15.** Vickers hardness (HV10, kg/mm²) of α/β-sialon ceramics as function of the α/(α+β) ratio. Prepared with 6 wt% Y₂O₃ as sintering additive by pressureless sintering at 1775°C [100].
Chapter 2

Fracture toughness

In Figures 2.15 and 2.16 the hardness and the fracture toughness are presented for reaction sintered α/β-sialon composites reported by Ekström [100]. These figures show that a tailor made material can be made by controlling the α/β ratio of the materials and thus a compromise can be made considering the hardness and toughness of the material.

Only a few data are known for Ca-α-sialon or Ca-α/β-sialon composites and therefore the dependence of the properties on the α/β-ratio has been investigated in this Ph.D. study (chapter 8).

2.6 Corrosion resistance of sialon materials

Silicon nitride and sialon materials are fairly corrosion resistant. For this reason silicon nitride and sialons have found an important application as cutting tools for cast iron and heat resistant alloys. The corrosion resistance of sialons in molten metals, particularly aluminium, is also applied in wear parts (for example extrusion dies) and for metal rolling and in parts for handling molten metals. Dower et al. [102] reported that sialon material with the following composition: 4 wt% Al₂O₃, 7.4 wt% Y₂O₃ and 88.6 wt% Si₃N₄ is well resistant against a molten aluminium lithium alloy. Corrosion of these ceramics by metal is a typical situation that arises in many industrial applications. Due to the corrosion resistance the pollution of the molten metal with the refractory phase is avoided or very much reduced. The resistance of sialon found for liquid aluminium attack is similar to what other workers [103,104] have...
found for silicon nitride type (sialon) ceramics. However, Dower et al. [102] did not find formation of an AlN layer as the other workers [103,104] did. The explanation can be the lower temperatures used in the work of Dower et al. or the use of an aluminium lithium alloy instead of pure aluminium [103] or an aluminium magnesium alloy [104].

Oxidation of pure silicon nitride as well as sialon materials in principle may occur by two mechanisms, depending on the oxygen partial pressure. The two mechanisms are called the ‘active’ and ‘passive’ oxidation. The former occurs at low oxygen concentrations leading to a ‘protective’ layer [105]. Various investigations [105,106,107,108,109,110,111] have shown that the reaction is diffusion-controlled and can be described by the parabolic function:

$$\Delta G/A = K_0 + B$$

(2.22)

where \((\Delta G/A)\) is the weight gain per unit area, \(t\) is the time of oxidation, \(K_p\) is the parabolic rate constant and \(B\) is an additive constant (ideally \(B = 0\)). Temperature, atmosphere, the type and amount of additives and impurities mainly influence the \(K_p\). Persson et al. [75] used a somewhat different law because the original (eq. 2.22) did not work for the system they used. This law takes into account a progressive crystallisation of the amorphous phases in the oxide layers. Oxygen diffuses less easily through the crystalline phase than through the amorphous layer and therefore the effective surface area decreases [75]. As a result Persson et al. [75] derived the following equation:

$$\Delta G/A = a \arctan(b/t) + c/t + d$$

(2.23)

where \(a\), \(b\), \(c\) and \(d\) are constants and \(K_p = (a^2b + c)^2\). The rate constant \(K_p\) is different from the usual rate constant \(K_p\) as defined in eq. (2.22). This new law was originally developed for the oxidation of \(Si_3N_4\) but it also appeared to be valid for \(\beta\)-sialon and \(\alpha\beta\)-sialon composites [110,111].

This arctan equation also applies for the results of oxidation of \(Y\)-\(\alpha\)/\(\beta\)-sialon composites found by van den Heuvel et al. [110]. From their measurements it was concluded that in all types of sialons measured, the oxidation rate rapidly increases at temperatures \(\geq 1400°C\) because a non-adherent oxide scale is formed. The oxidation resistance of the \(\alpha\)/\(\beta\) composite materials was found to be better than of single-phase \(Y\)-\(\alpha\)-sialon, probably due to the smaller amount of grain boundary phase in the composites [112].

The effect of the amount and type of sintering additive on the oxidation behaviour is illustrated in figure 2.19 by a comparison of the oxidation curves observed for three sialons with different overall composition. These compositions are prepared with pressureless sintering at 1825°C. From this figure the conclusion can be drawn that independent of the sintering additives used, the sialons with the highest \(\alpha\)-content are the most oxidation resistant and the \(\beta\)-sialons oxidise the easiest [111]. Furthermore the oxidation behaviour of the sialons prepared with yttria, as sintering aid is substantially better than those prepared with neodymia. The study of Cao [112] showed that the oxidation resistance is strongly influenced by the amount of amorphous grain boundary phase. However, in this study the highest oxidation resistance was obtained for mixed \(\alpha\)/\(\beta\)-sialon materials, which is due to the small amount of amorphous phase in these materials [112].

2.7 Potential and future prospects of sialon ceramics

The main advantage of sialon ceramics is that the densification of these materials is easier than for silicon nitride while the mechanical properties are similar as is shown before. From the subjects and applications reviewed above it can be concluded that investigating the \(\alpha\)/\(\beta\) composite sialons is worthwhile. These materials proved to have very good properties. They have high corrosion resistance, thermal shock resistance, and high hardness and fracture toughness. They can be very important in energy saving and substitution materials for super alloys in high temperature applications. However, for Ca-\(\alpha\)/\(\beta\)-sialon materials only few data are available. The potential advantages are the less expensive starting materials and lower processing costs (i.e. lower temperature to densify). These costs can even be more reduced by using the carbothermal preparation of the ceramic from oxide starting materials (chapter 6 and 7). Therefore it is of interest to investigate these materials in more detail.

References


Chapter 2

90. Ferguson, P., Rae, A.W.J.M., Sialons for Engineering and Refractory Applications, p1296-1304.

Literature review

Patience

Nothing grand starts suddenly. That won’t even happen to a grape or a fig. If you tell me that you want to have a fig now, I only can say that you’ll have to wait; first the tree has to blossom, then the fruit has to form and ripen. When even a fruit of a fig tree is not suddenly, or within the hour, edible, how would you reap the fruits of someone’s mind in such a short time and so effortlessly? Even if I myself told you that this is possible, don’t believe me.

Epictetus

Chapter 3
Relation between lattice parameters of Ca-α-sialon and its chemical composition

Abstract
A new model is proposed relating the lattice parameters of Ca-α-sialon (Ca_{m+2}Si_{12-(m+n)}Al_{(m+n)}O_{n}N_{16-n}) to its chemical composition, i.e. values of m and n. Its usefulness is shown by discussing several examples.

3.1 Introduction
Sialon materials are intensively studied because of their attractive mechanical properties [1]. Of current interest are especially the α/β-sialon composites due to their improved mechanical properties [2]. Fine tuning of the properties is possible by optimisation of the microstructure and chemical composition of the α/β-composite, i.e. the α/β ratio and the composition of the β-sialon (z-value in Si_{6-z}Al_{z}O_{2}N_{z}) and α-sialon (m and n-value in M_{m-val}Si_{12-(m+n)}Al_{(m+n)}O_{n}N_{16-n}, M = Li, Ca, Y, Rare earth, val = valency). Knowledge about the formation reaction and the two-phase α/β region in the phase diagram is required for this purpose. For the Ln-α-sialon (Ln = Y, rare earth) ample information is available (see e.g. [3,4]), in contrast to the Ca-α-sialon. Therefore we have investigated the phase formation of compounds within the Ca_{m+2}Si_{12-(m+n)}Al_{(m+n)}O_{n}N_{16-n} system, results of which have already been published elsewhere, showing the approximate boundaries of the single-phase Ca-α-sialon region [5, chapter 4]. The chemical composition of the Ca-α-sialon (i.e. m and n) during the formation yields information about the reaction mechanism and for the two-phase α/β region about the position of the tie lines. In order to determine the chemical composition from the lattice parameters, the relation between both should be known. The oldest model suggests that the lattice parameters of M-α-sialons are generally given by [6]:

\[ a (\text{Å}) = a (\text{Si}_3\text{N}_4) + 0.009 n + 0.045 m \]  

(3.1)
Chapter 3

\[ c (\text{Å}) = c (\text{Si}_2\text{N}_4) + 0.008 \, n + 0.040 \, m \]  

(3.2)

However, these equations are interdependent, resulting in only the value of \( 5m + n \).

So additionally, an assumption has to be made (e.g. \((m/\text{val})/(m+n) = [M]/[Al] \) of the starting mixture) to enable calculation of \( n \) and \( m \) separately from the lattice parameters \( a \) and \( c \). However, such an assumption is doubtful because considerable deviations may occur due to the formation of amorphous phase or non-equilibrium conditions. A subsequent refined model [7] takes into account the ionic radius of the M ion, and treats the index \( x \) of \( M \) (= \( m/\text{val} \)) in \( M^x\text{Sh}_{2-0.5}^z\text{Al}_{(m+n)}\text{O}_n\text{N}_{16-n} \) as an additional independent parameter. Therefore, besides two equations relating the lattice parameters \( a \) and \( c \) to the values of \( m, x \) and the ionic radius, a third equation was formulated giving the relationship between the lattice parameter \( c \) and the values of \( m, n \) and the ionic radius. However, compositions result that are not charge balanced (e.g. \( Yo_{48.3}Si_{94.9}4_{9.6}Ah_{55.10}OssoNtsA_{2} \)), and the illustrating example given in the paper could not be reproduced.

It is the objective of this chapter to present a new model, which describes the lattice parameters of Ca-\( \alpha \)-sialon very well as a function of the chemical composition.

3.2 New model and determination of the model parameters

The data used are restricted to samples that are well characterised. Data concerning the lattice parameters \( a \) and \( c \) of Ca-\( \alpha \)-sialon were gathered from the literature data and are given in table 3.1.

Table 3.1. Lattice parameters of Ca-\( \alpha \)-sialon with general composition \( Ca_{n_{12}}Si_{12-0.5}Al_{(m+n)}O_{n_{16-n}}N_{16-n} \) as collected from the literature.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( a )</th>
<th>( c )</th>
<th>( c/a )</th>
<th>( m )</th>
<th>( n )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Ca_{5.5}Si_{7.5}Al_{1.5}O_{16.5} )</td>
<td>7.82</td>
<td>5.68</td>
<td>0.726</td>
<td>1.0</td>
<td>0.5</td>
<td>6</td>
</tr>
<tr>
<td>( Ca_{6.5}Si_{6.5}Al_{2.5}O_{16.5} )</td>
<td>7.86</td>
<td>5.71</td>
<td>0.726</td>
<td>1.6</td>
<td>1.2</td>
<td>6</td>
</tr>
<tr>
<td>( Ca_{7.5}Si_{5.5}Al_{3.5}O_{16.5} )</td>
<td>7.85</td>
<td>5.708</td>
<td>0.727</td>
<td>1.4</td>
<td>1.2</td>
<td>8</td>
</tr>
<tr>
<td>( Ca_{8.5}Si_{4.5}Al_{4.5}O_{16.5} )</td>
<td>7.917</td>
<td>5.756</td>
<td>0.727</td>
<td>2.4</td>
<td>1.6</td>
<td>8</td>
</tr>
<tr>
<td>( Ca_{9.5}Si_{3.5}Al_{5.5}O_{16.5} )</td>
<td>7.838</td>
<td>5.703</td>
<td>0.728</td>
<td>1.3</td>
<td>0.7</td>
<td>9</td>
</tr>
<tr>
<td>( Ca_{10.5}Si_{2.5}Al_{6.5}O_{16.5} )</td>
<td>7.852</td>
<td>5.709</td>
<td>0.727</td>
<td>1.6</td>
<td>1.2</td>
<td>10</td>
</tr>
<tr>
<td>( Ca_{11.5}Si_{1.5}Al_{7.5}O_{16.5} )</td>
<td>7.838</td>
<td>5.703</td>
<td>0.728</td>
<td>1.3</td>
<td>0.7</td>
<td>11</td>
</tr>
</tbody>
</table>

The lattice parameters \( a \) and \( c \) are fitted with a linear regression formula containing two variables for both \( a \) (p and q) and \( c \) (r and s):

\[ a = a_0 + p \cdot n + q \cdot m \]  

(3.3)

\[ c = c_0 + r \cdot n + s \cdot m \]  

(3.4)

Relation between lattice parameters of Ca-\( \alpha \)-sialon and its chemical composition

A least squares fit yields:

\[ a_0 = 7.749 \, \text{Å}, \ p = 0.0023 \, \text{Å}, \ q = 0.0673 \, \text{Å} \]  

(3.5)

\[ c_0 = 5.632 \, \text{Å}, \ r = -0.0054 \, \text{Å}, \ s = 0.0550 \, \text{Å} \]  

(3.6)

3.3 Evaluation of the model parameters

Using the determined model parameters, the lattice parameters are calculated for a given composition and compared with the measured ones (tables 3.2 and 3.3).

Table 3.2. Comparison of the measured and calculated lattice parameter \( a \) (Å) of Ca-\( \alpha \)-sialon (conventional, 'old' model [6] versus new model).

<table>
<thead>
<tr>
<th>Ref.</th>
<th>( m )</th>
<th>( n )</th>
<th>Measured ( a ) (Å)</th>
<th>Calculated ( a ) (Å)</th>
<th>'Old' model difference</th>
<th>New model difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.0</td>
<td>0.5</td>
<td>7.82</td>
<td>7.810</td>
<td>0.010</td>
<td>0.002</td>
</tr>
<tr>
<td>6</td>
<td>1.6</td>
<td>1.2</td>
<td>7.86</td>
<td>7.843</td>
<td>0.017</td>
<td>0.000</td>
</tr>
<tr>
<td>8</td>
<td>1.4</td>
<td>1.2</td>
<td>7.851</td>
<td>7.834</td>
<td>0.017</td>
<td>0.005</td>
</tr>
<tr>
<td>8</td>
<td>2.4</td>
<td>1.6</td>
<td>7.917</td>
<td>7.882</td>
<td>0.035</td>
<td>0.002</td>
</tr>
<tr>
<td>9</td>
<td>1.3</td>
<td>0.7</td>
<td>7.838</td>
<td>7.825</td>
<td>0.013</td>
<td>7.839 -0.001</td>
</tr>
<tr>
<td>10</td>
<td>1.6</td>
<td>1.2</td>
<td>7.852</td>
<td>7.843</td>
<td>0.009</td>
<td>7.860 -0.008</td>
</tr>
<tr>
<td>11</td>
<td>1.3</td>
<td>0.7</td>
<td>7.838</td>
<td>7.825</td>
<td>0.013</td>
<td>7.839 -0.001</td>
</tr>
</tbody>
</table>

Figure 3.1. Predicted lattice parameter \( a \) of Ca-\( \alpha \)-sialon as a function of the measured lattice parameter \( a \). Comparison of conventional (old) model (A, equations 1 and 2 [6]) versus new model (O, equations 3 and 4). The drawn line represents the linear relationship \( a_{\text{predicted}} = a_{\text{measured}} \).
It can be observed that application of the conventional model [6] leads to very large deviations (Figs. 3.1 and 3.2). The agreement becomes even worse when using the lattice parameters more recently suggested to be used in the equations (3.1) and (3.2) of the conventional model \(a = 7.75 \, \text{Å} \) and \(c = 5.62 \, \text{Å} \) [7] instead of the original proposed ones \(a = 7.76 \, \text{Å} \) and \(c = 5.62 \, \text{Å} \) [6]. However, on the contrary for the new model the largest difference observed is only 0.008 Å for \(a\) (with respect to 7.8 Å is about 0.1% deviation) and 0.005 Å for \(c\) (with respect to 5.7 Å is also about 0.1% deviation).

Table 3.3. Comparison of the measured and calculated lattice parameter \(c\) (Å) of Ca-α-sialon (conventional, 'old' model [6] versus new model).

<table>
<thead>
<tr>
<th>Ref.</th>
<th>(m)</th>
<th>(n)</th>
<th>measured</th>
<th>calculated 'old' model</th>
<th>calculated difference</th>
<th>calculated new model</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.0</td>
<td>0.5</td>
<td>5.68</td>
<td>5.664</td>
<td>0.016</td>
<td>5.684</td>
<td>-0.004</td>
</tr>
<tr>
<td>6</td>
<td>1.6</td>
<td>1.2</td>
<td>5.71</td>
<td>5.694</td>
<td>0.016</td>
<td>5.714</td>
<td>-0.004</td>
</tr>
<tr>
<td>8</td>
<td>1.4</td>
<td>1.2</td>
<td>5.708</td>
<td>5.686</td>
<td>0.022</td>
<td>5.703</td>
<td>0.005</td>
</tr>
<tr>
<td>8</td>
<td>2.4</td>
<td>1.6</td>
<td>5.756</td>
<td>5.729</td>
<td>0.027</td>
<td>5.755</td>
<td>0.001</td>
</tr>
<tr>
<td>9</td>
<td>1.3</td>
<td>0.7</td>
<td>5.703</td>
<td>5.678</td>
<td>0.025</td>
<td>5.700</td>
<td>0.003</td>
</tr>
<tr>
<td>10</td>
<td>1.6</td>
<td>1.2</td>
<td>5.709</td>
<td>5.694</td>
<td>0.015</td>
<td>5.714</td>
<td>-0.005</td>
</tr>
<tr>
<td>11</td>
<td>1.3</td>
<td>0.7</td>
<td>5.703</td>
<td>5.678</td>
<td>0.025</td>
<td>5.700</td>
<td>0.003</td>
</tr>
</tbody>
</table>

It is very good (Figs. 3.1 and 3.2). As expected, for the new model the slope and intercept values belonging to this plot are close to 1 and 0, respectively, in contrast to the conventional model. Moreover, the correlation coefficient is higher for the new model as compared to the conventional model. Using the determined model parameters, also the composition is calculated for the measured lattice parameters and compared with the given one (Table 3.4).

The agreement between the measured and calculated \(m\) appears to be very good (± 0.1). The amount of Ca incorporated in the α-sialon matrix can thus be estimated quite accurately from the lattice parameters.

The \(m\)-values in Table 3.4 are calculated with the formula that is derived from equations 3.3-3.6:

\[
m = \frac{(0.0054/0.0023 \times (a - 7.749) + (c - 5.632))/0.213}{(0.0054/0.0023 \times (a - 7.749) + (c - 5.632))/0.213}
\]

On the contrary, the calculation of \(n\) appears to be quite unreliable: the difference between the measured and calculated \(n\) appears to be as high as 0.8. An inaccuracy of 0.001 Å in the lattice parameters already results in an \(n\)-value with an uncertainty of 0.3. For inaccurate lattice parameters (± 0.01 Å) or small values of \(n\) (< 1), the deviation can be even larger. This is a result of only a very slight dependence of the lattice parameters on \(n\), and therefore it is not possible to determine a reliable oxygen concentration in Ca-α-sialon from the lattice parameters.

### 3.4 Interpretation of the model parameters

The α-sialon system \(Ca_{12}(Si_{12}O_{16}N_{4})\) is considered as a solid solution of the hypothetical compounds \(Al_{12}O_{12}N_{4}\) (= \(Al_{12}O_{3}N\)) and \(Ca_{6}Al_{2}N_{16}\) (= \(Ca_{3}Al_{2}N_{16}\)) with the α-Si$_3$N$_4$ structure in Si$_{12}$N$_{16}$ (= Si$_3$N$_4$):

\[
Ca_{6}Al_{2}Si_{12}O_{16}N_{4} = \frac{[12-(m+n)]/12 \cdot Si_{12}N_{16} + n/12 \cdot Al_{12}O_{12}N_{4} + m/12 \cdot Ca_{6}Al_{2}N_{16}}{[12-(m+n)]/3 \cdot Si_{3}N_{4} + n/3 \cdot Al_{3}O_{3}N + m/3 \cdot Ca_{3}Al_{2}N_{4}}
\]

Or, abbreviated:
Chapter 3

3.5 Application of the new model

The developed model is applied for the determination of the composition of Ca-\(\alpha\)-sialon materials prepared in different ways, especially during the formation of it or in the two-phase \(\alpha/\beta\) sialon region.

The lattice parameters were calculated from the measured interplanar spacings (d-values) published for Ca-\(\alpha\)-sialon prepared by reaction hot pressing a mixture of Si\(_3\)N\(_4\), AlN and CaC\(_2\) at 1700 \(^\circ\)C [16], resulting in \(a = 7.851 \, \text{Å}\) and \(c = 5.712 \, \text{Å}\). Using these values as input parameters, the new model yields \(m = 1.5\) and \(n = 0.5\), as compared to the nominal starting composition \(m = 2\) and \(n = 1\). It implies that not all the Ca\(^{2+}\) ions are incorporated into the \(\alpha\)-sialon matrix, in agreement with the observation with TEM of amorphpous phase between the grains [16]. For another case the lattice parameters decrease from \(a = 7.883 \, \text{Å}\) and \(c = 5.731 \, \text{Å}\) at 1400 \(^\circ\)C to \(a = 7.830 \, \text{Å}\) and \(c = 5.694 \, \text{Å}\) at 1700 \(^\circ\)C during the formation of Ca-sialon by reaction sintering a mixture of Si\(_3\)N\(_4\), AlN and CaC\(_2\) [17]. According to the presented model the composition changes from a Ca-rich (\(m = 1.9\)) to a Ca-poor (\(m = 1.2\)) \(\alpha\)-sialon, which is in agreement with the decrease in the amount of Si\(_3\)N\(_4\) starting material observed during progress of the reaction [17]. The Ca concentration in the final product determined from the lattice parameters \((m = 1.2)\) again shows that not all the Ca ions weighed-out in the starting mixture \((m = 1.6)\) are incorporated in the \(\alpha\)-sialon matrix. For Ca-\(\alpha\)-sialon prepared by carbothermal reduction and nitridation of hydrolysed Ca, Si and Al oxides, the lattice parameters \(a = 7.834 \, \text{Å}\) and \(c = 5.703 \, \text{Å}\) were published [18]. The new model yields \(m = 1.3\) for this compound, as compared to \(m = 1.6\) expected from the weighed-out starting materials. As observed for the above-mentioned examples, less Ca\(^{2+}\) is incorporated than available in the starting mixture, and the remaining amount is in a non-crystalline phase. Another paper describing the carbothermal preparation of Ca-\(\alpha\)-sialon (from SiO\(_2\), Al\(_2\)O\(_3\) and CaSiO\(_3\)) gives \(a = 7.84 \, \text{Å}\) and \(c = 5.68 \, \text{Å}\) for the final product [19]. The composition calculated from these parameters using the new model is \(m = 1.2 \pm 0.2\). As the aimed value of \(m = 1.6\) [19] for this carbothermal route it is also found that not all the Ca\(^{2+}\) is incorporated. For the intermediate Ca-\(\alpha\)-sialon material formed at the beginning of the carbothermal reaction, the lattice parameters were found to be \(a = 7.87 \, \text{Å}\) and \(c = 5.72 \, \text{Å}\) [19]. Using the new model, \(m = 1.8 \pm 0.2\) results. This means that during the carbothermal preparation a transformation takes place from a Ca-rich \(\alpha\)-sialon to a Ca-poor \(\alpha\)-sialon, which is similar to what was observed for reaction sintering (see above).

Hot pressing materials in the two-phase Ca-\(\alpha/\beta\)-sialon region with different overall CaO/Si\(_3\)N\(_4\)/AlN/Al\(_2\)O\(_3\) starting compositions at 1600 \(^\circ\)C leads to \(\alpha/\beta\)-sialon composites, whose lattice parameters [20] indicate that the \(m\)-value according to the new model is about 0.5 in all cases. A constant value is expected for the two-phase \(\alpha/\beta\) sialon region, and resembles the minimum Ca concentration to be incorporated in a single-phase Ca-\(\alpha\)-sialon. Its value is in agreement with the minimum Ca\(^{2+}\) amount reported by Huang et al. for Ca-sialons prepared from compositions on the line Si\(_3\)N\(_4\)-CaO-3AlN at 1700\(^\circ\)C (\(m = 0.6\) [8]). This study also states that the maximum Ca-concentration in single-phase Ca-\(\alpha\)-sialon with a composition on this line corresponds with \(m = 2.8\) [8]. Powder synthesis of compositions on the line Si\(_3\)N\(_4\)-0.5Ca\(_4\)O\(_3\)-3AlN at 1700 \(^\circ\)C resulted in Ca-\(\alpha\)-sialon materials [5] with \(m_{\text{min}} = 1.1\) (minimum Ca-concentration) and \(m_{\text{max}} = 2.4\) (maximum Ca-concentration). As compared to
the corresponding $m$-values reported for the line Si$_3$N$_4$-CaO.3AlN, $m_{\text{min}} = 0.6$ and $m_{\text{max}} = 2.8$ [8]), these results suggest that during slow cooling down some composition shift occurs for higher amounts of oxygen incorporated in Ca-α-sialon. In another paper reaction sintering of mixed CaO/Si$_3$N$_4$/AlN/Al$_2$O$_3$ powder compacts in the two-phase $\alpha/\beta$-sialon region, yields $\beta$-sialon in combination with Ca-α-sialon whose lattice parameters are high at 1400 °C ($a = 7.852$ Å and $c = 5.693$ Å) and decrease for 1600 °C or higher temperatures to $a = 7.82$ Å and $c = 5.68$ Å [21]. According to the new model, the composition of the Ca-α-sialon material corresponds with $m = 1.4$ at 1400 °C (i.e. Ca-rich) and $m = 0.9$ at 1600 °C or higher temperatures (i.e. Ca-poor). In view of the above mentioned decreasing lattice parameters for reaction sintering Ca-α-sialon in the single-phase region at higher temperatures [17], it seems plausible that a similar reaction path is also valid for the two-phase $\alpha/\beta$ region. However, a temperature dependence of the width of the two-phase $\alpha/\beta$ region with higher $m_{\text{opt}}$-values for lower temperatures cannot be excluded. It has to be remarked that there is support into this direction from another study. Preparation of two-phase $\alpha/\beta$ mixtures by carbothermal reduction and nitridation of the starting oxides at higher amounts of oxygen incorporated in Ca-a-sialon. In another paper reaction sintering of Ca-a-sialon in the single-phase region at higher temperatures [17], it seems plausible that a similar reaction path is also valid for the two-phase $\alpha/\beta$ region. However, a temperature dependence of the width of the two-phase $\alpha/\beta$ region with higher $m_{\text{opt}}$-values for lower temperatures cannot be excluded.

An improved model has been presented to describe the lattice parameters of Ca-α-sialon as a function of its chemical composition. Evaluation of several data from the literature has shown its validity and usefulness.

### References

10. JCPDS Nr. 33-261.
11. JCPDS Nr. 42-252.

---

**Figure 3.3.** Cell dimensions versus actual Ca-α-sialon composition (x-value): a = a-axis, b = c-axis, o--- after Hampshire, - - - - our model
Chapter 4

Phase relations in the Ca-α/β-sialon system

Abstract

In this study the phase relations in the system Si$_{12}$N$_6$-Al$_2$O$_3$N$_4$-Ca$_6$Al$_{12}$N$_{16}$ are investigated, especially in the α/β-sialon region. In this two-phase region the position of some tie lines was established. In reaction sintering and reaction hot pressing experiments at 1700 °C the minimum $m$-value of the single-phase Ca-α-region (Ca$_{m+2}$Si$_{12}$O$_{6m}$N$_{16}$) was found to be $m = 0.9$ and the maximum was $m = 2.8$ for $n=0$. On the line $m = 2n$ where [Ca] = [O] the values were $1.0 \leq m \leq 2.4$. The single-phase area for Ca-α-sialon is larger than for other α-sialon systems. In the multiphase regions AlN polytypoids (12H, 21R), β-sialon and sometimes traces of α-Si$_3$N$_4$ starting material (indicating non-equilibrium) were found. A new preparation method involving in-situ nitridation of Ca-metal was used to prepare Ca-α-sialon on the line Si$_{12}$N$_6$-Ca$_6$Al$_{12}$N$_{16}$ ($n = 0$). Heat treatment shows no significant changes in the composition of the Ca-α/β-sialon. It seems that the Ca-α-sialon is more stable than other α-sialon systems during heat treatments at higher temperatures.

4.1 Introduction

Sialon ceramics are interesting materials for certain applications because of their good mechanical and chemical properties such as fracture toughness, hardness, thermal shock resistance and wear resistance [1,2]. Especially in high temperature regions the applications are promising as substitute for the super alloys [3]. There are two classes of sialons: β-sialon (Si$_{6-z}$AlO$_{3z}$N$_{8z}$, where $0 < z < 4$ [4]) and α-sialon (Me$_{m+2}$Si$_{12}$O$_{6m}$N$_{16m}$, where Me = metal like Y, lanthanide’s, Li, Ca, Mg, val = valency of the metal, $m, n$ are substitution numbers for Al and O [5]). Concerning α-sialon material the Y-compound has been studied most intensively [6]. Nowadays also the Sm-α-sialons are in the picture because of the
relatively easy densification [7,8,9,10]. However, the lanthanide's and yttrium are very expensive compared to for example calcium. That is one of the reasons why this study is focused on Ca-α-sialon. Recently, a number of papers have been published on this type of α-sialon [1,11,12,13,14,15]. In the present investigation more specific the Ca-α/β-sialon composite phase relations have been studied. Huang et al. [11] was one of the first who published results on this topic, but it was restricted to the line $m = 2n$. Hewett et al. [13] presented a behavioural diagram in the $\text{Si}_3\text{N}_4 - 4/3(\text{Al}_2\text{O}_3\text{N}) - \text{Ca}_1\text{5Al}_3\text{N}_4$ system at 1800°C. Phases in the part of the diagram where $m < 2n$ (oxygen rich) were reported but the part where $m > 2n$ (oxygen poor region) was not studied in detail.

Just recently Wood et al. [16] reported a more extended phase behavioural diagram where the higher $m$ and $n$-values are studied in more detail as well as the microstructure belonging to these compositions (figure 4.1).

For high temperature applications the $\alpha/\beta$ region is the most interesting one because the composite material combines the good properties of both the $\alpha$ and $\beta$ phase. $\alpha$-Sialon has high hardness, high wear resistance and good chemical resistance. The $\beta$-sialon has a lower hardness than $\alpha$-sialon but has higher fracture toughness. One of the additional advantages is

Phase relations in the Ca-α/β-sialon system the possibility to incorporate the sintering additives in the $\alpha$-matrix and so reducing the grain boundary phases that are detrimental for high temperature applications. In these high temperature applications it is important that the Ca-α/β-sialon composite maintains its phase composition during utilisation. In this study especially the $\alpha/\beta$ region is focused on and the influence of the temperature on it, whereas as a spin off information was obtained concerning the other regions.

4.2 EXPERIMENTAL METHODS

4.2.1 Starting materials

Ca-α-sialon materials can be prepared in various ways. For the determination of the phase stability area reaction hot pressing or reaction sintering are widely used. In this study both routes are used. These are convenient and quite fast ways to prepare the samples without too much difficulty. The starting materials for the reaction sintering experiments were $\text{Si}_3\text{N}_4$ (Starck, LC-12N, $\alpha/(\alpha+\beta) > 95\%$, oxygen content = 2 wt%), AlN (Starck, Grade 'C', oxygen content = 2 wt%), $\text{CaCO}_3$ (p.a., Merck) and $\text{Al}_2\text{O}_3$ (Sumitomo, AK-P-30) when $m \leq 2n$ ('oxygen-rich'). To prepare a composition where $m > 2n$ ('oxygen-poor') the Ca-starting material was Ca-metal granules (Cerac Inc.). With Thermogravimetric Analysis (TGA) and X-ray diffraction we showed that it is possible to use Ca-metal as one of the starting materials for the preparation of Ca-α-sialon. The starting compositions in reaction hot pressing experiments were corrected for oxygen present in the starting nitride materials. Depending on the desired starting composition different $\text{Si}_3\text{N}_4$ powders with various oxygen contents were used: Starck LC-12N ($\alpha/\alpha+\beta > 95\%$, oxygen content = 2 wt%), Silizot HQ (SKW Trostberg AG, $\alpha > 80\%$, oxygen content = 0.3 wt%) or $\text{Si}_3\text{N}_4$ S-1177 (Cerac Inc., ± 10% $\alpha$, oxygen content = 0.7 wt%). The rest of the starting materials were the same as for the reaction sintering experiments.

4.2.2 Reaction sintering

The reaction sintering method was used to get an overall impression of the single-phase Ca-α-sialon area and the Ca-α/β-sialon region. The starting compositions are presented in figure 4.2. The starting materials were mixed in two different ways, dry and wet. The compositions in the oxygen poor region are dry mixed with a mortar and pestle (porcelain), because Ca-metal is used. This mixing was performed in a glove box in a nitrogen atmosphere. These compositions were fired as powder. The compositions in the oxygen-rich part were wet mixed. To obtain a homogeneous mixture the powders were dispersed in isopropanol. The suspensions were 'milled' with silicon nitride milling balls in a polyethylene bottle on a roller bench for approximately 48h. Subsequently the isopropanol was removed by rotation evaporation.
Chapter 4

4.2.3 Reaction hot pressing

For the compositions expected to be situated in the α/β-sialon region (m=0.5, 0.75, n=0.25-1.5), based on the reaction sintering results, reaction hot pressing was used. As an additional advantage the tablets could also be used for mechanical testing. The mixtures were corrected for oxygen in the starting materials. The powders were mixed by mortar and pestle (agate, 15 min) to avoid extra contamination of oxygen by wet mixing. Then the powders were pressed uniaxially (Ø 33 mm, 10 MPa) and cold isostatically (250 MPa) into tablets, followed by heating in nitrogen at 900°C to decompose the CaCO₃. Subsequently the tablets were reaction hot pressed for one or three hours at 1700°C. The hot press apparatus used was an HP20 of Thermal Technology Ind. equipped with an Astro furnace model 100-4560-FP with graphite heating elements. The temperature was measured with a BGT-2 (graphite vs. B₄C) thermocouple. A graphite die (Ø 33 mm) and plunger were used. The heating rate was 10°C/min and no pressure was used before 1700°C was reached. At top temperature a pressure of 30 MPa was applied to densify the tablets. Cooling down was performed by switching off the furnace. The rate was 20-30°C/min from 1700°C to about 1000°C and slower to lower temperatures. Afterwards selected compositions were heat treated successively for 4 h at 1665°C, 1465°C and 1665°C in a nitrogen atmosphere. In these heat treatments the heating and cooling rate was 3°C/min.

4.2.4 Characterisation

To determine the phase composition of the obtained materials powder X-ray diffraction was applied (Rigaku Geigerflex and Philips PW1120, Cu-Kα radiation) at room temperature. The scanning angle ranged from 10-97° 20 and the scan speed was 0.012°/min. Cell parameters were calculated from the diffraction patterns. For calculating the z-value of β-sialon from its lattice parameters equations 4.1 and 4.2 were used [17]:

\[
a(nm) = 0.7599 + 0.00276 z \quad (4.1) \\
c(nm) = 0.2904 + 0.00244 z \quad (4.2)
\]

For the calculation of the m and n values of the Ca-α-sialon equations 4.3 and 4.4 are used. These are also based on an evaluation of literature data (see chapter 3, [18]).

\[
a(A) = 7.749 + 0.0023 n + 0.0637 m \quad (4.3) \\
c(A) = 5.632 - 0.0054 n + 0.0550 m \quad (4.4)
\]

From these equations the m-values of the Ca-α-sialon can be calculated more reliably than the n-values [18].

The α/β ratio of the samples are calculated using the following equation [19]:

\[
\alpha/\beta = 1/|10a(110) + 10b(210)|/|10a(101) + 10b(210)| \quad (4.5)
\]

This equation is applicable in the case of pure α and β-Si₃N₄ and is assumed to be valid for sialon materials too, because the structures are very similar.

The starting mixtures were fired in two ways, as tablets or powder in two different furnaces. The powders were fired in a vertical tube furnace (Isoheat, Eurotherm control) in molybdenum crucibles. The furnace was purged with a small constant flow of nitrogen (KCE, FPW 900°C). The atmosphere was raised with CO₂ (0.5 MPa). Up to 900°C the furnace was kept constant for 1 h. Subsequently the tablets were reaction hot pressed for 3 h in a static nitrogen atmosphere. In these experiments no correction is made for the oxygen in the starting material, as they were performed to get a quick overview of the stability area.
3.6. However, if equations 3 and 4 are used to calculate the values, this result is in excellent agreement with the values that we found. In our reaction sintering experiments on the line Si$_3$N$_4$, the nominal n-values were taken instead. Sometimes unreacted Si$_3$N$_4$ starting material is found which is ascribed to not fully settled equilibrium, because it was observed especially in the samples with a starting composition near the Si$_3$N$_4$ corner of the diagram. If only traces of one of the starting materials (e.g. AlN, although this also could be present as a compound in equilibrium, and α-Si$_3$N$_4$) are observed besides α-sialon, the samples are considered as single-phase Ca-α-sialon. In figure 4.3 the border of the single-phase Ca-α-sialon area is divided in 4 parts (a-d). These parts are the borders between single-phase α-sialon, and the regions in which α-sialon is present together with (a) β-sialon + 15R, (b) 12H + 21R, (c) 21R, (d) 21R + AlN.

![Diagram](image)

Figure 4.3. Single-phase Ca-α-sialon region in the Si$_3$N$_4$ - Ca$_6$Al$_{12}$N$_{16}$ - Al$_2$O$_3$N$_4$ system obtained by reaction sintering at 1700°C followed by slow cooling. I: m>2n (oxygen poor), II: m=2n, III: m<2n (oxygen rich). Phases present outside the α-sialon region: a. β-sialon + 15R, b. 12H + 21R, c. 21R, d. 21R + AlN.

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Reaction sintering

For the determination of the phase composition only samples with a low weight loss were used. For the powders a limit of 4 wt% is used and the weight loss limit for the tablets is 2 wt%. In figure 4.3 the observed single-phase Ca-α-sialon region is presented. Figure 4.3 is based on the observed phases and the calculated m-values of the Ca-α-sialon present in the samples. As the n-values cannot be determined in a reliable way from the lattice parameters the nominal n-values were taken instead. Sometimes unreacted Si$_3$N$_4$ starting material is found which is ascribed to not fully settled equilibrium, because it was observed especially in the samples with a starting composition near the Si$_3$N$_4$ corner of the diagram. If only traces of one of the starting materials (e.g. AlN, although this also could be present as a compound in equilibrium, and α-Si$_3$N$_4$) are observed besides α-sialon, the samples are considered as single-phase Ca-α-sialon. In figure 4.3 the border of the single-phase Ca-α-sialon area is divided in 4 parts (a-d). These parts are the borders between single-phase α-sialon, and the regions in which α-sialon is present together with (a) β-sialon + 15R, (b) 12H + 21R, (c) 21R, (d) 21R + AlN.

<table>
<thead>
<tr>
<th>Overall composition</th>
<th>m-value slow cooling</th>
<th>m-value fast cooling</th>
<th>Composition slow (α'/β'-ratio)</th>
<th>Composition fast (α'/β'-ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>0.9</td>
<td>1.0</td>
<td>α',α'</td>
<td>α'</td>
</tr>
<tr>
<td>1/1.5</td>
<td>1.2</td>
<td>0.9</td>
<td>α',β'(50)</td>
<td>α',β'(3.0)</td>
</tr>
<tr>
<td>1/2</td>
<td>1.2</td>
<td>1.0</td>
<td>α'</td>
<td>α',β'(2.6)</td>
</tr>
<tr>
<td>1/3</td>
<td>1.2</td>
<td>1.0</td>
<td>α',β',15R,12H(5.9)</td>
<td>α',β'(0.2)</td>
</tr>
</tbody>
</table>

Table 4.1. Overall composition of Ca-α/β-sialon and influence on m-value with different cooling rates (3 vs. 30°C/min). Phases besides α' and β'-sialon were observed in very small amounts (traces). α = α-Si$_3$N$_4$.

The borders between the various areas are not as accurate as presented in figure 4.3. As can be seen in figure 4.2 the chosen compositions are very near the border of the single-phase area. As a result the amounts of the polytype phases are very low. Therefore it is not easy to distinguish the polytypes in the X-ray diffractograms; moreover the polytype phases have very similar patterns. The 2H and 33R phases shown in figure 4.1 were not encountered but some other phases were observed instead (15R, 21R). According to the phase behavioural diagram in figure 4.1 this 15R phase is not in equilibrium with the α-sialon phase. The phases observed in figure 4.3 are in agreement with the results found by Wood et al. [16] and other α-sialon systems [7,8,9,20]. For example in both the Sm- and Y-α-sialon system the AlN polytypoids (15R, 12H, 21R) are found. These AlN polytypoids are sialons situated in the base plane of the Järnecke prism. The starting compositions are not corrected for oxygen with the consequence that the overall composition chosen is above the α-sialon plane. Besides the crystalline AlN polytypoid and α-sialon phases, a small amount of an amorphous glassy phase is observed in the X-ray diffraction patterns, which is assumed to balance the chemical composition in the plane. Stutz et al. [21] observed the same phenomenon where a glassy phase balances the composition for these polytype phases in the Y-α-sialon systems.

In the reaction sintering experiments at 1700°C single-phase Ca-α-sialon exists in the range m = 0.9 - 2.8 on the line Si$_3$N$_4$ - Ca$_6$Al$_{12}$N$_{16}$ (n = 0). Jack [22] reported on the same line (n = 0) an extension range of m = 0.9 - 3.65. However, if equations 3 and 4 are used to calculate the m-value from the lattice constants reported by Jack [22] then this range becomes m = 0.9 - 2.7. This result is in excellent agreement with the values that we found. In our reaction sintering experiments on the line m = 2n the extension ranges from m = 1.0 to m = 2.4. At 1700°C Huang et al. [11] found a minimum m-value of 0.6 on the line m = 2n and a maximum of m = 2.8 for Ca-α-sialon.

If equations 4.3 and 4.4 are used these values are about the same (0.6 and 2.9 respectively). Obviously, the extension range found by Huang et al. [11] on the line m = 2n is larger than the range we found. The difference is thought to be caused by the difference in cooling rate. Their cooling rate was about 200°C/min, while in our experiments it was 3 or approx. 30°C/min. It is shown that during slow cooling some phase transformation occurs. Consequently the minimum m-values are also influenced. This is even seen in the experiments that we carried out to check the influence on the extension range with a relatively small difference in cooling.
4.1.2 Reaction hot pressing

Due to the reaction / transformation during slow cooling down it was decided to use reaction hot pressing because a faster cooling rate (30°C/min) was possible. The hot pressed samples contained α and β-sialon with sometimes a trace of not reacted α-Si₃N₄ starting material. The nominal compositions of the samples, the α/β ratio, the z-values of β-sialon and the m-values of Ca-α-sialon formed at 1700°C are presented in table 4.2.

<table>
<thead>
<tr>
<th>Overall Composition m/n</th>
<th>z-value (β-sialon)</th>
<th>m-value (α-sialon)</th>
<th>α/β</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5/0.5</td>
<td>0.3</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td>0.5/1.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>0.5/1.5</td>
<td>1.1</td>
<td>0.9</td>
<td>1.6</td>
</tr>
<tr>
<td>0.75/1.5</td>
<td>1.1</td>
<td>0.9</td>
<td>18.2</td>
</tr>
</tbody>
</table>

When the starting n-value reaches a value of about 1.5 the border between the single-phase region and the multiphase region is attained. In this work in the samples with m <= 1 besides α-sialon a β-sialon phase is found. The z-values for this work in the samples with low cooling rate (3°C/min), as calculated with equations 4.1 and 4.2, vary in the range 0.5 - 2.2 (i.e. n = 1.0 - 4.4). These z-values are very high. The z-values for samples that are cooled down at a higher rate (30°C/min) are in the range 0.5 - 1.6. In the literature [24] these z-values for β-sialon in α/β-sialon composites generally are smaller than 1. Wood et al. [16] reported a highest z-value of 1.1 for the β-sialon in a Ca-sialon system. The presence of some amount of glassy phase may influence the results of the measurements somewhat. The XRD measurements are performed at room temperature and the glassy phase present disturbs the equilibrium established at 1700°C especially at low cooling rate.

Figure 4.4. Low m-value border of single-phase Ca-α-sialon, calculated with eq. 3 and 4 from literature lattice parameters [11, 18, 23], versus temperature.

Figure 4.5. Most probable phase behavioural diagram of Ca-α-sialon system at 1700°C based on our results and literature data [16]. •: calculated m-value; O: n-value (n = 2z) of β-sialon, x: nominal composition; △: calculated from α/β-ratio.
1.1. Ca$_{n}$-a-sialon, Sm$_{n}$-a-sialon

Experiments that were performed at 1700°C with slow cooling rate. The $z$-values of the $\beta$-sialon phases for the hot pressed samples were also lower. These were in the range 0.3 - 1.1. These $z$-values are in agreement with the values found for reaction sintering with high cooling rate. The trend in the $z$-values is consistent with the $n$-values for the various samples and the $z$-values are in accordance with the literature [24]. The calculated $m$-values of the Ca-\(\alpha\)-sialon phase are somewhat higher than the $m$-values of the overall starting composition, as is expected. In figure 4.5 the most likely phase behavioural diagram is constructed from our own results and literature data [16]. It has to be mentioned that the phase diagram does not seem to obey the phase rules. Some phases are 'missing' because the polytype phases are in fact not in the same plane as the \(\alpha\)-sialon phase. These polytype phases are situated in the baseplane of the Jänecke prism (see figure 2.7) and are projected in the \(\alpha\)-sialon plane.

When figures 4.3 and 4.5 are compared it is obvious that the minimum $m$-values in figure 4.5 are smaller due to the higher cooling rate used at reaction hot pressing. The phases have less time to transform during cooling. This makes the stability area of the single-phase Ca-$\alpha$-sialon larger on the minimum $m$-value side (see fig 4.4) when a fast cooling is performed. The tie lines that can be drawn in figure 4.5 are not exactly correct but give a very good impression of the $\alpha/\beta$ region. It is not very likely that the 0.5/1.5 and 0.75/1.5 compositions have the same $m$ and $z$-value as is experimentally observed. In fact 0.5/1.5 is least likely because the other 3 give a consistent trend. The inaccuracies are due to the slow establishment of the phases. When the single-phase areas of several \(\alpha\)-sialon systems are compared it is seen that the area for Ca-$\alpha$-sialon is larger than for Y and Sm-$\alpha$-sialon [25] (see figure 4.6).

> Figure 4.6. Comparison of the sizes of different single-phase $\alpha$-sialon stability areas at 1700°C.

### Phase relations in the Ca-$\alpha$/$\beta$-sialon system

#### 4.3.3 Heat treatment of Ca-$\alpha$/$\beta$-sialon

After hot pressing of the samples, as described in section 4.2.3, with a cooling rate of 30°C/min some $\alpha/\beta$-sialon composite materials were selected for heat treatment. The results of the heat treatment experiments for Ca-$\alpha$/$\beta$-sialon and single-phase Ca-$\alpha$-sialon show that the composition of the Ca-$\alpha$-sialon ($m$-value) does not change significantly during heat treatment (see table 4.3). To show the difference the calculated $m$-values are noted with two decimals, although the accuracy of the data is less. However, the composition changes in the right direction and is in agreement with figure 4.4.

**Table 4.3. Calculated $m$-values and $\alpha/\beta$-ratio of as prepared reaction hot pressed Ca-$\alpha$-sialon and after several subsequent annealing steps in nitrogen.**

<table>
<thead>
<tr>
<th>Overall Composition</th>
<th>no treatment</th>
<th>annealing 1 1665°C</th>
<th>annealing 2 1465°C</th>
<th>annealing 3 1665°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m/n$</td>
<td>$m/(\alpha/\beta)$</td>
<td>$m/(\alpha/\beta)$</td>
<td>$m/(\alpha/\beta)$</td>
<td>$m/(\alpha/\beta)$</td>
</tr>
<tr>
<td>0.5/1.0</td>
<td>0.65/1.0</td>
<td>0.66/0.7</td>
<td>0.75/0.7</td>
<td>0.71/0.6</td>
</tr>
<tr>
<td>0.5/1.5</td>
<td>0.87/2.1</td>
<td>0.87/1.8</td>
<td>0.92/1.5</td>
<td>0.91/1.5</td>
</tr>
<tr>
<td>0.75/1.5</td>
<td>0.88/9.7</td>
<td>0.95/18.6</td>
<td>1.04/35.8</td>
<td>1.03/21.3</td>
</tr>
<tr>
<td>1.6/1.4</td>
<td>1.26/oo</td>
<td>1.43/71</td>
<td>1.39/oo</td>
<td>1.44/oo</td>
</tr>
</tbody>
</table>

$m/(\alpha/\beta)$: $m$-value / $\alpha/\beta$-ratio

The $\alpha/\beta$ ratio of the samples with nominal values 0.5/1.0 and 0.5/1.5 is influenced by the fact that there was a certain amount of $\alpha$-Si$_3$N$_4$ in the as prepared samples. This amount decreased after the subsequent annealing steps. The $\alpha/\beta$ ratio approaches the final ratio after annealing step 3 because the ratio hardly changes anymore. For the sample with nominal $m/n$ value 0.75/1.5 the final ratio is not yet reached. It seems that the equilibrium is more difficult to reach than for the other samples. The composition of the $\alpha$-phase ($m$-value) does not change much although the $\alpha/\beta$ ratio changes drastically. The Ca-$\alpha$-sialon phase is stable in this temperature range, only the amount changes and not the composition. After the first annealing step some $\beta$-sialon phase is present in the nominally single-phase composition. In the subsequent steps this $\beta$-sialon is converted to 21R phase.

Camuscu et al. [26] showed that there is a relation between the ionic size of the stabilising metal ion (e.g. Nd, Sm, Dy, Yb) and the $\alpha$-sialon content after heat treatment at 1450°C. They showed that the larger the ionic size the faster the $\alpha$/$\beta$ composite material transforms to $\beta$-sialon or another phase. For Nd and Sm the content of $\alpha$-sialon decreases continuously and at the end there is no $\alpha$-phase left. The viscosity and the amount of liquid phase (if present) during heat treatment experiments can influence the transformation and so can $\beta$-sialon seeds. They reported that single-phase Dy- and Yb-$\alpha$-sialon are stable during heat treatment. After 150 h no transformation to $\beta$-sialon had occurred. The only change was a small increase in the amount of crystalline phases ($M^\ast$ or $J$) as a result of a decrease in $m$-values of the $\alpha$-phase during the first 7 days of heat treatment; this latter trend stopped. However, the single-phase Nd- and Sm-$\alpha$-sialon degraded during heat treatment. Depending on the composition the $\alpha$-sialon phase was completely transformed to another phase within 168 h.
Calcium ions, however, have almost the same size (0.99 Å) as the samarium and neodymium ions but the Ca-αβ-sialon composites and single-phase Ca-α-sialon behave similar to the Dy and Yb sialon systems during heat treatment. It seems that for Ca-αβ-sialon the structure of the Ca-α-sialon phase is more stable during heat treatment in this temperature range compared to Sm and Nd. There is no stable intermediate phase like mellitite in the Nd- and Sm-α-sialon systems to incorporate the stabilising ions in the Ca-α-sialon system. At low temperature (1465°C) still only α and β phase is found (no gehlenite) where in other systems besides these also other phases like mellitite are observed. This is confirmed by the study of Mandal et al. [27] where heat treatment experiments were performed with calcium containing α-sialon ceramics in the range 1450-1550°C. They did not observe α to β transformation in this range in mixed calcium containing α-sialons systems. In the nominal single-phase composition (1.6/1.4) some β-sialon phase is observed after the first annealing step. The m-value stays constant as well as the concentration of the single-phase Ca-α-sialon and the initially formed β-sialon is converted to 21R-phase during the following annealing steps.

Although the ion size is similar to those of Dy and Yb the charge of Ca ions is different. This is 2+ while in the above-mentioned systems (Dy and Yb) it is assumed to be 3+ although this also is under discussion [28].

4.4 CONCLUSIONS

A new method was developed for the preparation of oxygen-poor Ca-α-sialon. The in-situ nitridation of Ca-metal in the starting mixture proved to be effective to synthesise Ca-α-sialon materials on the line Si1.52N1.6-Ca12Al17N16 (n=0).

The single-phase area of Ca-α-sialon was roughly estimated with reaction sintering experiments. The border between single-phase Ca-α-sialon and multi-phase region can be separated in 4 parts, besides Ca-α-sialon 1. β-sialon + 15R, 2. 12H + 21R, 3. 21R and 4. 21R and AIN is observed. This is in agreement with the data reported in literature for Ca-αβ-sialon, although cooling influences cannot be ruled out. The 33R-phase as well as the 27R-phase is not encountered in this study.

It is shown that the cooling rate in reaction sintering experiments influences the composition of the samples. When a high cooling rate is used the observed m-values are lower than when a low cooling rate has been used. A change during cooling down is enhanced if more oxygen is present in the starting mixture. The calculated minimum m-value is higher at higher oxygen content.

The hot pressing experiments were performed with oxygen correction to investigate the Ca-αβ-sialon region in more detail. The border between the single-phase α-sialon and the αβ-sialon region is situated at m = 0.8. At a cooling rate of 30°C/min the m-values were a little higher than the nominal composition. Tentative tie lines were established in the two-phase region.

The composition after heat treatment at 1465°C of the Ca-αβ-sialon composites was not significantly different from the composition before the annealing. As well as the m-value the αβ ratio was the same before and after. It seems that the Ca-αβ-sialon is more stable than the other αβ-sialon systems where a significant difference in composition occurs after heat treatment at 1450°C. If a transformation takes place it will occur below 1450°C.

References

Fame

Statements like 'I'm richer than you are, so I'm superior', or 'I speak more swiftly than you do, so you're inferior' lack any logic. A logical conclusion would be: 'I'm richer than you are, so I apparently possess more than you do', or 'I speak more swiftly than you do, so your linguistic skill is less than mine'. Strictly speaking neither wealth nor eloquence has anything to do with any hierarchy among people.

Epictetus

Roem

Beweringen als 'Ik ben rijker dan jij, dus ben ik je meerdere', of 'Ik spreek vlotter dan jij, dus ben ik mijn mindere', missen elke logica. Een logische gevolgtrekking zou zijn: 'Ik ben rijker dan jij, dus zal ik wel meer bezitten dan jij', of 'Ik spreek vlotter dan jij, dus is jouw taalvaardigheid kleiner'. Maar strikt genomen hebben rijkdom of welsprekendheid niets te maken met enige rangorde onder de mensen.

Epictetus

Chapter 5
Phase formation of Ca-α-sialon by reaction sintering

Abstract

In this study the reaction sintering route for the formation of Ca-α-sialon with a composition on the line Si$_3$N$_4$ / CaO·3AlN ($Ca_9Si_9Al_2.4O_8N_{15.3}$, $m=1.6$, $n=0.8$) has been investigated. It is compared to hot pressing Ca-α-sialon and reaction sintering of Y or lanthanide α-sialons.

The reaction follows the same sequence, first the formation of a Ca-rich α-sialon phase ($m=1.9$) which is gradually transformed to a Ca-α-sialon with a lower Ca-concentration ($m=1.2$). The gehlenite phase (Ca$_2$Al$_2$SiO$_7$, mellite group) is observed as an intermediate product.

A potential advantage of Ca-α-sialon over Ln-α-sialon (Si$_3$N$_4$ / 1/3 Ln$_2$O$_3$·3AlN, Ln = Y, lanthanide) is a liquid phase formation at a lower temperature which influences the processing temperature positively. Moreover, Ca is cheaper than the lanthanide's. The Ca solubility in the α-sialon is in agreement with values found in literature.

5.1 INTRODUCTION

Sialon ceramic materials are interesting for application because of their good mechanical and chemical properties such as strength, hardness, thermo-shock resistivity and wear resistance. The sialon ceramics can be divided into two categories: β-sialon with the general formula: Si$_6$Al$_2$O$_2$N$_4$, where $0 < z < 4.2$ [1,2] and α-sialon with the general formula: Me$_{6}$-$\text{Si}_{2}$(2-2m)Al$_{2}$O$_{3}$N$_{16}$-$4$, (Me = metal like Y, lanthanides, Ca, Mg, Li, val = valency of the metal)[3]. The α and β sialon materials have similar structures as α and β Si$_3$N$_4$. The $z$, $m$ and $n$ parameters are substitution numbers for Al and O. From the α-sialon materials Y-α-sialon is studied most intensively [3,4,5,6]. The Ln-α-sialon (Ln = lanthanide) materials are less intensively studied. However, most lanthanides are quite expensive, therefore this work is focused on a less expensive alternative, i.e. Ca-α-sialon. In a previous paper the preparation of Ca-α-sialon by a carbothermal reduction and nitridation process has been reported [7]. In this
Chapter 5

paper the reaction route for the formation of Ca-α-sialon by reaction sintering is described. The results are compared with results found in literature concerning hot pressing Ca-α-sialon and reaction sintering Ln-α-sialon (Ln = Y, lanthanide) to see what are similarities and differences in reaction paths.

5.2 EXPERIMENTAL METHODS
To determine the reaction sequence during reaction sintering several experiments were carried out. The composition, which was aimed at, is Ca$_{0.8}$Si$_{0.8}$Al$_{2.4}$O$_{0.8}$N$_{13.2}$ ($m=1.6, \; m=0.8$). As starting materials Si$_3$N$_4$ (LC-12N, Starck, $\alpha/(\alpha+\beta) > 95$%, oxygen content 2 wt%), AlN (Starck, grade C, oxygen content 2 wt%) and CaO (freshly decomposed CaCO$_3$ (Merck p.a.)) were used. No correction was made for the oxygen content of the nitride starting materials. All firing experiments were performed with the same batch of mixed starting materials. The mixing of these powders was performed in isopropanol in polyethylene bottles on a roller bench (for 48 h) with Si$_3$N$_4$ milling balls. Subsequently the powder was dried and pressed into tablets; first uniaxially at 51.7 MPa followed by isostatic pressing at 250 MPa. The firing of the samples was performed in a graphite resistance nitriding furnace at a pressure of at maximum 0.13 MPa of nitrogen. The temperature was increased from room temperature to 800°C with 10°C/min in vacuum, keeping it constant for a quarter of an hour to decompose the CaCO$_3$. Then the temperature was raised (10°C/min) to the top temperature which was varied in the range of 1300-1700°C. At 900°C the vacuum was replaced by a nitrogen atmosphere. After reaching the top temperature the samples were cooled down immediately (10°C/min), so no soaking time was used. The tablets (5 for each temperature) were embedded in a powder mixture of 55 wt.% Si$_3$N$_4$, 20 wt.% AlN, 5 wt.% CaO (decomposed CaCO$_3$) and 20% BN to prevent decomposition of the starting materials at elevated temperatures. BN was added to this mixture to prevent sintering of the powder bed mixture. Densification during heating up was measured using dilatometry. This was performed in a graphite resistance furnace in a static nitrogen atmosphere (heating rate 5°C/min, no soaking time at top temperature). A 15-min holding time at 1350°C was implemented till the shrinkage rate started to drop. The difference in heating rate used in the dilatometry experiments as compared to the reaction sintering experiments was used to get a clear separation of the different shrinkage rate maxima. The dilatometer was set up to measure horizontal displacement. The samples were pressed into bars with the aid of polyethylene glycol as a binder material, first uniaxially and then isostatically at 250 MPa. The size of the bars was approximately 15x5x5 mm$^3$. To remove the binder and decompose the CaCO$_3$ to CaO and CO$_2$ the bars were carefully heated up in air to 900°C and soaked for 1 hour. The dilatometer samples were not used for further investigation. Only samples with a weight loss smaller than 5% were used for further analysis.

The samples were analysed by X-ray diffraction (Rigaku, Geigerflex, CuK$_\alpha$, 0.0125°/min, 10-97° 2θ, 5 sec. counting time, 35 kV, 20 mA). For X-ray diffraction the tablets were powdered as fine as possible by mortar and pestle. The determination of the phase composition by X-ray diffraction was qualitatively performed by estimation of the intensities of the peaks in the diffractograms belonging to various compounds. To determine the cell parameters generally the peaks with the highest intensity are chosen. It would be better to use the peaks at high reflection angles, but the intensity of these peaks is too low. The computer program Refcel [8] was used to calculate the cell parameters. The d or 2 $\theta$-values and the hkl-values of the ten strongest peaks (hkl = 101, 201, 102, 210, 211, 301, 222, 311, 411, 322) were used as input for these programs.

5.3 RESULTS AND DISCUSSION

5.3.1 Shrinkage behaviour
It is generally accepted that the shrinkage during densification of α-sialon occurs as a consequence of liquid phase sintering, which proceeds in three stages [3]:
1. primary particle rearrangement, immediately following the formation of liquid phase, is brought about by solid particles sliding over each other under action of capillary forces;
2. solution / precipitation process which will occur if the solid particles have sufficient solubility in the liquid phase; and
3. coalescence and closed pore elimination.

By reaction of SiO$_2$ and Al$_2$O$_3$ on the surface of the nitride starting materials with CaO, a liquid phase can be formed at the eutectic temperature. According to the CaO – SiO$_2$ – Al$_2$O$_3$ phase diagram, the lowest eutectic temperature is 1170°C [9]. To increase the amount of liquid phase, the temperature should be somewhat higher, in agreement with the fact that the shrinkage starts at about 1225°C (fig. 5.1) due to particle rearrangement. The amount of liquid

![Figure 5.1 Dilatometer curve of reaction mixture of CaO, Si$_3$N$_4$ and AlN with a composition Ca$_{0.8}$Si$_{0.8}$Al$_{2.4}$O$_{0.8}$N$_{13.2}$](image_url)
phase further increases at higher temperatures, the more because dissolution of nitrogen lowers the eutectic temperature [10]. As a result, a maximum shrinkage rate is observed at about 1350°C (fig. 5.1), which corresponds with the temperature (1360°C) reported for this stage during reaction hot pressing of Ca-α-sialon [11]. Reaction sintering of Si₃N₄ / AlN / Y₂O₃ compositions on the line Si₃N₄ / 1/3 Y₂O₃ · 3 AlN shows the first shrinkage rate maximum at a significantly higher temperature of 1500°C [12] to 1550°C [13]. At about 1450°C the second shrinkage rate maximum can be discerned for Ca-α-sialon (fig. 5.1), which is ascribed to the occurrence of the solution / precipitation mechanism (stage 2). The temperature observed for this stage agrees with the value reported for the second shrinkage step during reaction hot pressing Ca-α-sialon [11]. Chen and co-workers [11,14,15] pointed out that the position of the second peak is closely related to the temperature where the major nitride component in the mixture is wetted by the liquid phase. For Si₃N₄, which is the major component in our reaction mixture, complete wetting was observed at 1450°C, corresponding with the second peak in fig. 1. For the Ca-system preferential wetting of the nitride starting material being present in the largest amount, i.e. Si₃N₄, takes place [14], whereas for the Y-system preferential wetting of the AlN starting material occurs [15]. From the present study and our earlier research on Y-α-sialon [16] we conclude that the densification during reaction sintering is quite similar to that during reaction hot pressing observed by Chen et al. [11,14,15].

5.3.2 Phase formation

To analyse the phase composition of the tablets powder X-ray diffraction was used. The amounts of the crystalline phases are presented in figure 5.2 as a function of the reaction sintering temperature. The figure shows that the formation of Ca-α-sialon starts at a temperature between 1300 and 1400°C. This is related with the formation of a significant amount of liquid phase at 1350°C as deduced from the first peak in the shrinkage curve. From the dilatometer curve it was concluded that at 1450°C the solution / precipitation mechanism plays a dominant role. This corresponds with the temperature in figure 5.2 where the amounts of the raw materials Si₃N₄ as well as AlN start to decrease significantly. β-Si₃N₄, which was near the detection limit, was already not detectable anymore above 1300°C. AlN disappears in the range 1500-1600°C. α-Si₃N₄ can still be determined at 1600°C. The amount of Ca-α-sialon increases with increasing temperature till near complete conversion at 1700°C. Only one crystalline intermediate product could be determined. This is Ca₃Al₂SiO₇ (gehlenite) or more likely a compound with the general formula Ca₃Al₂-xSibN₄-xO₇, according to the calculated cell parameter that is different from that of pure gehlenite. It is already observed at 1300°C and can be determined till 1600°C, at which temperature it is completely dissolved. The amount, however, is near the detection limit. The presence of this intermediate phase is in agreement with the results Hewett et al. [17] reported for reaction hot pressing of Ca-α-sialon. Besides this gehlenite intermediate they found a very small amount of M-phase (2CaO·Si₃N₄·AlN) at low temperatures (till about 1400°C), which is not detected in our samples. In our investigation CaSiO₃ appears between 1400°C and 1500°C and remains in the mixture even at 1700°C. It may be formed during cooling down, and its presence in the end product is assigned to the surface oxygen present on the nitride starting materials. It can be calculated that the oxygen content of the nitride raw materials corresponds with 2-3 wt% CaSiO₃ in the end product. According to this calculation m-value of the resulting Ca-α-sialon shifts a little bit, from 1.6 to 1.4 at minimum. According to Hintzen et al. [18] the m and n-value can be calculated from the relations:

\[ a (\text{Å}) = 7.749 + 0.0023 n + 0.0673 m \]  
\[ c (\text{Å}) = 5.632 - 0.0054 n + 0.0550 m \]  

From these relations it can be seen that the m-value is the dominant parameter, therefore the n-value is not calculated. At the beginning of the reaction (1400°C) the cell parameters of the Ca-α-sialon material are large (a = 7.883 Å, c = 5.731 Å, see table 5.1) which is ascribed to formation of a Ca-rich Ca-α-sialon material. From equations 5.1 and 5.2 the m-value can be calculated to be 1.9. This m-value is smaller than 2.8, which is reported as the upper limit of solubility of Ca in α-sialon [19]. The presence of still large amounts of Si₃N₄ and AlN at 1400°C also is in agreement with the presence of Ca-α-sialon with a high Ca-concentration. For increasing sintering temperatures the lattice parameters of the Ca-α-sialon become smaller (table 5.1). This corresponds with a decreasing m-value (figure 5.3).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>m-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>7.883</td>
<td>5.731</td>
<td>1.9</td>
</tr>
<tr>
<td>1500</td>
<td>7.865</td>
<td>5.725</td>
<td>1.7</td>
</tr>
<tr>
<td>1550</td>
<td>7.845</td>
<td>5.700</td>
<td>1.4</td>
</tr>
<tr>
<td>1600</td>
<td>7.842</td>
<td>5.685</td>
<td>1.3</td>
</tr>
<tr>
<td>1700</td>
<td>7.830</td>
<td>5.694</td>
<td>1.2</td>
</tr>
</tbody>
</table>
and indicates formation of a Ca–α-sialon with lower Ca-concentrations at higher temperatures. The final Ca–α-sialon composition (1700°C) has small lattice parameters \( (a = 7.830 \text{ Å}, c = 5.694 \text{ Å}) \) resulting in \( m = 1.2 \). From the comparison of the experimentally found \( m \)-value (1.2) with the \( m \)-value expected from the weighed-out starting composition (1.4–1.6), it can be concluded that 75–85% of the amount of calcium is incorporated in the Ca–α-sialon lattice. Such percentages are generally found for Ca–α-sialon systems \[18\]. The reaction is finished according to these cell parameters calculated from the samples fired at 1700°C, in agreement with the presence of nearly single-phase Ca–α-sialon. The decrease of the cell parameters of Ca–α-sialon during the reaction corresponds with the results Sun et al. \[20\] reported for reaction sintering of Ca–α/β-sialon composite materials. In this last case, however, also the shift of the boundary between the single-phase α-region and the two-phase α/β region with temperature, may play a role of importance.

5.3.3 Reaction mechanism

From the results discussed so far the following reaction mechanism can be derived.

\[
\begin{align*}
\text{CaO} + \text{Al}_2\text{O}_3 / \text{AIN} + \text{SiO}_2 / \text{Si}_3\text{N}_4 &\rightarrow \text{Ca-Si-Al-O-N liquid + gehlenite} \quad (1) \\
&\quad -1350°C \\
\text{Ca-Si-Al-O-N liquid} + \text{Si}_3\text{N}_4 + \text{AIN} + \text{gehlenite} &\rightarrow \\
\text{Ca-α-sialon} (m = 1.9) + \text{Ca-Si-Al-O-N liquid} + \text{gehlenite} &\rightarrow \\
&\quad -1400°C \\
\end{align*}
\]

**Phase formation of Ca–α-sialon by reaction sintering**

\[
\begin{align*}
\text{Ca-α-sialon} (m = 1.9) + \text{Si}_3\text{N}_4 + \text{AIN} + \text{Ca-Si-Al-O-N liquid + gehlenite} &\rightarrow \\
\text{Ca-α-sialon} (1.2 < m < 1.9) + \text{Ca-Si-Al-O-N liquid + gehlenite} &\rightarrow \\
&\quad -1400-1550°C \\
\text{Ca-α-sialon} (1.2 < m < 1.9) + \text{Ca-Si-Al-O-N liquid + gehlenite} &\rightarrow \\
&\quad -1700°C \\
\text{Ca-α-sialon} (m = 1.2) + \text{CaSiO}_3 &\rightarrow \\
&\quad >1550°C
\end{align*}
\]

Reaction 1 occurs at about 1350°C, reaction 2 in the range 1400–1550°C and the last one takes place if the temperature is higher than 1550°C. The SiO₂ and Al₂O₃ in equation 1 are present on the surface of the starting Si₃N₄ and AlN powder.

The reaction scheme proposed in this study is similar to that observed by Watari et al. \[13\] for reaction sintering of Ln–α-sialons \((\text{Ln} = \text{Y}, \text{Er}, \text{Yb})\). They proposed a reaction sequence, starting with lanthanide oxides \((\text{Y}, \text{Er}, \text{Yb})\), in which first a liquid phase is formed, subsequently α-sialons with high concentrations of lanthanide ions and finally α-sialons with low lanthanide concentrations. In this case also a melilite like compound \((\text{Ln}_2\text{Si}_2\text{O}_6\text{N}_2)\) is found as an intermediate, in agreement with results Cao et al. found for reaction sintering of Y-sialon materials \[3,12,16\]. There are strong similarities between this reaction sequence proposed for Ln–α-sialons and the work described in the present paper for Ca–α-sialon. In both cases a melilite like compound \(M_2(\text{Al},\text{Si})_2(\text{O},\text{N})_7\) \((M = \text{Ca}, \text{Y}, \text{lanthanide})\) was observed as an intermediate product. Only there is no end product present that can be exchanged by CaSiO₃ in their reaction sequence.

Potential advantages of Ca–α-sialon are the lower processing temperature (densification temperature 1550°C vs >1600°C) and the much cheaper starting materials as compared to the Ln-α-sialons.

5.4 CONCLUSIONS

Reaction sintering of a mixture of CaO, Si₃N₄, and AIN on the line Si₃N₄ / CaO-3AIN \((\text{CaO}_9\text{Si}_6\text{Al}_2\text{O}_{15}\text{N}_{52}, m = 1.6, n = 0.8)\) starts at a temperature of about 1350°C due to formation of a Ca-Si-Al-O-N liquid, as deduced from shrinkage rate measurements. At about 1450°C the solution precipitation mechanism is dominant promoting the formation of Ca–α-sialon. First, a Ca–α-sialon is formed which contains more Ca than aimed at \((m = 1.9)\). Subsequently this Ca-rich α-sialon reacts with the Si3N4 and AIN that are still present until finally \(m = 1.2\) is reached, indicating that not the total amount of Ca is incorporated in the α-sialon matrix. As an intermediate product Ca₂Al₂Si₁₋₂O₃₋₄N₄ (gehlenite, belonging to the melilite group) was found. This is comparable to the intermediate products in the formation of Ln-α-sialon \((\text{Ln} = \text{Y}, \text{lanthanide})\) where Ln₂Si₂O₆N₂ melilite phases are formed. In the final product, besides Ca–α-sialon, CaSiO₃ was observed due to the presence of oxygen in the nitride starting materials, which was not corrected for. Potential advantages of Ca–α-sialon over Ln-α-sialon are the lower processing temperature (1550°C vs >1600°C) and the much cheaper starting materials.
Chapter 6

Carbothermal preparation and characterisation of Ca-α-sialon

Abstract
Ca-α-sialon can be synthesised by simultaneous carbothermal reduction-nitridation of a mixture of fine SiO₂, Al₂O₃, CaSiO₃ and carbon black powder at 1500°C. For the first time a single-phase material is obtained in a one step process. The main intermediate product in these processes is a β-sialon with a low z-value (z < 1.2). After formation of this β-sialon the calcium is incorporated in the lattice to form the Ca-α-sialon.

6.1 INTRODUCTION
Si₃N₄ and Si₃N₄ based ceramics like sialon materials are interesting for high temperature engineering applications. These materials have very good thermal shock behaviour, high wear resistance, good corrosion resistivity, oxidation resistance and high strength [1,2,3,4]. The preparation of the sialon materials, either α or β, can be performed along several different routes. Reaction sintering is the most widely used method among them. The disadvantages are the relatively expensive starting materials and the limited possibilities to produce complex shapes of fully densified materials. An alternative way of producing sialon starting with relatively inexpensive materials is the route of carbothermal reduction and nitridation of oxide materials. The carbothermal reduction and nitridation of kaolin clay is well known for the synthesis of β-sialon [5,6,7]. The overall reaction for the production of β-sialon (Si₆-z Al₃O₃N₅z) when z=3 is:

$$3 (2 \text{SiO}_2 \text{Al}_2 \text{O}_3 2 \text{H}_2 \text{O}) + 15 \text{C} + 5 \text{N}_2 \rightarrow 2 \text{Si}_3\text{Al}_2\text{O}_7 + 15 \text{CO} + 6 \text{H}_2 \text{O} \quad (6.1)$$

This reaction can be separated into several stages. Some of the intermediate products are mullite and SiC [5,6].

References
As mentioned besides the β-sialon also α-sialon exists. The structure of these latter materials is stabilised by a modifying cation such as Y, Li, Mg and Ca. The general formula for α-sialon is $\text{M}_{m+n}\text{Si}_{2m+n}\text{Al}_m\text{O}_{3m+n}\text{N}_{16-n}$ where $m$ and $n$ indicate the replacement of (Si-N) by (Al-O) and $v/f$ is the valency of the metal ion. The synthesis of α-sialon materials by reaction sintering is widely used. Especially the β-sialon materials, however, is hardly investigated and reported. In the study described here the possibility is investigated to prepare Ca-α-sialon by carbothermal reduction in a single step from oxidic starting powders. To determine which are the most convenient starting materials, it is important to know what kind of intermediate products are formed. This is one of the reasons why the mechanism of the carbothermal reaction has been studied here. The composition that is aimed at is $\text{Ca}_0.8\text{Si}_{0.8}\text{Al}_{2.8}\text{O}_{14.8}$. When starting with CaSiO$_3$ the overall reaction can be described as:

$$0.8 \text{CaSiO}_3 + 8.4 \text{SiO}_2 + 1.4 \text{Al}_2\text{O}_3 + 22.2 \text{C} + 7.4 \text{N}_2 \rightarrow \text{Ca}_0.8\text{Si}_{0.8}\text{Al}_{2.8}\text{O}_{14.8} + 22.2 \text{CO} \quad (6.2)$$

The composition has been chosen for practical reasons because it is well within the single-phase area of Ca-α-sialon [8], and single-phase material is likely to be obtained. Some years ago, Mitomo et al. [9] prepared α-sialon (Ca and Y) by carbothermal reduction and nitridation. In that study relative expensive starting materials like tetraethyl-orthosilicate, cristobalite, mullite, aluminium-isopropoxide, calcium-ethoxide and yttrium nitrate were used. These were mixed with carbon black, precipitated and dried at different temperatures. This study showed that α-cristobalite, mullite, Si$_3$N$_4$ and β-Si$_3$N$_4$ were the main intermediate crystalline products. These were obtained, next to some amount of α-sialon, after firing at temperatures at 1450°C or lower. In a second step the material was transformed to single-phase α-sialon by firing it at higher temperatures.

### 6.2 EXPERIMENTAL METHODS

#### 6.2.1 Preparation

Pure oxide materials were used to investigate the formation of single-phase Ca-α-sialon. The starting materials were SiO$_2$ (Aerosil OX-50, Degussa), Al$_2$O$_3$ (grade 'C', γ + δ Al$_2$O$_3$, Degussa) and CaSiO$_3$ (Wollastonite SG, Rheinische Kalksteinwerke). In some experiments CaCO$_3$ (Merck p.a., purity > 99%) or CaO (decomposed CaCO$_3$) were used as a source for calcium. The SiO$_2$ and Al$_2$O$_3$ powders have a high specific surface area (approx. 50 m$^2$/g). This means a high reactivity that can cause sintering of particles during the powder preparation.

An important parameter in carbothermal processes is the mixing of the powders to improve the contact between reactants and reduce the diffusion path length. Wet mixing and dry mixing are the two methods that have been used. They are described briefly below.

#### 6.2.2 Wet mixing

The starting powders are dispersed in water or isopropanol in a polyethylene bottle with SI$_2$N$_4$ milling balls on a roller bench for approx. 48 h. The next stage is evaporation of the isopropanol and mostly pressing tablets of the powder, or slip casting the aqueous suspension. For slip casting tablets, the suspension has to meet certain requirements. The powder particle size distribution should be narrow and if possible the particle size should be below 1 mm. It is important that the suspension is stable and not too viscous. To obtain a stable suspension with SiO$_2$, Al$_2$O$_3$ the pH should be either below pH = 2 (otherwise the SiO$_2$ and Al$_2$O$_3$ will form a gel) or above 9. However, in the latter case a very small amount of the SiO$_2$ will dissolve, the ionic strength will increase which will flocculate the suspension. In order to check these properties in all cases sedimentation experiments were done. For dispersing the carbon a surfactant is required. Several surfactants were tried and among these CG-6 (i.e. ammonium salt of poly-acrylic acid) supplied by ICI worked best for this system. It also helped to disperse the other powders. The suspensions which were used for slip casting had a pH < 2 because the surfactant worked better at this pH than at higher pH-values. After mixing, the suspension was ultrasonically treated to break the agglomerates and then slip cast in a plastic ring (Ø 45 mm) placed on a gypsum plate.

#### 6.2.3 Dry mixing

Pelletising is another way to produce green bodies that can be fired. The starting powders were dry mixed in an Eiger mixer (Labor Mixer R02) until the mixture looked homogeneous. Then water was sprayed on the powder that caused agglomeration of the powder. The size of the pellets which are obtained is related to the amount of water added and the speed of the mixer (typical values 5-10 mm). These pellets were dried at 100°C and could be used for the synthesis of Ca-α-sialon.

The density of the tablets and pellets were roughly estimated by measuring the weight and volume (pellets = 1.0 g/cm$^3$, tablets = 0.7 g/cm$^3$). The slip cast tablets are less dense, so more porous, than the pellets, so the influence of porosity on the reaction can be observed.

#### 6.2.4 Synthesis

The different experiments and conditions are summarised in table 1. For these experiments a constant amount of slip cast tablets was used in a horizontal tube furnace with flowing nitrogen. Except experiment 'A' during which pieces of mixed starting powder bonded with binder were used (this can be considered as being pellets, agglomerates are formed after evaporation of isopropanol) and 'E' in which pellets were used. The experiments with starting mixtures A-D were carried out in a horizontal tube furnace with a diameter of 25 mm. Experiment e was carried out in a tube furnace with a diameter of 50 mm. The amount of pellets was 200 g and the bed length was 20 cm. The temperature was in the range 1350 - 1650°C for 3 - 65 hours. The progress of the reaction was followed by measuring the CO content in the exhaust gas mixture with a CO-monitor (Defor Gas Analyser, Maihak).
Additionally some of the tablets were re-fired for one or two hours between 1550 and 1700°C in a graphite resistance furnace in a static nitrogen atmosphere to see if the amount of α-sialon would increase. The tablets were embedded in a mixture of BN, Si₃N₄ and AlN powder to prevent dissociation at these relatively high temperatures. The influence of a milling step between the first and second firing was investigated as well. The milling could be performed in a mortar, because the material was not very hard. This powder was pressed uniaxially followed by isostatic pressing.

To get some insight in the mechanism of the carbothermal reduction several experiments were carried out at 1500°C as a function of the firing time. In these experiments pellets were used and all the reaction parameters were kept constant, except the time, which varied from 20-1000 minutes. The volume of the reaction bed in the horizontal tube furnace (Ø 25 mm) was 10 ml and the N₂ flow was 12.5 l/h.

6.3 Characterisation

To investigate the phase compositions in the product material X-ray diffraction was applied (Rigaku Geigerflex diffractometer) using Cu-Kα radiation. To determine the ratio of α-sialon to β-sialon the following equation was used [10]:

\[
\alpha/\beta = \frac{I_{100} + I_{210}}{I_{101} + I_{220}}
\]

(6.3)

This equation is applicable in the case of pure α and β Si₃N₄ and is assumed to be valid for sialon materials too, because the structures are very similar. To estimate the α-sialon content only α and β sialon phases were taken into account. Amorphous phases and (traces of) secondary phases were neglected. Therefore in table 1 only an indication is given of the compounds present in the sample, the concentration for each component is not calculated. The lattice parameters of the materials were determined from slow scans (0.0125°/sec). The ten strongest reflections observed were applied to calculate the lattice parameters using a computer program based on the SIMPLEX method [11].

To determine the relation between the nitrogen content and the content of α-sialon the nitrogen content was determined by a reverse Kjeldall titration [12]. The sample is destructed with molten lithium hydroxide, the formed NH₃ is dissolved in boric acid which was titrated with hydrochloric acid to determine the nitrogen-content. Particle size was determined by sedigraph measurements (Micromeritics Sedigraph 5100). The powder was suspended in water and ultrasonically treated before the measurements.

6.4 RESULTS AND DISCUSSION

6.4.1 Synthesis of Ca-α-sialon

The conditions of the experiments and the results are displayed in table 6.1. As can be seen, the applied conditions at 1450°C or lower temperatures are not appropriate for preparing single-phase α-sialon from the starting SiO₂, Al₂O₃ and CaSiO₃ powders. The main products

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Temperature [°C]</th>
<th>Time [hrs]</th>
<th>N₂-flow [l/hr]</th>
<th>α/β ratio</th>
<th>Composition *</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1450</td>
<td>14</td>
<td>12</td>
<td>0.27</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>B</td>
<td>1450</td>
<td>14</td>
<td>12</td>
<td>0.39</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>C</td>
<td>1450</td>
<td>6</td>
<td>12</td>
<td>0.79</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>D</td>
<td>1450</td>
<td>6</td>
<td>12</td>
<td>0.25</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>E</td>
<td>1450</td>
<td>6</td>
<td>12</td>
<td>0.49</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>F</td>
<td>1450</td>
<td>7.5</td>
<td>12</td>
<td>0.67</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>G</td>
<td>1450</td>
<td>7.5</td>
<td>6</td>
<td>0.33</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>H</td>
<td>1450</td>
<td>3</td>
<td>12</td>
<td>0.45</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>I</td>
<td>1350</td>
<td>6</td>
<td>12</td>
<td>0.33</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>J</td>
<td>1350</td>
<td>6</td>
<td>12</td>
<td>0.45</td>
<td>α-sialon, β-sialon</td>
</tr>
<tr>
<td>K</td>
<td>1350</td>
<td>12</td>
<td>12</td>
<td>0.33</td>
<td>SiO₂</td>
</tr>
<tr>
<td>L</td>
<td>1450</td>
<td>6</td>
<td>5</td>
<td>0.33</td>
<td>Si₃N₄</td>
</tr>
<tr>
<td>M</td>
<td>1500</td>
<td>65</td>
<td>30</td>
<td>&gt;20</td>
<td>α-sialon</td>
</tr>
<tr>
<td>N</td>
<td>1500/1650</td>
<td>15/2</td>
<td>30</td>
<td>0</td>
<td>SiC</td>
</tr>
</tbody>
</table>

* Amorphous and secondary phases neglected

This amorphous phase cannot be characterised by X-ray diffraction, the phase is assumed to consist of aluminates and silicates. Evaporation of SiO influences the yield of the sialon material. When the reaction time is longer there is more probability that this occurs. This explains the higher ratio after 6 hrs compared to the ratio after 14 hours (experiments 2 and 3). Although in experiments 3 and 4 the circumstances were the same, the results are quite different. This is probably due to the fact of using two different batches of tablets. Apparently one batch was not as homogeneously mixed as should have been. This could explain the large difference in the α/β ratio. According to the results of experiments 13 and 14 (main products SiO₂ and Si₃N₄) the temperature of 1350°C is not sufficient for the reaction to have
proceeded far enough for the sialon materials to be detected. In experiment 14 the N$_2$-flow is too low to supply a sufficient amount of nitrogen in 6 hrs to form sialon material. In the shortly reacted samples also remains of starting materials are present. The z-values of the formed β-sialon material in the samples fired below 1500°C vary between approximately 0.4 and 1.2. A value of 1.4 at the most can be expected from the starting composition. At a temperature below 1500°C the highest content of α-sialon is about 40% both for the slip cast tablets and pelletised starting material. Increasing the temperature to 1500°C resulted in an almost single-phase Ca-α-sialon (>95 wt%). The rest (5 wt%) is uncertain because of the detection limit of the X-ray diffraction analysis. However, when the holding time at 1500°C is not long enough a significant amount of residual carbon is left in the mixture. The mixture hardly contains sialon material (at least not above the detection limit). When the temperature is raised to 1650°C the main product is SiC instead of α-sialon. After firing at temperatures below 1500°C, the tablets were fired again at elevated temperatures (1550-1700°C). This resulted in a decrease of the α-sialon content. On the contrary milling and pressing tablets and refiring these tablets in the same temperature range results in products with high α-sialon content. α-Sialon contents of up to 95 wt% are achieved (see table 2). This means that on the one hand it has been confirmed that Ca-α-sialon can be obtained in a two step process [9], but it also has been shown in this work that it is possible to use a single step process.

Table 6.2. Comparison of α-sialon content between first and second firing of tablets and pellets with intermediate grinding. (The numbers are averages).

<table>
<thead>
<tr>
<th></th>
<th>First firing (1450°C)</th>
<th>Second firing (1700°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tablets</td>
<td>30% α-sialon, 70% β-sialon</td>
<td>&gt; 95% α-sialon</td>
</tr>
<tr>
<td>pellets</td>
<td>35% α-sialon, 65% β-sialon</td>
<td>&gt; 95% α-sialon</td>
</tr>
</tbody>
</table>

In figure 6.1 is shown the transformation percentage to α-sialon after milling and a second firing at higher temperatures. The highest amount of Ca-α-sialon was obtained at 1700°C. No SiC could be detected, indicating a complete consumption of carbon in the first step. The phase change during the refiring process is shown in figure 6.2. The lower part presents a diffractogram of a sample fired at 1450°C. According to the baseline (which is not straight) a significant amount of amorphous phase is still present after firing at 1450°C. The diffractogram in figure 6.2 after refiring at 1700°C shows narrow and sharp peaks and a straight baseline. The unit cell dimensions of α-sialon calculated from this diffractogram are $a = 0.784$ nm and $c = 0.571$ nm. From these lattice parameters an $m$-value in the general formula for α-sialon of approx. 1.4 can be estimated. This means that most of CaO is incorporated in the crystalline material and the rest is present in the amorphous or unidentified phase.

Figure 6.1. Transformation to α-sialon after second firing. (start = initial amount of Ca-α-sialon before second firing).

Figure 6.2. X-ray diffraction patterns of material after first firing at 1450°C (bottom) and firing at 1700°C (top). The circles indicate peaks of β-sialon.
The powder which is obtained after firing two times is more difficult to mill than powder which is synthesised at 1500°C. The particle size (in fact agglomerate size) of this powder as synthesised is approximately 5-8 μm while the agglomerate size of the re-fired powder is about 10-20 μm.

6.4.2 Reaction mechanism

The results from the experiments concerning the investigation of the mechanism of the reaction are presented in figure 6.3 and discussed in the next paragraph. In a relatively short time the sialon products are formed. From X-ray diffraction patterns it follows that in the beginning of the reaction a significant amount of amorphous phase is present.

This complicates the identification and quantitative determination of the several components during this initial period. The main intermediate product is β-sialon material with low $z$-values ($z<1.2$). In shortly reacted samples some SiC seems to be present. Sometimes the samples contain O-sialon. Calcium aluminates or silicates were hardly found except the starting CaSiO$_3$. The intermediate products are consumed very fast otherwise there should be a plateau at a certain level in the curves. To monitor the progress of the reaction also the cell parameters of Ca-α-sialon are calculated. The values are shown in table 6.3. These show that the further the reaction proceeds the smaller the cell parameters become. The cell parameters of the α-sialon converge to the values of the desired product. As expected if the amount of nitrogen increases the cell parameters will decrease [13].

In figure 6.4 the data from the nitrogen determination are plotted, showing that even at a low (40 wt%) Ca-α-sialon concentration the nitrogen content is high. This means that the nitridation has so far proceeded that most of the nitrogen that is required for the formation of the Ca-α-sialon is available in the sample. Approaching 100 wt% of Ca-α-sialon the nitrogen content rises up to almost the theoretical value (35.0 wt%).

On the basis of the previously mentioned results the following mechanism of the formation of Ca-α-sialon is proposed. The first step is the formation of a β-sialon with a $z$-value of 1.2 (Theoretically $z = 1.4$, because there was aimed at Si$_{9.2}$/Al$_{12.8}$). The theoretical value of the nitrogen content of a β-sialon is 33.8 wt% if the $z$-value is 1.2. In figure 6.4 it is shown that with a low (40 wt%) Ca-α-sialon concentration combined with a high content of β-sialon (60 wt%) the nitrogen content nearly reaches the theoretical value for a β-sialon material with a $z$-value of 1.2. The end of the curve shows that the nitrogen content rises to the theoretical value of Ca-α-sialon which is 35.0 wt%. The mole concentration of nitrogen is increased from 13.2 to 14.8 (see equations 6.4 and 6.5). In summary, the first step is:
4.6 SiO<sub>2</sub> + 0.7 Al₂O₃ + 9.9 C + 3.3 N₂ → Si₄₆Al₄₀O₄₃N₆₆ + 9.9 CO (β-sialon)  

(6.4)

In the second step calcium and the extra nitrogen are being incorporated:

0.8 CaO + 2 Si₄₆Al₄₀O₄₃N₆₆ + 2.4 C + 0.8 N₂ → Ca₈₀Si₄₆Al₄₀O₃₂N₁₄₆ + 2.4 CO (α-sialon)  

(6.5)

It is assumed that an eutectic liquid of CaO and β-sialon promotes the formation of Ca-α-sialon. During this formation it is expected that Si-N as well as Al-O bonds have to be broken but how exactly the formation takes place is not in the scope of this work and is not investigated. The conversion of the mixed α/β-sialon which was obtained after firing at a temperature lower than 1500°C to a single-phase α-sialon by firing it at a higher temperature can be compared to reaction sintering [13]. The carbon was fully consumed in the first step due to complete nitridation. Then the Ca is incorporated in the material in the second step at higher temperature without further nitridation, in contradiction with equation 6.5.

### 6.5 Conclusions

The carbothermal reduction and nitridation of oxidic powder precursors is a possible route to prepare single-phase Ca-α-sialon in a relatively inexpensive way. There are two methods to obtain single-phase material. The first route is firing first at 1450°C, milling the obtained α/β mixture and refiring it at 1550-1700°C. Results from this route are comparable with the results found in literature. The second route is firing at 1500°C where the reaction can be completed in one step to form single-phase materials. The main intermediate product in the carbothermal reduction of the oxides is β-sialon with low z-value (< 1.2). A proposal for the formation mechanism of single-phase Ca-α-sialon has been made. First a β-sialon with low z-value is formed followed by the incorporation of the Ca-ions. Nitrogen contents determination and calculation of the cell parameters support this proposed mechanism. In contrast with the formation of β-sialon, SiC is not a major intermediate product.

**Note**

Although these results are published a few years ago, the subject is still attracting attention. Recently Komeya et al. [14] reported the synthesis of nanosize Ca-α-sialon grains using the carbothermal reduction/nitridation method.

### References


---

Carbothermal preparation and characterisation of Ca-α-sialon

8. JCPDS-card 33-261.
Tolerance

If only one opinion can be stated, there is no possibility to choose the best: one has to follow that opinion, wherever it leads. But if conflicting opinions are stated, one can choose. If there was only gold, we would not be able to tell its worth; but if we can compare it with other metals we see directly what is best.

Herodotus

Chapter 7
Densification behaviour of Ca-α-sialons

Abstract

In this chapter three methods of densification of Ca-α-sialon are compared. It is shown that both reaction hot pressing and reaction sintering are convenient methods to obtain densities close to theoretical values. For the densification of carbothermally prepared Ca-α-sialon powders the influence of the amount of CaO as a sintering additive has been shown to be significant. The highest density was reached with 15 wt% CaO (~97% relative density). The ‘mechanisms’ of sintering using the three mentioned methods (reaction hot pressing, reaction sintering and sintering Ca-α-sialon powder with CaO as a sintering additive) appear to be similar. First a rearrangement of the particles takes place due to the presence of a liquid phase, followed by a solution/precipitation mechanism. The mechanism for liquid phase sintering of Ca-α-sialon is similar to that described in literature for other Ln-α-sialon (Ln = Y, lanthanide's) materials.

7.1 INTRODUCTION

Silicon nitride has been of interest as a ceramic material for already quite a long time. The interest is due to the combination of several very good properties like high strength and fracture toughness, low thermal expansion, relatively high thermal conductivity and good oxidation/corrosion resistance at elevated temperatures in air [1,2]. Early work demonstrated that fully dense silicon nitride is hard to achieve and this is one of the major drawbacks of silicon nitride ceramics. However, with the development of β-sialon (Si₆₋₂Al₄O₁₄N₉₋₄) materials a new and very important approach for densification of silicon nitride based ceramics was taken [3]. To obtain fully dense silicon nitride based ceramic materials often the addition of alumina and/or yttria as sintering additives is applied, resulting in a liquid phase at the sintering temperature. The overall chemical composition and way of processing determine the microstructure and the mechanical properties of the final sialon materials [4,5]. Besides β-sialon also α-sialon material was discovered. This material with a similar structure as α-Si₃N₄
has the general formula: \( \text{M}_{m+n}\text{Si}_{4n+1}\text{Al}_{m+n}\text{O}_{2n}\) where \( M = \text{Li, Mg, Ca, Y or lanthanide,} \)
m, n are substitution coefficients and \( \text{val} = \text{valency of the metal ion} \). Since some 15 years these materials are intensively studied, especially the \( Y - \alpha\)-sialon materials [7]. Last years also more effort is put in study of the lanthanide \( \alpha\)-sialon materials [8-10]. On the contrary, only just recently more interest in Ca-\( \alpha\)-sialon systems was displayed. Papers were published for the Ca-\( \alpha\)-sialon materials concerning thermal stability [11] and more general dealing with these materials [11] and more general dealing with phases, properties and microstructure [12]. The Ca-\( \alpha\)-sialon system becomes even more interesting because it enables to incorporate other cations that were earlier thought to be impossible to substitute in the lattice [13]. Another application is adding luminescent cations [14]. From a scientific point of view one of the reasons to focus in our study on the Ca-\( \alpha\)-sialon system is the still fairly large unexplored area of this system. Another reason from an application point of view is that Ca sources like CaO or CaCO\(_3\) are much cheaper than yttria and the lanthanide oxides. Also, we showed that the waste material fly ash could be used to prepare Ca-\( \alpha\)-sialon materials with carbothermal synthesis [15].

In this chapter a comparison is made between various sintering procedures of Ca-\( \alpha\)-sialon materials viz: 1. Reaction hot uniaxial pressing; this is an expensive method with inflexibility concerning shaping possibilities. On the other hand it is a very convenient route to prepare fully densified samples that can be used to determine the properties of dense ceramic materials. 2. Reaction sintering; the starting materials are the same as mentioned for the first route, but there is more flexibility in shaping possibilities like slip casting (as we have used for the preparation of \( \beta\)-sialon [16,17]). 3. Sintering of carbothermally prepared powders. Besides the advantage of the flexibility in shaping, another advantage of this method is the use of cheaper oxide starting materials [18] compared to the other methods mentioned above.

### 7.2 Experimental methods

#### 7.2.1 Reaction hot-uniaxial-pressing and reaction sintering

The starting materials used were: Si\(_3\)N\(_4\) (LC-12N, Starck, \( \alpha/\beta\geq 95\% \), oxygen content \( \leq 2 \) wt%), Al\(_2\)O\(_3\) (APK30, 99.9% \( \alpha\)-Al\(_2\)O\(_3\), Sumitomo) and CaCO\(_3\) (Merck p.a.). The starting powders with the appropriate compositions (table 7.1) were mixed for 48 h in isopropanol (IPA) using Si\(_3\)N\(_4\) balls (powder : balls ratio = 2:1) in a polythene bottle on a roller bench. As binder material a mixture of 1 wt% of PEG 400 (Polyglykol 400 DAB8, Hoechst) and 1 wt% PEG 8000 (Polyglykol 8000S DAB8, Hoechst) was added for obtaining a better running powder. Then the isopropanol was removed by evaporation and the resulting powders were dried and fractionated by sieving (0.5 < \( x \) < 1 mm). Subsequently the powders were pressed uniaxially (10 MPa) followed by cold isostatic pressing at 250 MPa. Before hot pressing, the tablets were calcined at 900°C for 1 h in air in a special furnace to remove the binder and decompose the CaCO\(_3\) into CaO. Finally the tablets were hot pressed at 1700°C for 1 h at 35 MPa in a nitrogen atmosphere. The shrinkage during reaction hot pressing was determined by monitoring the displacement of the piston. The hot press used was a HP20 of Thermal Technology Ind. equipped with an Astor furnace model 100-4560-FP with graphite heating elements. The temperature was measured with a BGT-2 thermocouple. A graphite die (Ø 30 mm) and plunger were used. The heating rate was 10°C/min and no pressure was used before 1700°C was reached. Cooling down was performed naturally which means 20-30°C/min from 1700°C to about 1000°C. The reaction sintering experiments were carried out either in the dilatometer with bars (section 7.2.3) or in a graphite resistance furnace with tablets. The tablets (Ø 12 mm), mixed and pressed as described above, were heated in vacuum till 900°C, then nitrogen pressure (0.5 MPa) was applied. The sintering temperature was varied in the range 1700 - 1850°C and the heating rate was 10°C/min. In some experiments when the temperature had reached 1800°C, a high nitrogen pressure (10 MPa) was applied. The tablets were embedded in a powder bed consisting of a mixture of Si\(_3\)N\(_4\) and BN. Cooling down was also performed naturally (20-30°C/min).

#### Table 7.1. Starting compositions of powders used for reaction hot pressing (A, B, C) and reaction sintering (RS).

<table>
<thead>
<tr>
<th>m</th>
<th>n</th>
<th>( \text{CaCO}_3 ) (wt%)</th>
<th>Si(_3)N(_4) (wt%)</th>
<th>Al(_2)O(_3) (wt%)</th>
<th>( \text{Al}_2\text{O}_3 ) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>1</td>
<td>15.5</td>
<td>65.4</td>
<td>19.1</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1.5</td>
<td>15.5</td>
<td>61.8</td>
<td>20.1</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>2</td>
<td>8.3</td>
<td>69.7</td>
<td>13.6</td>
</tr>
<tr>
<td>RS</td>
<td>1.6</td>
<td>0.8</td>
<td>12.8</td>
<td>71.5</td>
<td>15.7</td>
</tr>
</tbody>
</table>

According to the phase behavioural diagram, the compositions A and B should give a single-phase \( \alpha\)-sialon material and C should be an \( \alpha/\beta\)-sialon composite material.

#### 7.2.2 Sintering of carbothermally prepared Ca-\( \alpha\)-sialon powder

Details with respect to the carbothermal preparation of Ca-\( \alpha\)-sialon powder are given in chapter 6 [18]. The grain size of the powder (attrition milled) measured using the sedigraph method is less than 1 \( \mu \text{m} \) \((d_{50} = 0.96 \mu \text{m})\). To determine the optimal processing conditions for sintering carbothermally produced Ca-\( \alpha\)-sialon powder (composition aimed at \( m = 1.6, n = 0.8 \) [18]) the influence of a number of variables was checked. An important parameter is the amount of sintering additive. This was studied using 10 and 15 wt% CaO as a sintering additive. Three types of experiments were done in the dilatometer with bars (section 7.2.3): 1. Carbothermally prepared powder was mixed (Si\(_3\)N\(_4\) balls, IPA, roller bench, 48h) with CaCO\(_3\) (to be decomposed to obtain CaO), pressed in bars and sintered, the decomposition of CaCO\(_3\) was performed in vacuum at 900°C; 2. To check the influence of residual carbon left after the carbothermal preparation the powder was first calcined at 700°C in air to remove the carbon, mixed as mentioned above with CaCO\(_3\), pressed in bars and sintered, the decomposition of CaCO\(_3\) was performed in vacuum at 900°C; 3. To check the additional influence of granulation and fractionation, carbothermally produced powder (calcined at 700°C in air), CaCO\(_3\) and PEG (section 7.2.1) as binder were mixed as above, pressed in bars, binder removed and CaCO\(_3\) decomposition at 900°C in air (as described in paragraph 7.2.1), and sintered. In addition to the bars for the dilatometer experiments tablets (Ø 12 mm) were
sintered in the same way as mentioned in step 3. All green tablets were sintered at 1700°C for 2 hrs in 0.5 MPa or 10 MPa of nitrogen in a graphite resistance furnace with a heating rate of 10°C/min. The tablets were embedded in a powder bed consisting of a mixture of Si₃N₄ and BN to avoid decomposition of the starting materials. Cooling down was performed naturally (20-30°C/min).

7.2.3 Dilatometry
To determine the optimal sintering temperature several dilatometry experiments were performed. They were carried out with bars in a graphite resistance furnace in a static nitrogen atmosphere (0.5 MPa). Heating rate was 5°C/min to get a good separation of the shrinkage rate peaks (in contrast with the sintering experiments using tablets where 10°C/min was used), temperature was held constant at the maximum shrinkage rate and no soaking time was applied at the top temperature. In the dilatometry experiments no protective powder bed was used, only a layer of BN. The dilatometer was set up to measure horizontal displacement. Mixtures for reaction sintering (section 7.2.1) and for sintering of carbothermally prepared powders (section 7.2.2) were pressed into bars (approximately 15x5x5 mm³), in some cases with the aid of PEG as a binder material (see above), first uniaxially (10 MPa) and then cold isostatically at 250 MPa. To remove the binder and decompose CaCO₃, the bars were carefully heated up in air to 900°C and soaked for one hour.

7.2.4 Characterisation
To characterise the different phases present in the samples X-ray diffraction was used (Rigaku Geigerflex, Cu-Kα radiation). The ceramic samples were polished and placed in the sample holder of the diffractometer. The scanning angle ranged from 10° to 90° 2θ and the scan speed was 0.002°/s (0.01°/step, 5 sec counting time). The density of the samples was measured using the Archimedes method by immersion in water. If the samples had still open porosity the density was determined from size and weight of the samples. The theoretical density is 3.22 g/cm³ [19].

7.3 RESULTS AND DISCUSSION

7.3.1 Phase Composition
During sintering no significant decomposition took place (weight loss < 2 wt%) for all three methods. From the X-ray diffraction pattern it was determined that both reaction hot pressed samples A and B were single-phase Ca-cα-sialon. Sample C was multi-phase, besides Ca-cα-sialon also traces of a cβ-sialon with low z-value and 12H were observed. This phase composition is in agreement with the results found by Hewett et al. [11], Wood et al. [20] and our own results (see chapter 4). From the diffractograms the cell parameters of the materials were calculated. With equation 3.7 the m-values were calculated to be m = 1.5 for A (a = 0.7851 nm, c = 0.5713 nm), m = 1.4 for B (a = 0.7844 nm, c = 0.5708 nm) and m = 0.9 for C.

7.3.2 Densification mechanism
The 'mechanism' of sintering appears to be rather similar for the three methods used. For our reaction hot pressing experiments it is not possible to determine the temperature of liquid phase formation due to the set up of the experiment. For the densification rate during reaction hot pressing of the materials no information was obtained before the pressure was applied at the top temperature of 1700°C. The shrinkage behaviour of the three different compositions can be qualitatively compared with each other at that temperature. The order in decreasing densification rate during reaction hot pressing is: sample B (m = 2, n = 1.5) = C (m = 1, n = 2) > A (m = 2, n = 1). The rate difference between sample B and C is very small but the rate difference of these two is significant compared to the densification rate of sample A (B = C > A). This is in agreement with what is expected if the rate is controlled by the oxygen content. Sample A is on the line n = m/2 and has the lowest amount of oxygen compared to the other two; moreover, the intentionally added oxygen originates only from CaO. Samples B and C meet the requirement n > m/2, the oxygen is present due to CaO and the addition of extra Al₂O₃. This means that a larger amount of liquid phase which causes a faster densification compared to sample A. The density of the reaction hot pressed tablets (3.20, 3.18 and 3.19 g/cm³ for samples A, B and C, respectively) was about 99% of the theoretical density.

The densification during reaction sintering of the composition m = 1.6, n = 0.8 as followed by dilatometry shows two major peaks in the shrinkage rate (figure 7.1). The first peak can be ascribed to particle rearrangement due to the eutectic formation at about 1350°C of a liquid phase from CaO and the oxide layers on the surface of the nitride starting materials. Between 1400 and 1500°C solution / precipitation of the nitride starting materials takes place. This temperature range is in agreement with the results reported by Hewett et al. [22].
hot pressing Ca-α-sialon where they found an increasing fraction of liquid phase due to redissolution of gehlenite to support densification. This gehlenite formation/redissolution is also observed with X-ray diffraction in our reaction sintering experiments (see chapter 5, [23]). Besides these major peaks some smaller peaks can be recognised. At ± 1560°C a small but clear peak is visible. Less pronounced peaks can be observed at ± 1610°C and ± 1660°C. Menon et al. [24] suggested several reactions to occur during densification of Ca-α-sialon by reaction hot pressing Ca-a-sialon where they found an increasing fraction of liquid phase due to also observed with X-ray diffraction in our reaction sintering experiments (see chapter 5, Menon et al. [24] suggested several reactions to occur during densification of Ca-α-sialon by the formation of the final Ca-α-sialon phase [24], corresponding with a similar reaction in our reaction hot pressing based on the shrinkage curves. The temperatures of the reactions identified in their study are in good agreement with the values we have found: 1. 1560°C, the eutectic formation [24] as in our case; 2. 1410 - 1450°C, ascribed to wetting of Si₃N₄ [24] corresponding with the start of the solution / precipitation mechanism; 3. 1550°C assigned to the formation of the final Ca-α-sialon phase [24], corresponding with a similar reaction in our reaction scheme proposed for reaction sintering (chapter 5). In results recently reported by Zhou et al. [25] for hot pressed Ca-α-sialon ceramics the gehlenite phase has disappeared at a similar temperature (1500°C) as in our experiments and they find the same trend of densification. Moreover, their results indicate that nearly full densification can be obtained at 1600°C and higher [25], in agreement with figure 1 and the densities we have obtained for the sintered tablets (95%, [23]).

**Figure 7.1.** Dilatometer curve of reaction mixture of CaO, Si₃N₄ and AlN with a composition Ca₆₀Si₃₀Al₂O₃N₁₅. The kink in the shrinkage curve at the holding temperature of 1350°C (15 min) is a result of an overshoot when it is reached. Final density of this sample is 90% of the theoretical density.

The influence of the different processing parameters (as the burn out of residual carbon and granulation) on the densification of carbothermally prepared Ca-α-sialon powders with 10 wt% CaO as sintering additive is shown in figure 7.2. Without treatment the powder hardly densifies; the relative density of the green samples is about 50% and the final relative density is about 65%. After only burn out of the residual carbon the relative density increases from 52% (green density) to 68% (ceramics). No oxygen is consumed anymore by the carbon during sintering resulting in a larger amount of liquid phase. A full treatment, meaning carbon removal as well as granulation (green density 55%), gives a relative density of 73% (ceramics). It is clear that both removal of residual carbon as well as granulation have a positive effect on the density of the Ca-α-sialon material. The granulation makes the density of the green body higher and consequently that of the sintered product. Densification is drastically enhanced if more sintering additive is used. The maximum density of the dilatometer samples achieved with 10 wt% CaO is 2.34 g/cm³ whereas for 15 wt% CaO a density of 3.06 g/cm³ is obtained. These values correspond to 73% and 95% of the theoretical density, respectively (ceramics). These densities are obtained for dilatometer samples and are always lower than densities obtained with tablets using a protective powder bed. When applying a higher pressure or a protective powder bed mixture as is the case in the furnace experiments for sintering carbothermally prepared powders the density becomes 3.11 g/cm³ (~97%) for samples with 15 wt% CaO as sintering additive. This value is obtained by a not yet optimised sintering process. Recently, another possibility was suggested to increase the densification by using dual cation sialons [26].

**Figure 7.2.** Comparison of dilatometer curves of carbothermally prepared Ca-α-sialon powders with 10 wt% CaO as sintering additive; not processed (1, 3) and processed (2, 4: i.e. calcined at 700°C in air to remove residual carbon and granulated before pressing).
If the dilatometer curves obtained with carbothermally prepared powder (figure 7.2) are compared to the curve obtained for reaction sintering (figure 7.1) several similarities and differences can be recognised. The formation of the eutectic liquid (first peak) is at the same temperature (1350°C) as in reaction sintering, this is obvious because the same melt is formed from CaO and Al-Si-O compounds present at the surface of the nitride or sialon starting materials. The wetting of the sialon starting material inducing the solution / precipitation mechanism (peak 2), however, takes place at a significantly higher temperature indicating a higher wetting temperature for sialon material (1500-1550°C) as compared to Si₃N₄ (1450°C). In the curves also other minor peaks are recognisable in the range 1650 - 1700°C. It seems that here also an intermediate phase dissolves similar to the reaction sintering route. As a final remark, we want to mention that the shapes of the measured sintering curves (carbothermal powders and reaction sintering) are similar to shrinkage curves reported for other α-sialon materials (containing lanthanide’s or Y) for both low pressure reaction sintering [27] as well as for reaction hot pressing [24]. This indicates similar densification mechanisms for all these materials.

7.4 CONCLUSIONS

Reaction hot pressing is a very efficient and convenient method to obtain almost fully dense Ca-α-sialon materials (~99% relative density). Reaction sintering is also a good method to achieve almost full densification (~95% relative density). The influence of the amount of CaO as a sintering additive on the densification of carbothermally prepared Ca-α-sialon powder has been shown to be significant. The highest density was reached with 15 wt% CaO (~97% relative density). It was shown that removal of residual carbon and granulation has a positive effect on the final density of the material. Use of a protective powder bed and higher nitrogen pressures further improves densification. The mechanisms of liquid phase sintering using the three mentioned methods (reaction hot pressing, reaction sintering and sintering of carbothermally prepared Ca-α-sialon powder with CaO as a sintering additive) are similar to each other. First a rearrangement of the particles takes place due to liquid formation at about 1350°C followed by a solution / precipitation mechanism at 1450-1550°C depending on the starting materials. The mechanism for sintering Ca-α-sialon is similar to the mechanism described in literature for other Ln-α-sialon (Ln = Y, lanthanide’s) materials. Full densification of the material can be accomplished by either higher nitrogen pressure or addition of more sintering additives. The former has the disadvantage of higher processing costs while the latter could influence the high temperature properties in a negative way, although this is not so significant for the Ca-α-sialon ceramics. Combination of Ca with other cations may further increase the density or ease the processing conditions.

References

19. JCPDS-card 33-261.
Joy and grief

Even mourning or lament over a deceased gives a certain peace. Certainly there is grief over the loss, but thinking of him, and seeing him as it were in what he has realised in life and remembering how he has lived, gives joy.

Aristoteles

Chapter 8
Influence of the $\alpha/\beta$-ratio on the properties of Ca-$\alpha/\beta$-sialon ceramics

Abstract

Ca-$\alpha$-sialon and Ca-$\alpha/\beta$-sialon ceramics with overall $m$-values in the range 0.25-1.6 and $n$-values from 0.5-4 were prepared by uniaxial hot pressing. The measured properties like hardness (15-23 GPa), fracture toughness (3.5-5.0 MPa$\cdot$m$^{0.5}$), Young’s modulus (250-325 GPa) and thermal conductivity (between 4 and 15 W/m K) are in fair agreement with literature data. The hardness and the Young’s modulus of the Ca-$\alpha/\beta$-sialon materials increase with increasing $\alpha/\beta$-ratio, while the thermal conductivity decreases and the fracture toughness remains more or less constant.

8.1 INTRODUCTION

It has been shown that selected non-oxide ceramic materials have similar or better properties compared to super alloys, except fracture toughness. Especially the high temperature mechanical properties are very good. Besides this, the chemical resistance and inertness is characteristic for these ceramic materials. Sialon ceramics have similar or even better properties than silicon nitride materials. In the literature so far only a few data are reported for fracture toughness and hardness for single-phase Ca-$\alpha$-sialon ceramics [1]. In this study several properties of Ca-$\alpha/\beta$-sialon ceramics with varying $\alpha/\beta$-ratio are investigated and compared to those of other sialon materials and $\text{Si}_3\text{N}_4$ ceramics.
8.2 EXPERIMENTAL METHODS

8.2.1 Preparation
To test the mechanical properties dense Ca-α-sialon and Ca-αβ-sialon ceramics were used. These samples were made by uniaxial reaction hot pressing (see chapter 4 + 7). The starting materials used are summarised in table 8.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>Oxygen [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si₃N₄ LC12-N</td>
<td>Starck</td>
<td>α/α+β&gt;95%</td>
<td>2</td>
</tr>
<tr>
<td>Si₃N₄ S-1177</td>
<td>Cerac Inc.</td>
<td>10%α, 90%β</td>
<td>0.7</td>
</tr>
<tr>
<td>SiO₂ Aerosil OX50</td>
<td>Degussa</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AlN grade ’C’</td>
<td>Starck</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Al₂O₃ AKP-30</td>
<td>Sumitomo</td>
<td>99.9% α-Al₂O₃</td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Merck</td>
<td>p.a.</td>
<td></td>
</tr>
</tbody>
</table>

The weighed-out compositions were corrected for the oxygen content in the starting materials. The amounts of starting materials used for the various compositions are presented in table 8.2.

<table>
<thead>
<tr>
<th>Nr</th>
<th>m/n</th>
<th>Si₃N₄ (1) [wt%]</th>
<th>Si₃N₄ (2) [wt%]</th>
<th>SiO₂ [wt%]</th>
<th>AlN [wt%]</th>
<th>Al₂O₃ [wt%]</th>
<th>CaCO₃ [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25/4</td>
<td>63.4</td>
<td>-</td>
<td>14.1</td>
<td>20.3</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.5/0.25</td>
<td>90.5</td>
<td>-</td>
<td>5.2</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.5/0.5</td>
<td>2.1</td>
<td>86.3</td>
<td>7.2</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.5/1</td>
<td>87.0</td>
<td>-</td>
<td>8.3</td>
<td>0.9</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.5/1.5</td>
<td>80.7</td>
<td>-</td>
<td>10.8</td>
<td>4.2</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.5/1.5</td>
<td>77.8</td>
<td>3.7</td>
<td>14.2</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5/1.5</td>
<td>80.7</td>
<td>-</td>
<td>10.8</td>
<td>4.2</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.5/1.5</td>
<td>80.7</td>
<td>-</td>
<td>10.8</td>
<td>4.2</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.75/1.5</td>
<td>77.3</td>
<td>-</td>
<td>12.9</td>
<td>3.4</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.6/1.36</td>
<td>67.7</td>
<td>-</td>
<td>19.4</td>
<td>12.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.2. Amounts of starting materials for reaction hot pressing Ca-αβ-sialon ceramics.

The weighed-out compositions were corrected for the oxygen content in the starting materials. The amounts of starting materials used for the various compositions are presented in table 8.2.

8.2.2 Characterisation
The phase composition of the samples was determined using X-ray diffraction. The hot pressed samples were ground, polished and placed in the sample holder of the diffractometer (Rigaku, Geigerflex, Cu-Kα). The scanning angle ranged from 10° to 97° 2θ and the scan speed was 0.012°/min, stepsize 0.01°, 5 s counting time, 35 kV, 20 mA. The approximate weight fraction was calculated from the distinguishable crystalline compounds. The density of the hot pressed samples was measured using the Archimedes method by immersion in water.

8.2.3 Hardness
The Vickers hardness of the various compositions is measured with a Leitz Miniload 2 with computer printer counter RZD-DO. The hardness was measured with equation 8.1 [3]:

\[ H_v = 1856.12 \cdot \frac{L}{d^2} \]

with: \( H_v \) : Vickers hardness (GPa)
\( L \) : Indentation load (N)
\( d \) : Indentation diagonal (μm)

The elasticity of the investigated materials causes some recovery capabilities after indentation. This recovery behaviour results in an apparently higher hardness. To determine this effect the Vickers hardness was measured for one sample (nr 2) at different loads (2, 3, 5, 10, 20N). For each load 10 indentations were made. The influence of recovery on the values of the hardness decreases with higher loads. For the other specimens the hardness was measured at 3 different loads (5N, 10N, 20N) to determine this influence. At lower loads the indentation size was so small that it was very difficult to measure the size accurately.

8.2.4 Young’s modulus
The Young’s modulus was determined by the pulse echo method (Panametrics 5223 ultrasonic equipment) measuring sound velocities. Besides this modulus the Poisson’s ratio can be determined also with this technique. From the sound velocities (longitudinal wave velocity, \( v_L \) and transversal wave velocity, \( v_T \)) the Poisson’s ratio and the Young’s modulus were calculated with [4]:

Influence of the α/β-ratio on the properties of Ca-αβ-sialon ceramics

earlier literature data. The hot pressing experiments are described in more detail in chapter 4. The heating rate was 10°C/min and no pressure was used before 1700°C was reached. Cooling down was performed by switching off the furnace, from 1700°C to about 1000°C with a rate of 20-30°C/min and slower at lower temperatures. At the top temperature a pressure of 35 MPa was applied to densify the tablets. This pressure was held for one or three hours. One of the samples was subsequently heated at 1500°C for three hours in the hot press equipment.
v = 1/2 - \frac{v_i^2}{2(v_i^2 - v_i^2)} \\
E = 2p v_i^2 (1 + v) 

where \( p \) is the density.

8.2.5 Fracture toughness

With the Young's modulus and the Vickers hardness the fracture toughness can be derived from indentation measurements. In literature many equations are reported [5, 6, 7, 8]. The equation commonly used in the literature is equation 8.4 reported by Anstis et al. [5]. It is calibrated for ceramics, glasses, glass ceramic and polycrystalline ceramics and therefore assumed to be suitable for sialon ceramics.

\[
K_{ic} = 0.016 \left( \frac{E}{H_v} \right)^{1/2} \left( \frac{L}{c_i} \right)^{3/2} 
\]

with:
- \( K_{ic} \): Fracture toughness (MPa \cdot m^{1/2})
- \( E \): Young's modulus (GPa)
- \( H_v \): Vickers hardness (GPa)
- \( L \): Indentation load (N)
- \( c_i \): Mean crack length (m)

Although it is known that the absolute value of the fracture toughness is strongly influenced by the type of measuring method, the indentation method is sufficiently reliable for direct comparison of several samples in order to determine the influence of the \( \alpha/\beta \)-ratio.

8.2.6 Thermal conductivity

The thermal conductivity of a ceramic, which is a very important property when used in thermal applications, is related to its thermal diffusivity by [9]:

\[
\lambda = c_v \cdot \rho_{bulk} \cdot a 
\]

with:
- \( \lambda \): Thermal conductivity (W\cdot m^{-1}\cdot K^{-1})
- \( c_v \): Specific heat capacity at constant volume (J\cdot kg^{-1}\cdot K^{-1})
- \( \rho_{bulk} \): Bulk density (kg\cdot m^{-3})
- \( a \): Thermal diffusivity (m^{2}\cdot s^{-1})

The thermal diffusivity \( a \) was measured with the photo flash method [10, 11] (XP20/XP, Compo Therm Oberflächentechnik GmbH). In this method the topside of the sample is irradiated with a light flash and the temperature is then measured as a function of time at the bottom side. The density was measured and the heat capacity data were taken from [12].

8.3 RESULTS AND DISCUSSION

8.3.1 Phase composition

The approximate weight fractions of the various phases in the composite materials are, together with their density, presented in table 8.3. In most of the samples residual \( \alpha \)-Si_{3}N_{4} is found, suggesting non-equilibrium situation.

<table>
<thead>
<tr>
<th>Nr</th>
<th>( m/n )</th>
<th>( \alpha )-Si_{3}N_{4}</th>
<th>( \alpha )-sialon</th>
<th>( \beta )-sialon</th>
<th>1SR/21R</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.25/4</td>
<td>-</td>
<td>-</td>
<td>88</td>
<td>12</td>
<td>3174</td>
</tr>
<tr>
<td></td>
<td>(1700/1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.5/0.25</td>
<td>12</td>
<td>-</td>
<td>88</td>
<td>-</td>
<td>3145</td>
</tr>
<tr>
<td></td>
<td>(1700/1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.5/0.5</td>
<td>6</td>
<td>-</td>
<td>94</td>
<td>-</td>
<td>3145</td>
</tr>
<tr>
<td></td>
<td>(1750/1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.5/1</td>
<td>30</td>
<td>36</td>
<td>34</td>
<td>-</td>
<td>3165</td>
</tr>
<tr>
<td></td>
<td>(1700/1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.5/1.5</td>
<td>17</td>
<td>56</td>
<td>27</td>
<td>-</td>
<td>3171</td>
</tr>
<tr>
<td></td>
<td>(1700/1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.5/1.5</td>
<td>13</td>
<td>57</td>
<td>30</td>
<td>-</td>
<td>3180</td>
</tr>
<tr>
<td></td>
<td>(1700/1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5/1.5</td>
<td>9</td>
<td>56</td>
<td>35</td>
<td>-</td>
<td>3180</td>
</tr>
<tr>
<td></td>
<td>(1700/3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.5/1.5</td>
<td>10</td>
<td>55</td>
<td>35</td>
<td>-</td>
<td>3185</td>
</tr>
<tr>
<td></td>
<td>(1700/3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.5/1.5</td>
<td>7</td>
<td>84</td>
<td>9</td>
<td>-</td>
<td>3187</td>
</tr>
<tr>
<td></td>
<td>(1700/3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.6/1.36</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>3199</td>
</tr>
<tr>
<td></td>
<td>(1700/3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. T: temperature [°C] / t: soaking time [hours].
b. SiO_{2} instead of Al_{2}O_{3} (see table 2).

Sample 1 is close to the \( \beta \)-sialon line far from the Si_{3}N_{4} corner and has no detectable \( \alpha \)-sialon phase; it consists of \( \beta \)-sialon and 1SR/21R phase. These results are in agreement with the results reported by Hewett et al. [13], Wood et al. [14] and chapter 4. Samples 2 and 3 are much closer to the Si_{3}N_{4} corner and contain \( \beta \)-sialon and \( \alpha \)-Si_{3}N_{4}. As samples 2 and 3 are in the \( \alpha/\beta \) region of the diagram (chapter 4) some \( \alpha \)-sialon phase was expected in these samples and no Si_{3}N_{4}, indicating incomplete reaction. In sample 4 besides \( \alpha \)-sialon, also a relatively large amount of \( \alpha \)-Si_{3}N_{4} is found although the composition is further from the Si_{3}N_{4} corner than samples 2 and 3. The phase compositions of samples 5 - 8 \( (m/n = 0.5/1.5) \) are not significantly different as well as the densities of the samples. There is no difference between the use of SiO_{2} or Al_{2}O_{3} to accomplish the desired composition (5 vs 6). The \( \alpha/\beta \) ratio of these samples is also corresponding with the phase behavioural diagram presented in chapter
the lever rule predicts a composition ratio of 5:3 and all specimens (5-8) satisfy this ratio despite the presence of α-Si₃N₄. Increasing the m-value leads to an increase in the α-sialon fraction. From 0% if $m = 0.25$ (sample 1) to 100% when $m = 1.6$ (sample 10). The $\alpha/\beta$-ratio increases for the samples with $m = 0.5$ with increasing n-value due to more oxygen present in the sample. Sample 9 has the highest $\alpha/\beta$ ratio, this corresponds with the expectation because the border of the single-phase area is at $m = 0.9$ (see chapter 4).

8.3.2 Mechanical and thermal properties

An example of the influence of the load on the apparent hardness is shown in figure 8.1. It shows that with increasing load the apparent hardness decreases and at 20N the load hardly influences the hardness value for this specimen. At 20N the maximum load was not reached yet because there were no cracks observed outside the indentations.

![Figure 8.1. Influence of the applied load on the apparent hardness of sample 2 (0.5/0.25).](image)

The dependence of the hardness on the load was described with the model of Bull et al. [15]:

$$H_m = H_0 \left(1 + \frac{\delta}{d_m}\right)^2 \quad (8.6)$$

In this equation $H_m$ and $d_m$ are the measured values for hardness (GPa) and indentation diameter (µm) respectively. The $\delta$-value is the amount of elastic recovery (µm) and $H_0$ is the true hardness. At high loads $d_m \gg \delta$ and $H_m$ tends to $H_0$. This $\delta$-value and $H_0$ were determined by a non-linear least mean squares method by fitting $H_m$ versus $d_m$ measurements (table 8.4).

<table>
<thead>
<tr>
<th>Nr</th>
<th>$H_v$ (20N) [GPa]</th>
<th>$H_0/\delta$ [GPa/µm]</th>
<th>$E$ [GPa]</th>
<th>$K_{IC}$ [MPa·m²]</th>
<th>$\lambda$ [W/m·K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.1±0.4</td>
<td>16.7/1.2</td>
<td>246</td>
<td>3.6±0.5</td>
<td>7.6</td>
</tr>
<tr>
<td>2</td>
<td>16.1±0.4</td>
<td>15.2/1.2</td>
<td>273</td>
<td>4.9±0.5</td>
<td>4.4</td>
</tr>
<tr>
<td>3</td>
<td>15.3±1.3</td>
<td>14.2/1.8</td>
<td>282</td>
<td>4.6±0.2</td>
<td>15.4</td>
</tr>
<tr>
<td>4</td>
<td>21.0±2.1</td>
<td>18.9/2.0</td>
<td>310</td>
<td>4.3±0.6</td>
<td>15.1</td>
</tr>
<tr>
<td>5</td>
<td>21.3±1.7</td>
<td>20.1/1.3</td>
<td>305</td>
<td>3.9±0.7</td>
<td>11.1</td>
</tr>
<tr>
<td>6</td>
<td>22.5±1.0</td>
<td>21.7/1.6</td>
<td>313</td>
<td>3.9±0.5</td>
<td>11.3</td>
</tr>
<tr>
<td>7</td>
<td>22.0±1.7</td>
<td>20.6/1.2</td>
<td>306</td>
<td>3.8±0.4</td>
<td>12.0</td>
</tr>
<tr>
<td>8</td>
<td>22.2±1.6</td>
<td>21.3/0.8</td>
<td>312</td>
<td>3.4±0.4</td>
<td>12.1</td>
</tr>
<tr>
<td>9</td>
<td>22.5±0.6</td>
<td>22.0/1.6</td>
<td>316</td>
<td>4.0±0.8</td>
<td>10.7</td>
</tr>
<tr>
<td>10</td>
<td>21.1±0.5</td>
<td>20.6/1.7</td>
<td>306</td>
<td>4.3±0.8</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table 8.4. Overview of properties of Ca-α/β-sialon ceramics with different overall compositions.

a. Hardness at load of infinity / recovery zone.

As is well known that generally β-sialon has a higher fracture toughness, and α-sialon has a higher hardness [16], we have evaluated the dependence of the measured properties on the α-sialon content. Figure 8.2 shows that with increasing amount of α-sialon phase in the ceramic the Vickers hardness of the material indeed increases till about 60 wt% α-sialon and above it is almost constant. A similar trend has been reported for Y-α/β-sialon materials, but with

![Figure 8.2. Relation between Vickers hardness $H_0$ or Young's modulus $E$ of Ca-α/β-sialon materials and the α-sialon content.](image)
lower absolute values [17]. Due to the presence of Ca-α-sialon the Young’s modulus also increases and becomes constant for higher α-sialon concentrations.

For the fracture toughness, no clear influence of the α-sialon content could be observed (figure 8.3). The highest values were found for the samples without Ca-α-sialon, while with increasing Ca-α-sialon content the fracture toughness more or less remains constant. Obviously, improvement of the hardness without decrease of the fracture toughness is possible. A further improvement in $K_{1c}$ can be achieved by optimisation of the processing resulting in acicular grains [18].

Our maximum value of 4.9 MPa·m$^{1/2}$ agrees fairly well with the fracture toughness measured with indentation reported for Si$_3$N$_4$ ceramics (4.7-5.2 MPa·m$^{1/2}$ [19]) and for β-sialon (5.4 MPa·m$^{1/2}$ [20]). However, it is significantly lower than 5.1 - 7.5 MPa·m$^{1/2}$ determined for Y-α/β-sialon materials with 3 and 4 point bending tests [21, 22], making a direct comparison with indentation results difficult.

The thermal conductivity of the Ca-α/β-sialon materials decreases for higher α-sialon contents (figure 8.4), as was also found for Y-α/β-sialon composites [12]. It can be understood from the fact that β-sialon has a higher thermal conductivity than α-sialon, which has more atoms in the unit cell resulting in enhanced phonon-phonon scattering. The maximum thermal conductivity (ca. 15 W/m·K) is higher than the values reported for α/β-sialon composite materials by Mitomo et al. [23]. All these values are significantly smaller than the maximum thermal conductivity reported for Si$_3$N$_4$ (150 W/mK [24]), because in sialon the O atoms on the N-sites and the Al atoms on the Si-sites act as scattering centres for phonons.

8.4 CONCLUSIONS

It has been shown that the properties of Ca-α/β-sialon composite materials are influenced by the composition of the materials i.e. the α/β-ratio. The Young’s modulus (245 GPa to 315 GPa) and the Vickers hardness (15-23 GPa) increase with increasing amount of α-phase in the composite, while the thermal conductivity (15-4 W/m·K) decreases and the fracture toughness remains more or less constant.

The Young’s modulus of Ca-α/β-sialon ceramics is higher than for β-sialon and similar to that of Si$_3$N$_4$ ceramics and Y-α-sialon. The Vickers hardness of single-phase Ca-α-sialon is much higher than for β-sialon and similar to the values of Si$_3$N$_4$ ceramics and Y-α-sialon, whereas the thermal conductivity of Si$_3$N$_4$ ceramics is much higher than for Ca-α/β-sialon ceramics.

When the properties of Ca-α/β-sialon materials are compared with related ceramics such as Si$_3$N$_4$, β-sialon and Y-α/β-sialon the properties are in the same order of magnitude. The main advantage of Ca-α/β-sialon materials is the price of raw materials and the high sinterability of the material compared to Si$_3$N$_4$ ceramics. Ca-α/β-sialon is a good competitor with Si$_3$N$_4$ ceramics and Y-α-sialon concerning the mechanical properties, but is not suitable for purposes where a high thermal conductivity is important.
Chapter 8

References


Summary

The research described in this thesis deals with the investigation of the preparation, characterisation and properties of Ca-α/β-sialon composite materials. In this work a comparison is presented between silicon nitride, β-sialon and rare earth α/β sialon and Ca-α-sialon and Ca-α/β-sialon composite materials.

In the literature review (chapter 2) several aspects of ceramics, particularly Si₃N₄ and related ceramics such as sialon are presented. The crystallographic structure and crystal chemistry is described and some uncertainties arise when looking at the relation between the cell parameters and the composition. Studies on the phase diagrams of silicon nitride based ceramics are focused on the rare earth sialons, especially the Y-sialon system. Only recently the interest in the Ca-sialon system increased and till now only a few parts of the phase diagram have been published. One of the interesting phenomena that have drawn a lot of attention is the transformation of α-sialon to another phase and reverse as a function of temperature. Again mainly rare earth materials are studied and the Ca-α-sialon system is hardly mentioned. If the properties of Ca-α/β-sialon materials are considered and compared to other ceramic materials it can be concluded that these are equally good or even better, based on the few data reported. However, the costs of the starting materials are considerably lower, even more when the carbothermal preparation can be used.

As mentioned above serious uncertainties about the relation between cell parameters and composition of Ca-α-sialon were encountered. In literature some relations were reported to describe the lattice parameters as a function of the composition (e.g. m and n-value) of α-sialons in general. However, these relations do not include the possibility to determine the m and n-value independently. In chapter 3 we propose improved relationships for describing the composition of Ca-α-sialon as a function of the lattice parameters. It is based on a linear regression fit from literature data. The m-value can be determined quite accurately while the n-value is not reliable. The validity is evaluated with several examples and the new model proved to describe the composition much better than the existing relations do.
The phase behavioural diagram of the Si₃N₄-Si₃O₆-Al₂O₃-AlN₄ system (β-sialon) is known as well as the line \( m = 2n \) in the \( \text{Si}_2\text{N}_2\text{O}_6\cdot\text{M}_4\text{Al}_3\text{N}_6\cdot\text{Al}_2\text{O}_{12}\cdot \text{N}_4 \) (α-sialon) systems at 1700°C with respect to the existing phases. For most of the rare earth α-sialon systems the shape of the single-phase α-sialon area is approximately known, but not the exact borders. In chapter 4 the borders of the single-phase Ca-α-sialon area are given in terms of \( m \) and \( n \)-values. To achieve these borders a new synthesis method was developed to obtain oxygen-poor Ca-α-sialon. This involves the in-situ nitridation of calcium metal. The most probable phase behavioural diagram was constructed on the basis of our results and literature data. It is shown that the cooling rate in reaction sintering experiments influences the composition of the samples. In the \( \alpha/\beta \) region temperature influences the composition. When a high cooling rate is used the observed \( m \)-values are lower than when a low cooling rate has been used. A transformation during cooling down is enhanced if more oxygen is present in the starting mixture (more liquid phase). As a consequence the calculated minimum \( m \)-value is higher at higher oxygen content. Hot pressing experiments were performed with oxygen correction to investigate the Ca-α-β-sialon region in more detail. Tentative tie lines were established in the \( \alpha/\beta \)-phase region.

In chapter 5 we describe the reaction sintering process of Ca-α-sialon. The reaction sintering starts at a temperature of 1350°C due to the formation of a Ca-Si-Al-O-N liquid resulting in particle rearrangement. At about 1450°C the solution precipitation mechanism is dominant promoting the formation of Ca-α-sialon. First, a Ca-rich α-sialon is formed \( (m = 1.9) \). Subsequently this Ca-rich α-sialon reacts with the Si₃N₄ and AlN that are still present until finally \( m = 1.2 \) is reached, indicating that not the total amount of Ca is incorporated in the α-sialon matrix (weighed-out composition \( m = 1.6 \)). As an intermediate product \( \text{Ca}_2\text{Al}_2\cdot\text{Si}_3\cdot\text{O}_7\cdot\text{N}_4 \) (gehlenite, belonging to the melilite group) was found. This is comparable to the intermediate products observed during the formation of Ln-α-sialon (Ln = Y, lanthanide) where \( \text{Ln}_2\text{Si}_3\text{O}_4\text{N}_4 \) melilite phases are formed. In the final product, besides Ca-α-sialon, some CaSiO₂ was observed due to the presence of oxygen in the nitride starting materials, which was not corrected for. From this chapter it can be concluded that a potential advantage of Ca-α-sialon over Ln-α-sialon is the lower processing temperature and the lower price of starting materials.

One of the objectives was to produce Ca-α-sialon and composite Ca-α/β-sialon material in a relatively inexpensive way. We know from literature that the material can be produced by reaction sintering, but the required starting materials are rather expensive. That is why a study was performed to investigate the carbothermal reduction and nitridation route to produce Ca-α-sialon for which the use of expensive starting powders is not necessary. This is a relatively cheap route where the possibility is available to use natural starting materials such as clay. In chapter 6 we showed that it is possible to prepare single-phase Ca-α-sialon in this way. There are two methods to realise the single-phase material. The first way is firing first at 1450°C, milling the obtained α/β mixture and fire it again at 1550-1700°C. The second way is firing at 1500°C where the reaction can be completed in ONE step. Furthermore we proposed a formation mechanism for obtaining this single-phase Ca-α-sialon by carbothermal reduction / nitridation. The main intermediate product in the carbothermal conversion of the oxides is β-sialon with a low \( z \)-value (<1.2). This is followed by the incorporation of Ca-ions, resulting in Ca-α-sialon. Nitrogen content determination and calculation of the cell parameters support this proposed mechanism. In contrast to the carbothermal synthesis of β-sialon, SiC is not a major intermediate product.

For most applications of the material it is necessary to be able to densify the material. In chapter 7 results are presented from different densification methods. Reaction hot pressing is a very efficient and convenient (for testing purposes) method to obtain almost fully dense materials (-99% relative density). Reaction sintering (0.5 MPa or 10 MPa nitrogen pressure) is also a good method to achieve almost full densification (-95%). However, this can be even further optimised by e.g. higher pressure. The influence of the amount of CaO as a sintering additive on the densification of carbothermally prepared Ca-α-sialon powder has been shown to be significant. The highest density was reached with 15 wt% CaO (-97% relative density). Moreover it was shown that removal of residual carbon and granulation had a positive effect on the final density of the material. The mechanisms of liquid phase sintering using the three mentioned methods (reaction hot pressing, reaction sintering and sintering of carbothermally prepared Ca-α-sialon powder with CaO as a sintering additive) are comparable to each other. First a rearrangement of the particles due to liquid formation at about 1350°C followed by a solution / precipitation mechanism at 1450-1550°C depending on the starting materials (mixture oxides/nitrides vs. sialons).

Chapter 8 shows that the properties of Ca-α/β-sialon composite materials are influenced by the composition of the materials i.e. the \( \alpha/\beta \)-ratio. The Young’s modulus (245 GPa to 315 GPa) and the Vickers hardness (15-23 GPa) increase with increasing amount of α-phase in the composite, while the thermal conductivity (15-4 W/m·K) decreases and the fracture toughness remains more or less constant. This enables to make a compromise between hardness and toughness and a tailor-made ceramics can be obtained.

When the properties are compared with those of materials such as Si₃N₄, β-sialon and Y-α/β-sialon ceramics the properties are in the same order of magnitude. The Young’s modulus is higher than for β-sialon and similar to that of Si₃N₄ and Y-α/β-sialon ceramics. The Vickers hardness of single-phase Ca-α-sialon is much higher than for β-sialon, and similar to the values of Si₃N₄ and Y-α/β-sialon ceramics. The thermal conductivity of Si₃N₄ ceramics is much higher than for Ca-α/β-sialon ceramics. Ca-α/β-sialon is a good competitor with Si₃N₄ and Y-α-sialon ceramics concerning the mechanical properties, but with Y-α/β-sialon it is not suitable for purposes where thermal conductivity is important.
In conclusion when the Ca-α-sialon and Ca-α/β-sialon materials are compared to the well-known 'traditional' structural ceramic materials they are equally good or even better. Especially the mechanical properties are very good. However, the properties of the Ca-sialon materials do not completely justify the right to say that it is better to use Ca-sialon materials instead of other materials. There are other considerations to prefer Ca-sialon materials over for example Si₃N₄ ceramics. The sinterability of Ca-α/β-sialon is very high, even compared to Y-sialon and other rare earth sialon systems. To sinter Si₃N₄ sintering additives have to be used. Alumina and yttria are commonly used, so it is even questionable if you can refer to the material as sintered Si₃N₄ ceramics. It is more likely to speak of a sialon material.

Another advantage is the higher stability of the Ca-α/β-sialon ceramics if temperature is considered. Many rare earth sialon materials transform from α to β phase more easily than in the Ca-sialon system. Moreover, it is possible to incorporate cations in combination with Ca that cannot be incorporated on their own. This is opening new perspectives for other applications that were never thought of before.

The main advantage of the Ca-α-sialon and Ca-α/β-sialon materials is the price of the starting materials. The price is much lower than for rare earth sialon materials and when the carbothermal reduction/nitridation route is used it is even more favourable. Si₃N₄ powder can also be produced with a carbothermal reduction/nitridation process. But the fact of the lower sinterability is still present and this will phase out the profit of the less expensive production process.

Main conclusions of this work
Apart from the general results similar to those reported for other α-sialon systems the following specific original results can be shown.

The phase diagram of the Si₁₂N₁₆-Μ₆Al₁₂N₁₆-Al₂O₃N₄ system is temperature dependent. This causes implications for the processing and the application of the materials.

A new model for the relation between composition and lattice parameters was derived. Independent and external results showed the successfullness of the model.

The influence of the α/β-ratio on the properties shows that a reasonable compromise can be obtained between the hardness and the toughness of the material.

The feasibility of the carbothermal synthesis is shown for the preparation of Ca-α-sialon in ONE step. This makes the advantage in cost price of Ca-α-sialon over other sialon materials even bigger.
betrouwbaar. De geldigheid is geëvalueerd met verscheidene monsters en het nieuwe model bleek de compartiment te beschrijven van de bestaande relaties.

Zowel het fasegedragsdiagram van het Si₃N₄-Si₃O₆-Al₂O₃-Al₂N₄ systeem (β-sialon) als dat van de lijn m = 2n in de Si₃N₄-MₓAl₁₅-N₁₆-Al₂O₃N₄ (α-sialon) systemen bij 1700°C zijn bekend ten aanzien van de voorkomende fasen. De vorm van het eenvoudig gebied van de meeste zeldzame aard sialon systemen is ongeveer bekend, maar niet de exacte grenzen. In hoofdstuk 4 zijn de grenzen van het eenvoudig Ca-α-sialon aangegeven in termen van m en n-waarden. Om deze grenzen te realiseren is er een nieuwe synthetische methode ontwikkeld om zuurstof-arme Ca-α-sialon te verkrijgen. Deze bevat een in-situ nitrering van calcium metaal. Zowel het fasegedragsdiagram van het Si₃N₄-Si₃O₆-Al₂O₃-Al₂N₄ systeem van de lijn temperatuur de samenstelling. Als er een hoge afkoelsnelheid wordt gebruikt zijn de bleek de compositie veel beter te beschrijven dan de bestaande relaties. Experimenten de samenstelling van de monsters en literatuurgegevens. Er is aangetoond dat de afkoelsnelheid in de reactie-sinter mechanismen van het eenvoudig Ca-α-sialon is ongeveer bekend, maar niet de exacte grenzen. In hoofdstuk 6 hebben we aangetoond dat eenfasig Ca-α-sialon op deze manier gemaakt kan worden. Er zijn twee mogelijkheden om het eenvoudig materiaal te verkrijgen. De eerste manier is om eerst te stoken bij 1450°C, dan het α/β mengsel te malen en het opnieuw te stoken bij 1550-1700°C. Een tweede manier is stoken bij 1500°C waar de reactie in EEN stap vrijwel voltooid. Verder hebben we een vormingsmechanisme voorgesteld om deze eenfasige Ca-α-sialon door carbothermische reductie / nitrering te verkrijgen. Het voornaamste product in de carbothermische omzetting van de oxides is een β-sialon met een lage z-waarde (-1.2). Dit wordt gevolgd door de inbouw van Ca-ioni, leidend tot Ca-α-sialon. Stikstofgehaltebepaling en berekening van de roostoparameters ondersteunen dit mechanisme. In tegenstelling tot de carbothermische synthese van β-sialon is hier SiC geen belangrijk tussenproduct.

Voer de meeste toepassingen van het materiaal is het noodzakelijk om het materiaal te kunnen verdichten. In hoofdstuk 7 zijn resultaten gepresenteerd van een aantal verschillende verdichtingsmethoden. Heetpersen is een erg efficiënte en handige (voor testdoeleinden) manier om bijna volledig verdicht materiaal (-99% relatieve dichtheid) te verkrijgen. Reactie sinten (0.5 MPa of 10 MPa stikstofdruk) is ook een goede methode om een bijna volledige verdichting te krijgen (-95%). Echter, dit kan nog verder geoptimaliseerd worden door bijvoorbeeld hogere druk en sneller temperatuur afkoelen. De invloed van het gehalte CaO als sinteradditief op de verdichting van carbothermisch geproduceerd Ca-α-sialon poeder is significant. De hoogste dichtheid werd bereikt met 15 w% CaO (-97%). Daarbij is laten zien dat verwijdering van restkoolstof en granuleren een positief effect heeft op de uiteindelijke dichtheid van het materiaal. De mechanismen van het vloeibare fase sinten voor de drie genoemde methoden (reactie heetpersen, reactie sinten en sinten van carbothermisch bereid Ca-α-sialon poeder met CaO als sinteradditief) zijn met elkaar vergelijkbaar. Eerst een beschouwing van de uitgangsmaterialen (mengsel oxides/nitrides vs. sialons).

Een van de doelen was de productie van Ca-α-sialon en Ca-α/β-sialon composiet materiaal op een relatief goedkope manier. We weten uit de literatuur dat het materiaal gemaakt kan worden door reactie-sinteren, maar de benodigde uitgangsmaterialen zijn tamelijk duur. Daarom is er een studie uitgevoerd om de carbothermische reductie en nitreringroute als bereidingsmethode voor Ca-α-sialon te bestuderen. Dit is een relatief goedkope manier met de mogelijkheid om natuurlijke uitgangsmaterialen zoals klei te gebruiken. In hoofdstuk 6 hebben we aangetoond dat eenfasig Ca-α-sialon op deze manier gemaakt kan worden. Er zijn twee mogelijkheden om het eenvoudig materiaal te verkrijgen. De eerste manier is om eerst te stoken bij 1450°C, dan het α/β mengsel te malen en het opnieuw te stoken bij 1550-1700°C. Een tweede manier is stoken bij 1500°C waar de reactie in EEN stap vrijwel voltooid. Verder hebben we een vormingsmechanisme voorgesteld om deze eenfasige Ca-α-sialon door carbothermische reductie / nitrering te verkrijgen. Het voornaamste product in de carbothermische omzetting van de oxides is een β-sialon met een lage z-waarde (-1.2). Dit wordt gevolgd door de inbouw van Ca-ioni, leidend tot Ca-α-sialon. Stikstofgehaltebepaling en berekening van de roostoparameters ondersteunen dit mechanisme. In tegenstelling tot de carbothermische synthese van β-sialon is hier SiC geen belangrijk tussenproduct.

Voor de meeste toepassingen van het materiaal is het noodzakelijk om het materiaal te kunnen verdichten. In hoofdstuk 7 zijn resultaten gepresenteerd van een aantal verschillende verdichtingsmethoden. Heetpersen is een erg efficiënte en handige (voor testdoeleinden) manier om bijna volledig verdicht materiaal (-99% relatieve dichtheid) te verkrijgen. Reactie sinten (0.5 MPa of 10 MPa stikstofdruk) is ook een goede methode om een bijna volledige verdichting te krijgen (-95%). Echter, dit kan nog verder geoptimaliseerd worden door bijvoorbeeld hogere druk. De invloed van het gehalte CaO als sinteradditief op de verdichting van carbothermisch geproduceerd Ca-α-sialon poeder is significant. De hoogste dichtheid werd bereikt met 15 w% CaO (-97%). Daarbij is laten zien dat verwijdering van restkoolstof en granuleren een positief effect heeft op de uiteindelijke dichtheid van het materiaal. De mechanismen van het vloeibare fase sinten voor de drie genoemde methoden (reactie heetpersen, reactie sinten en sinten van carbothermisch bereid Ca-α-sialon poeder met CaO als sinteradditief) zijn met elkaar vergelijkbaar. Eerst een beschouwing van de uitgangsmaterialen (mengsel oxides/nitrides vs. sialons).

In hoofdstuk 5 beschrijven we het reactie-sinter proces van Ca-α-sialon. Het reactie-sinteren begint bij een temperatuur van 1350°C door de vorming van een Ca-Si-Al-O-N vloeistof met als resultaat een deeltjesverschuiving. Bij ongeveer 1450°C is het solutie/precipitatie mechanisme dominant waardoor de vorming van Ca-α-sialon wordt stimuleerd. Eerst wordt er een Ca-rijke α-sialon gevormd (m = 1.9). Vervolgens reageert deze Ca-rijke α-sialon met de aanwezige Si₃N₃ en AlN totdat uiteindelijk m = 1.2 wordt bereikt, wat wijst op een niet volledige inbouw van Ca in de α-sialon matrix (inweegsamenstelling m = 1.6). Als een tussenproduct werd Ca₂Al₅Si₃N₃O₇N₂ (gelehteniet, behorend tot de meliliet groep) gevonden. Dit is vergelijkbaar met de tussenproducten die gevonden zijn tijdens de vorming van Ln-α-sialon (Ln = Y, lanthanide) waar Ln₂Si₃O₃N₄ (gelehteniet) behorend tot de meliliet groep) gevonden. In het eindproduct is naast Ca-α-sialon ook iets CaSiO₃ gevonden als gevolg van de aanwezige zuurstof in de nitridische uitgangsmaterialen waar niet voor was gecorrigeerd. Uit de resultaten van deze hoofdstuk kunnen we de conclusie trekken dat een potentieel voordeel van Ca-α-sialon de lagere proces temperatuur en de lagere kookpunt van de uitgangsmaterialen is tegenover de Ln-α-sialon.
hardheid van eenfasig Ca-α-sialon is veel hoger dan die van β-sialon en vergelijkbaar met die van Si₃N₄ en Y-α/β-sialon keramiek. De thermische geleiding van Si₃N₄ is veel hoger dan die van Ca-α/β-sialon. Ca-α/β-sialon is een goede rivaal van Si₃N₄ en Y-α/β-sialon keramiek wanneer gekeken wordt naar de mechanische eigenschappen, maar samen met Y-α/β-sialon is het niet geschikt in toepassingen waar de thermische geleiding een belangrijke rol speelt.

Samenvattend: als de Ca-α-sialon en Ca-α/β-sialon materialen vergeleken worden met de algemeen bekende ‘traditionele’ structurele keramiek dan zijn ze even goed of zelfs beter. Vooral de mechanische eigenschappen zijn erg goed. Echter, de eigenschappen van het Ca-sialon materiaal rechtvaardigen het niet volledig om te zeggen dat het beter is om Ca-sialon materiaal te gebruiken in plaats van een ander materiaal. Er zijn andere overwegingen om Ca-α/β-sialon materiaal te verkiesgen boven bijvoorbeeld Si₃N₄. De sinterbaarheid van Ca-α/β-sialon is erg hoog, zelfs vergeleken met Y-sialon en andere zeldzame aard sialon systemen. Om Si₃N₄ te sinteren moeten sinteradditieven toegevoegd worden. Over het algemeen worden alumina en yttria gebruikt en is het zelfs de vraag of het materiaal aangeduid moet worden met gesinterd Si₃N₄. Het zou misschien beter zijn om spreken van een sialon.

Een ander voordeel is de hogere stabiliteit van Ca-α/β-sialon materiaal met betrekking tot de temperatuur. Veel zeldzame aard sialon materialen zetten makkelijker om van de α-fase naar de β en andere fasen dan het Ca-α/β-sialon systeem. Daarnaast is het mogelijk om cationen in te bouwen in combinatie met Ca die op zichzelf niet in het rooster kunnen worden ingebouwd. Dit opent perspectieven voor toepassingen waar nu nog niet aan gedacht is.

Het grootste voordeel van Ca-α-sialon en Ca-α/β-sialon is de prijs van de uitgangsstoffen. De prijs is veel lager dan die voor zeldzame aard sialon materialen en als de carbothermische synthese route wordt gebruikt is dit nog voordeliger. Si₃N₄ poeder kan ook carbothermisch gemaakt worden, maar het feit van de lagere sinterbaarheid blijft. Dit zal het voordeel van de lagere productiekosten weer tenietdoen.

Belangrijkste conclusies uit dit werk

Apart van de algemene resultaten vergelijkbaar met die gerapporteerd voor andere α-sialon systemen kunnen de volgende specifieke originele resultaten worden gepresenteerd.

Het fasediagram van het Si₁₂N₁₆-M₆Al₁₂N₁₆-Al₁₂O₁₂N₄ systeem is temperatuur afhankelijk. Dit veroorzaakt implicaties ten aanzien van het bereidingsproces en de toepassingen van het materiaal.

Een nieuw model voor de beschrijving van de relatie tussen roosterparameters en de samenstelling is ontwikkeld. Onafhankelijke externe resultaten hebben het succes van het model al laten zien.

De invloed van de α/β-verhouding in de α/β-sialon materialen op de eigenschappen laten zien dat een redelijke compromis gekregen kan worden tussen de hardheid en de taaiheid van het materiaal. Het is aangetoond dat de carbothermische synthese geschikt is om Ca-α-sialon in EEN stap te maken. Dit maakt het voordeel van de kostprijs van Ca-α-sialon ten opzichte van andere sialon materialen nog groter.
Self-knowledge

We are all beautiful as long as we dare to be ourselves. We become ugly when we want to be someone else. In other words: our self-knowledge is our beauty; people that don’t know themselves are ugly.

Plotinus

Zelfkennis

Wij zijn allemaal mooi zolang wij onszelf durven zijn. Lelijk worden we pas wanneer we iemand anders willen wezen. Met andere woorden: onze zelfkennis is onze schoonheid; wie zichzelf niet kent is lelijk.

Plotinus

Dankwoord

Hoewel mijn naam als enige op dit proefschrift staat kan een omvangrijk werk als dit natuurlijk niet zijn volbracht zonder de inzet en belangstelling van velen. Hierbij wil ik graag een aantal mensen in het bijzonder bedanken voor hun bijdrage.

Allereerst mijn promotor Prof. Dr. R. Metselaar, Dr. R.A. Terpstra (TNO/TPD) en de IOP-commissie (financiële gedeelte) voor de mogelijkheid die zij mij geboden hebben om het onderzoek te mogen doen en de belangstelling die ze gesteld hebben in het onderzoek. I am grateful to Prof. Dr. S. Hampshire of the University of Limerick that he wants to act as the second promoter for this thesis. Mijn copromotor Dr. Bert Hintzen voor de inhoudelijke discussies, ideeën over experimenten, adviezen en zijn niet aflatende enthousiasme en steun die hij mij in het werk heeft gegeven.

Het onderzoek is in samenwerking uitgevoerd met TNO/TPD afdeling Technisch Keramiek. Ik ben Rinse Terpstra en Han van der Heijde dankbaar voor de prettige samenwerking en voor het opstarten van dit onderzoek. Het heeft mij wat meer houvast gegeven bij de start van mijn onderzoek. Tevens ben ik Joost van Eijk en Han erkentelijk voor de technische ondersteuning bij tal van experimenten en de hulp die ze verleend hebben aan ‘mijn’ studenten. Ook de rest van de medewerkers van TNO/TPD zal ik niet vergeten vanwege de fijne sfeer.

Een flink gedeelte van het praktische werk is uit gevoerd door studenten in het kader van hetzij hun afstuderen, hetzij hun stage. Ik kan hun namen hier natuurlijk niet vergeten en ik wil ze hier dan ook in min of meer chronologische volgorde noemen: Djoni Sutanto, Peter Paul Geluk, John Klok, Slobodan Markovski, Miroslav Kollar, Cornel Schreuders en Erwin Dits.

Dr. Inz. Malgorzata Sopicka Lizer and Prof. Mingyuan Chen for their pleasant company as my roommates and the discussions we had. Although their work is not reported in this thesis, they gave me supplementary information that contributed to my work.

Voor de preparatie en analyses van mijn materiaal en andere zaakjes kon ik altijd een beroep doen op Marco Hendrix, Hans Heijligers, Gerrit Bezemer, Henk van der Weijden en Toon Rooijakkers.

Mijn collega’s bij de vakgroep Vaste Stof Chemie en Materialen, die de periode van het onderzoek tot een aangename periode maakte. Dan bedoel ik niet alleen tijdens werkuren, maar ook de verbeten strijd tijdens de lunchpauze en de gezellige uitsjes buiten werktijd.

Prof. Dr. G. de With ben ik erkentelijk voor de mogelijkheid die hij mij geboden heeft om het proefschrift af te maken.

Natuurlijk Judith, die mij het laatste zetje heeft gegeven om het tot een goed einde te brengen. En laat but not least mijn ouders zonder wie ik er niet zou zijn en dus ook dit werk niet en familie en vrienden die mij tijdens de gehele periode hebben ondersteund.
Relaxation

I enjoy myself because I also like to do other things than to work.

Euripides

List of publications and conference presentations


2. **Poster presentation**: Carbothermal preparation and characterisation of Ca-α-sialon, 3rd Meeting European Ceramic Society (ECERS), Madrid 1993.


---

### Curriculum Vitae


Na deze studie verhuisde hij opnieuw, nu naar Eindhoven om daar een promotieonderzoek te starten. Het onderwerp was 'Processing of non-oxide ceramics'. Het promotieonderzoek is in samenwerking gedaan met TPD/TNO afdeling Technische Keramiek. Hij onderzocht de bereiding, karakterisering en verwerking van Ca-α-sialon en Ca-α/β-sialon composiet materialen. De resultaten van dit onderzoek staan beschreven in dit proefschrift. In deze tijd heeft hij veel plezier gehad in het begeleiden van studenten (zowel buitenlandse als Nederlandse) die in het kader van een stage of afstuderen een gedeelte van het onderzoek hebben uitgevoerd.

Tussen het praktische werk en de uiteindelijke verschijning van dit proefschrift heeft hij 2 jaar bij Philips, bij het Centrum voor Fabricage Technologie gewerkt. Hij heeft daar een aantal projecten uitgevoerd op het gebied van zeefdrukken. Daaronder valt onder andere hoge resolutie zeefdrukken, meerlaagszeefdrukken, bereiding en aanpassen van pasta’s en bestudering van de reologie van pasta’s en inkten.
1. The synthesis of Ca-α-sialon can be performed in ONE step by the carbothermal reduction / nitridation route.


2. The model described in this thesis considering the relations between the composition and lattice parameters of Ca-α-sialon works better than the models reported in literature for Ca-α-sialon systems.

Chapter 3.

3. The border of the single-phase α-sialon area shifts to the β-sialon line when the temperature increases.

Chapter 4.

4. In the future no snooker player will dominate the sport as Steve Davis did in the eighties and Stephen Hendry in the nineties.

5. Positive discrimination is also discrimination and therefore does not contribute to a solution in striving for equality.
6. Hoge resolutie zeefdrukken wordt voornamelijk gestuurd door de reologie van de inkt i.p.v. de instellingen van de zeefdrukmachine en de gebruikte zeef.

High-resolution screen-printing is mainly controlled by the rheology of the ink or paste and not by the settings of the screen printer and screen used.

7. Er zijn geen regels voor naamgeving van keramiek als sialon en siliciumnitride, het lijkt nu een persoonlijke voorkeur en daarom is er een normalisatie nodig.

There are no rules for denomination of ceramics like sialon and silicon nitride, it seems a personal preference and therefore a normalisation is necessary.

8. De gemeente Eindhoven zegt te streven naar een vlotte doorstroming van het verkeer, maar door de genomen maatregelen is die niet toegenomen, eerder afgenomen.

The Eindhoven city council states it pursues a better management of traffic, but the measures taken have not improved traffic but caused even more problems.

9. Mensen die bewust hebben gekozen om bij een vliegveld of industrieterrein te gaan wonen hebben niet het recht te klagen over overlast.

People that consciously chose to live near an airport or industrial estate do not have the right to complain about inconvenience.

10. De dingen die we moeten leren voordat we ze kunnen doen, leren we door ze te doen.

The things we have to learn before we can do them, we learn by doing them. 

*Aristoteles.*