Spark Plasma Sintering of Si$_3$N$_4$-Based Ceramics
-Sintering mechanism-Tailoring microstructure-Evaluating properties-

BY

HONG PENG

Department of Inorganic Chemistry
Stockholm University

2004
In the memory of my father

To my mother

Work while you work;

Play while you play;

This is the way;

To be cheerful and gay.

—— A. D. Stoddart
Spark Plasma Sintering (SPS) is a promising rapid consolidation technique that allows a better understanding and manipulating of sintering kinetics and therefore makes it possible to obtain Si$_3$N$_4$-based ceramics with tailored microstructures, consisting of grains with either equiaxed or elongated morphology.

The presence of an extra liquid phase is necessary for forming tough interlocking microstructures in Yb/Y-stabilised $\alpha$-sialon by HP. The liquid is introduced by a new method, namely by increasing the O/N ratio in the general formula RE$_x$Si$_{12-(3x+n)}$Al$_{3x+n}$O$_n$N$_{16-n}$ while keeping the cation ratios of RE, Si and Al constant.

Monophasic $\alpha$-sialon ceramics with tailored microstructures, consisting of either fine equiaxed or elongated grains, have been obtained by using SPS, whether or not such an extra liquid phase is involved. The three processes, namely densification, phase transformation and grain growth, which usually occur simultaneously during conventional HP consolidation of Si$_3$N$_4$-based ceramics, have been precisely followed and separately investigated in the SPS process.

The enhanced densification is attributed to the non-equilibrium nature of the liquid phase formed during heating. The dominating mechanism during densification is the enhanced grain boundary sliding accompanied by diffusion- and/or reaction-controlled processes. The rapid grain growth is ascribed to a dynamic ripening mechanism based on the formation of a liquid phase that is grossly out of equilibrium, which in turn generates an extra chemical driving force for mass transfer.

Monophasic $\alpha$-sialon ceramics with interlocking microstructures exhibit improved damage tolerance. Y/Yb- stabilised monophasic $\alpha$-sialon ceramics containing approximately 3 vol% liquid with refined interlocking microstructures have excellent thermal-shock resistance, comparable to the best $\beta$-sialon ceramics with 20 vol% additional liquid phase prepared by HP.

The obtained sialon ceramics with fine-grained microstructure show formidably improved superplasticity in the presence of an electric field. The compressive strain rate reaches the order of 10$^{-2}$ s$^{-1}$ at temperatures above 1500°C, that is, two orders of magnitude higher than that has been realised so far by any other conventional approaches. The high deformation rate recorded in this work opens up possibilities for making ceramic components with complex shapes through super-plastic forming.
This thesis is based on the following papers:


Papers not included in this thesis:


The papers have been reprinted with kind permissions.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>I</td>
</tr>
<tr>
<td>LIST OF PAPERS</td>
<td>III</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>1.1 Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.1.1 Si₃N₄ phases</td>
<td>1</td>
</tr>
<tr>
<td>1.1.2 α-sialon and β-sialon</td>
<td>3</td>
</tr>
<tr>
<td>1.1.3 Conventional sintering methods</td>
<td>4</td>
</tr>
<tr>
<td>1.2 Liquid phase sintering</td>
<td>6</td>
</tr>
<tr>
<td>1.2.1 Classic liquid phase sintering</td>
<td>6</td>
</tr>
<tr>
<td>1.2.2 Liquid-phase sintering of sialon ceramics</td>
<td>8</td>
</tr>
<tr>
<td>1.2.3 Densification mechanisms of Si₃N₄-based ceramics</td>
<td>10</td>
</tr>
<tr>
<td>1.3 Spark Plasma Sintering (SPS)</td>
<td>12</td>
</tr>
<tr>
<td>1.3.1 General background</td>
<td>12</td>
</tr>
<tr>
<td>1.3.2 SPS instrument</td>
<td>13</td>
</tr>
<tr>
<td>1.3.3 Consolidation mechanism</td>
<td>14</td>
</tr>
<tr>
<td>1.3.4 Features and applications of SPS</td>
<td>15</td>
</tr>
<tr>
<td>1.4 Properties of Si₃N₄-based ceramics</td>
<td>17</td>
</tr>
<tr>
<td>1.4.1 Mechanical properties</td>
<td>18</td>
</tr>
<tr>
<td>1.4.2 Thermal-shock resistance</td>
<td>18</td>
</tr>
<tr>
<td>1.4.3 Superplasticity of ceramics</td>
<td>19</td>
</tr>
<tr>
<td>2. AIM OF THIS THESIS</td>
<td>22</td>
</tr>
<tr>
<td>3. EXPERIMENTAL</td>
<td>23</td>
</tr>
<tr>
<td>3.1 Starting materials</td>
<td>23</td>
</tr>
<tr>
<td>3.2 Composition design</td>
<td>23</td>
</tr>
<tr>
<td>3.2.1 Rare-earth stabilised α-sialons</td>
<td>23</td>
</tr>
<tr>
<td>3.2.2 Lithium stabilised monolithic α- and duplex α/β-sialon</td>
<td>25</td>
</tr>
<tr>
<td>3.2.3 Monolithic β-sialon</td>
<td>25</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 Overview

Silicon nitride (Si$_3$N$_4$) based ceramics have been intensively studied for more than 40 years due to their potential application in high-temperature structural components. They can withstand very harsh environments where metals and polymers fail. The principal excellent properties of silicon nitride (Si$_3$N$_4$) based ceramics are: high strength and wear resistance, low density, high decomposition temperature and oxidation resistance, low coefficient of friction and high resistance to chemical corrosion$^{1-11}$.

1.1.1 Si$_3$N$_4$ phases

Silicon nitride occurs in three modifications, the well-known $\alpha$- and $\beta$-Si$_3$N$_4$, and a newly observed $\gamma$-Si$_3$N$_4$ modification$^{12,13}$. $\alpha$- and $\beta$-Si$_3$N$_4$ have hexagonal structures, which are built up by corner-sharing SiN$_4$ tetrahedra. They can be regarded as consisting of layers of silicon and nitrogen atoms in the sequence ABAB... or ABCDABCD... in $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$, respectively (see Figure 1.1a and b). The AB layer is the same in the $\alpha$ and $\beta$ phases, and the CD layer in the $\alpha$ phase is related to AB by a $c$-glide plane. The SiN$_4$ tetrahedra in $\beta$-Si$_3$N$_4$ are interconnected in such a way that tunnels are formed, running parallel with the $c$ axis of the unit cell. Due to the $c$-glide plane that relates AB to CD, the $\alpha$ structure contains cavities instead of tunnels. The cubic $\gamma$-Si$_3$N$_4$ is often designated as c modification in the literature, in analogy with the cubic modification of boron nitride (c-BN). It has a spinel-type structure in which two silicon atoms each coordinate six nitrogen atoms octahedrally, and one silicon atom coordinates four nitrogen atoms tetrahedrally, as seen in Figure 1.1c.
Figure 1.1 Crystal structure stacking model of $\alpha$-Si$_3$N$_4$, $\beta$-Si$_3$N$_4$ and $\gamma$-Si$_3$N$_4$: a) The ABCD layer stacking in $\alpha$-Si$_3$N$_4$, showing that each unit contains two interstitial sites; b) The ABAB layer stacking in $\beta$-Si$_3$N$_4$ along the c axis, illustrating the continuous channel along the c axis; c) The spinel structure of $\gamma$-Si$_3$N$_4$. 
The space group of $\alpha$-Si$_3$N$_4$ is $P31c$, with the following lattice parameters: $a = 7.748(1) \, \text{Å}$ and $c = 5.617(1) \, \text{Å}$. The corresponding datum for the $\beta$ modification is $P6_3$ with $a = 7.608(1) \, \text{Å}$ and $c = 2.911(1) \, \text{Å} \, \textsuperscript{12}$. The symmetry of $\gamma$-Si$_3$N$_4$ is $Fd-3m$ with $a = 7.738(1) \, \text{Å}$. Whilst $\alpha$- and $\beta$-Si$_3$N$_4$ can be prepared under normal nitrogen pressure and hence may be widely used commercially, cubic $\gamma$-Si$_3$N$_4$ can only be prepared in a diamond anvil cell$^{13}$ or by shock transformation$^{14}$ at high pressures and temperatures.

1.1.2 $\alpha$-sialon and $\beta$-sialon

$\alpha$-sialon$^{15}$ and $\beta$-sialon$^{16,17}$ are two important solid solutions, isostructural with $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$, respectively. By substitution of Al-O for Si-N in $\beta$-Si$_3$N$_4$, a solid solution is formed, which was originally named $\beta'$-Si$_3$N$_4$, later $\beta'$-SIALON, and nowadays $\beta$-sialon. The overall formula of $\beta$-sialon is Si$_{6-z}$Al$_z$O$_z$N$_{8-z}$, where, the $z$ value varies continuously from zero to 4.2; and its unit cell contains two “Si$_3$N$_4$” units. $\alpha$-sialon is another solid solution based on the $\alpha$-Si$_3$N$_4$ structure. The formula of this solid solution is RE$_x$Si$_{12-(m+n)}$Al$_{(m+n)}$O$_n$N$_{16-n}$, where RE is a metal ion with a valence of $p^+$ and $m = px$. The unit cell of $\alpha$-sialon comprises four “Si$_3$N$_4$” units, which are formed by replacement of $(m+n)$Si-N by $m$(Al-N) and $n$(Al-O). There are two interstitial sites per unit cell in $\alpha$-sialon, which constrains $x$ to be $\leq 2$ in the formula given above. The added RE$^{p^+}$ cations compensate for the valence discrepancy created by the replacement of m(Si-N) by m(Al-N). Thus, the $\alpha$-sialon solid solution range has a two-dimensional extension in the Si$_3$N$_4$–Al$_2$O$_3$–AlN–REN·3AlN plane located in the Jänecke prism that is commonly used to visualise the phase relationships among $\alpha$-sialon and other phases in the RE-Si-Al-O-N system, as seen in Figure 1.2. In the $\beta$-sialon case the replacement of Si-N by Al-O results in a very small change of the unit cell, because the Si-N and Al-O bond lengths are very similar; whereas the replacement of $(m+n)$(Si-N) by $m$ (Al-N) and $n$(Al-O) in $\alpha$-sialon results in a considerable increase of the unit cell size, because the Al-N bond (1.87 Å) is much longer than Si-N (1.72–1.74 Å).
Figure 1.2 The commonly used Jänecke prism, showing the main phases present in the Si-Al-O-N-RE system.

It is commonly accepted that the β-sialon phase often occurs with a whisker-like morphology, which promotes the formation of interlocking microstructures. It has been shown that this type of microstructure yields improved mechanical properties, e.g. high fracture toughness. For a long time α-sialon was believed to exist only in an equiaxed shape, until it was experimentally proved in 1995 that elongated grain morphology can be developed in α-sialon as well\(^{18-21}\). α- and β-sialon ceramics have been intensively studied during the recent two decades. However, up to now, only β-Si\(_3\)N\(_4\) and β-sialon have been widely used commercially, mainly because they are sufficiently hard and can more easily form microstructures with high fracture toughness values.

1.1.3 Conventional sintering methods

Si\(_3\)N\(_4\) is a highly covalently bonded synthetic material exhibiting very low diffusivity, so conventional pressureless solid-state sintering methods are not applicable to producing pure, dense Si\(_3\)N\(_4\)-based ceramics. Full density in these
ceramics is achieved by applying pressure and/or by introducing sintering aids to create a liquid phase that assists the densification.

Dense Si$_3$N$_4$-based ceramics can only be produced, on a technologically interesting scale, in combination with addition of sintering aids. MgO, Al$_2$O$_3$, AlN, Y$_2$O$_3$ or a mixture of Al$_2$O$_3$ and Y$_2$O$_3$ are frequently used as sintering aids. The most common sintering methods used to consolidate Si$_3$N$_4$-based ceramics are the following: reaction bonding (RB), pressureless sintering (PLS), hot pressing (HP), hot isostatic pressing (HIP) and gas pressure sintering (GPS). Reaction bonding implies a direct reaction between Si and N$_2$ during the sintering, but this process often results in materials with high porosity. It is very difficult to get fully dense Si$_3$N$_4$-based ceramics without introducing a large amount of liquid phase, using pressureless sintering.

Hot pressing is the most established pressure-assisted sintering method, in which the specimen is placed in a die and an axial pressure is applied by punches. Both the die and the punches are made of graphite or boron nitride-coated graphite, and the whole assembly is placed in a furnace. Although the applied pressure promotes the densification of the specimen, the method has severe limitations when it comes to preparation of specimens of complex shapes.

In the HIP process the isostatic pressure is applied via a gaseous or liquid medium, which allows manufacturing of more complicated-shape components in large quantities. For silicon nitride ceramics, the green bodies are usually coated with a glass that acts as a gas-tight protective membrane against the gas used as pressure medium. The furnace is placed in a pressure vessel, and a high-pressurised gas (normally argon) is pumped into the vessel during the sintering cycle. The entire set-up is quite complicated and costly, and the glass coating and de-glassing procedures are also very time-consuming.
Gas pressure sintering implies that the specimens are sintered in an appropriate gas atmosphere at high pressures, but without using membranes. High nitrogen pressures are used in connection with gas pressure sintering of Si$_3$N$_4$ based ceramics, which prevents decomposition of Si$_3$N$_4$, and higher sintering temperatures can accordingly be applied.

1.2 Liquid phase sintering

Liquid-phase sintering (LPS) is defined as a sintering process that involves liquid and solid particles. The liquid can be present during the entire sintering process or during a specific stage of the sintering cycle. There are two basic ways to obtain a liquid phase: (i) Using mixed powders of differing characteristics; and (ii) Taking advantage of the interaction between two or more of the components involved. The liquid can result from the melting of one component or from the formation of a eutectic liquid. Furthermore, this liquid can be either transient or permanent during the entire sintering cycle, depending on the solubility relationships as discussed below.

1.2.1 Classic liquid phase sintering

According to Kingery’s model, the classic liquid-phase sintering process can be divided into three steps that may in certain cases be partly overlapped, see Figure 1.3.

![Figure 1.3 A schematic drawing showing the microstructural evolution during classic liquid-phase sintering of powder mixtures: I) Rearrangement, II) Solution–precipitation; and III) Microstructure coarsening and solid-state sintering.](image)

6
The initial stage of classic liquid-phase sintering is a *particle rearrangement* process. Rearrangement takes place immediately after the liquid phase forms, accompanied by rapid partial densification due to the capillary force exerted by the wetting liquid on the solid particles. The elimination of porosity takes place as the system minimises its surface energy. The most favourable features for rearrangement are: (i) A homogeneous distribution of a congruently melting liquid that wets the particles present; (ii) The solid particles are soluble in the liquid; (iii) A large solubility ratio. The rate and extent of shrinkage depend upon the viscosity and quantity of liquid phase formed and on its wetting properties. A relative density of about 0.65 can be achieved by particle rearrangement. For complete densification, provided that the amount of liquid phase is less than 35 vol%, additional sintering processes are necessary.

The second step of this process is termed the *solution–reprecipitation* step. The small grains are more soluble than the large ones, and the difference in solubility establishes a concentration gradient in liquid. Material is therefore transported from small grains to large grains by diffusion, so that the large grains grow at the expense of the small during the liquid-phase sintering. This process is known as *coarsening*, or *static Ostwald ripening* (abbreviated as *static ripening* below)\(^{24-26}\). The major driving forces for static ripening is the reduction of interfacial energy and the capillary force. This process relies strongly on two critical steps: dissolution of solid into the liquid and diffusion through the liquid. If the transport is limited by mass transfer from the source to the sink, this process is diffusion-controlled; if the transport is confined by interfacial dissolution or precipitation, the process is reaction-controlled. Static ripening plays an important role during the solution–reprecipitation step. It contributes not only to grain growth but also to densification.

The final step of this sintering process is termed the *solid-state sintering controlled step*. A solid skeleton is formed, and grain coalescence occurs. The rigidity of the solid skeleton hinders further rearrangement, although microstructure coarsening continues by diffusion. In this case, the residual pores will enlarge if they contain
entrapped gas that results in swelling. The densification rate is greatly decreased during this part of the sintering cycle.

1.2.2 Liquid-phase sintering of sialon ceramics

The densification of silicon nitride based ceramics with sintering additives takes place via a liquid-phase sintering process\textsuperscript{5}. At high temperatures the introduced metal oxides react with the oxygen-rich layer (SiO\textsubscript{2}) that is always present at the surface of each Si\textsubscript{3}N\textsubscript{4} particle, and with the small Si\textsubscript{3}N\textsubscript{4} particles to form an oxy-nitride liquid phase, which wets solid particles and allows rearrangement of them. With increasing temperature, more nitride particles dissolve in the liquid, β-Si\textsubscript{3}N\textsubscript{4} or sialon phases (if possible) will precipitate when the liquid has become supersaturated, and this promotes densification by the mechanism of liquid-phase sintering.

The mechanism of sintering Si\textsubscript{3}N\textsubscript{4}-based ceramics is much more complicated than that of liquid-phase sintering of hard metals, because intermediate compounds can be formed and phase transformations occur during the sintering process, which all consume the liquid phase and/or alter the composition of the liquid\textsuperscript{9,27-33}. Sintering α-sialon ceramics is thus a complicated process, during which densification, phase transformation and grain growth normally take place simultaneously. It is not an easy task to clarify the true mechanism of each stage, e.g. the mechanism governing grain growth.

The densification of α-sialon in the presence of a liquid phase during the hot-pressing process can be divided into three steps (frequently overlapped) in terms of the microstructure development: (i) Particles are rearranged as soon as a melt forms by reaction between the oxides present on the surfaces of Si\textsubscript{3}N\textsubscript{4} and AlN and the sintering additives (metal oxides) around 1350°C; (ii) AlN and Si\textsubscript{3}N\textsubscript{4} dissolve into the liquid as they are wetted by the melt, and the α-sialon grains precipitate when the liquid has become supersaturated; (iii) Finally, coalescence and grain growth take place.
It has been commonly accepted that the formation of elongated morphology of Si$_3$N$_4$ grains can be ascribed to the inherent differences in interfacial energy between various facets of the crystals. However, the relation between the densification, phase transformation and grain growth during hot pressing of Si$_3$N$_4$-based ceramics is very complicated, and there are many factors that may influence the elongation of resultant grains. On the one hand, phase transformation is expected to enhance the elongation of the grains owing to the enhancement of the dissolution of $\alpha$-Si$_3$N$_4$ into the liquid phase. On the other hand, the grain elongation is inhibited by full densification due to impingement of particles in fully dense ceramic bodies$^{20,34-37}$.

Based on the understanding of the processes given above, the following strategic steps have been taken with the aim to form a tough interlocking microstructures of sialon ceramics: (i) Seeding; (ii) Varying the amount and composition of the liquid phase present; (iii) Promoting the dissolution process by using fine-grained precursor powders; (iv) Controlling nucleation rate via monitoring the phase transformations taking place during the sintering process$^{20,38,39}$. Although it has been observed that, under high nitrogen pressure, a few grains grow dramatically fast above 1900$^\circ$C$^{40,41}$, and that the growth of anisotropic grains is directly related to the difference in solubility between small and large grains$^{42}$, it is generally accepted that growth of elongated grains is predominantly diffusion controlled$^{43}$. This implies that extended holding at high temperature is a necessary requirement to develop a tough interlocking microstructure.

Microstructure design is crucial for improving the fracture toughness and strength of silicon nitride-based ceramics, however, the kinetics of the formation of elongated grains, particularly during or after the phase transformation period, is still not well understood.
1.2.3 Densification mechanisms of Si$_3$N$_4$-based ceramics

Many investigations have been performed concerning the densification mechanism of Si$_3$N$_4$-based ceramics. Generally, the Kingery sintering model has been used in describing the densification results$^{44-51}$. As mentioned above, the first step is a rearrangement of the particles that takes place immediately after the liquid phase is formed and is accompanied by a rapid partial densification due to the capillary force. The elimination of porosity takes place as the system minimises its surface energy. Kingery concluded that viscous flow was a dominant mechanism for the densification at this stage, and used the following equation to describe the time dependence of the compaction:

$$\Delta L/L_0 \propto t^{1+y} \quad (1-1)$$

where $\Delta L/L_0$ is the relative linear shrinkage, $t$ the holding time at the sintering temperature and $1+y$ an exponent somewhat larger than one.

A corresponding equation for diffusion-controlled densification that Kingery derived for the solution–reprecipitation process, assuming spherical particles, reads:

$$\Delta L/L_0 = \left(6k_2\cdot D\cdot C_0 \cdot \gamma_{LV} \cdot V_0 / k_1 \cdot R \cdot T\right)^{1/3} \cdot r^{-4/3} \cdot t^{1/3} \quad (1-2)$$

where $\Delta L/L_0$ is the relative linear shrinkage, $k_2$ a proportionality constant, $\delta$ the grain boundary’s thickness, $D$ the diffusivity of the solid in the liquid, $C_0$ solid concentration in the liquid, $\gamma_{LV}$ the liquid/solid surface energy, $V_0$ the initial volume, $k_1$ a constant, $R$ the gas constant, $T$ the temperature, $r$ the initial grain radius and $t$ the sintering time.

With a grain-boundary reaction-controlled densification:

$$\Delta L/L_0 = \left(2 \cdot k_3 \cdot k_2^2 \cdot C_0 \cdot \gamma_{LV} \cdot V_0 / k_1 \cdot R \cdot T\right)^{1/2} \cdot r^{-1} \cdot t^{1/2} \quad (1-3)$$

where $k_3$ is a constant.

This implies that, when the shrinkage is proportional to the cube root of the sintering time, the sintering process is diffusion controlled; and when the shrinkage
is proportional to the square root of the sintering time, it is controlled by grain boundary reactions.

For prismatic particles, the shrinkage ($\Delta L/L_0$) is $\propto t^{1/5}$ for diffusion-controlled densification and ($\Delta L/L_0$) $\propto t^{1/3}$ for grain boundary reaction-controlled densification.

Finally, the third step involves solid-state diffusion process, and diffusion within the solid is less rapid than that along grain boundaries, so that the diffusion rate decreases.

The logarithm of shrinkage is usually plotted versus logarithm of time in order to determine the densification mechanism. In this type of diagram, the slope of the line reveals the time exponent. For instance, Hampshire and Jack reported an exponent of 1/3 for MgO-doped silicon nitride and 1/5 for $Y_2O_3$-doped silicon nitride$^{45,52,53}$, indicating that the densification is reaction-controlled for MgO-doped silicon nitride and diffusion-controlled for $Y_2O_3$-doped silicon nitride.

Densification during hot pressing of $Si_3N_4$-based ceramics has been analysed with other equations/models than those derived by Kingery. Bowen et al.$^{32,33}$ used the Coble equation in a simplified form to describe the obtained densification data in the MgO-doped silicon nitride system, and thereby to determine the densification mechanism. The equation used reads:

$$\frac{d\rho}{dt} = 47.5 \cdot P \cdot D_b \cdot a^3 \cdot W/G^3 \cdot k \cdot T$$  \hspace{1cm} (1-4)

where $\rho$ is the relative density, $P$ the applied pressure, $D_b$ the grain-boundary diffusion coefficient and $a^3$ the volume of the rate-controlling species transported; $W$ is the grain boundary thickness and $G$ the grain size; $k$ is the Boltzmann constant and $T$ the temperature. It is assumed that the surface energy term may be neglected in the early densification stage. They found that the densification rate varied with the applied pressure and the content of MgO additive, confirming that the densification was controlled by diffusion of Si/N through a magnesium silicate grain-boundary phase away from the grain-boundary contact region.
That the densification rate during hot pressing is related to the applied stress was reported by Rahaman and his colleagues \(^5^4\). With appreciable amounts of liquid phase, the grain-boundary sliding process is relatively fast and dominates during the initial part of the shrinkage, but full density is not obtained by this mechanism alone. In order to yield fully dense samples a solution–reprecipitation process ought to be operative, and since this process is slower than grain-boundary sliding, the former process must be the rate-controlling one. The densification rate at a given density increases linearly with the applied stress. For compositions comprising less liquid, the grain-boundary sliding process is retarded, and for compositions with even smaller amounts of liquid the grain-boundary sliding mechanism might become rate-controlling.

1.3 Spark Plasma Sintering (SPS)

1.3.1 General background
A spark sintering method was investigated and patented in the 1960s and used to compact metal powders, but due to high equipment cost and low sintering efficiency it was not put to wider use \(^5^5\). The concept was further developed during the mid 1980s to the early 1990s, and a new generation of sintering apparatus appeared named Plasma Activated Sintering (abbreviated PAS) and Spark Plasma Sintering (abbreviated SPS). Common to these systems is the use of pulsed direct current to heat the specimens. These sintering techniques currently attract growing attention among productions engineers as well as materials researchers. Whether plasma is generated has not been confirmed yet, especially when non-conduction ceramic powders are compacted. It has, however, been experimentally verified that densification is enhanced by the use of a pulsed DC current or field \(^5^6\). This family of techniques is in academia also named as pulsed electric current sintering (PECS) \(^5^7-5^9\) or electric pulse assisted consolidation (EPAC) \(^6^0\). SPS allows compaction of ceramic and metal powders at low temperature and in short time (within minutes).
1.3.2 SPS instrument

The basic configuration of a SPS unit is shown in Figure 1.4. It consists of a uniaxial pressure device, where the water-cooled punches also serve as electrodes, a water-cooled reaction chamber that can be evacuated, a pulsed DC generator, pressure-, position- and temperature-regulating systems. Figure 1.5 illustrates the used ON–OFF pulsed direct current during the entire sintering cycle, with a standard on–off time relation of 12:2. Spark Plasma Sintering resembles the hot pressing process in several respects, i.e. the precursor powder (green body) is loaded in a die, and a uniaxial pressure is applied during sintering process. However, instead of using an external heating source, a pulsed direct current is allowed to pass through the electrically conducting pressure die and, in appropriate cases, also through the sample. This implies that the die also acts as a heating source and that the sample is heated from both outside and inside. The use of a pulsed direct current also implies that the samples are exposed to a pulsed electric field during the sintering process.
1.3.3 Consolidation mechanism

SPS is a pressure-assisted sintering method that is thought to be based on momentary high-temperature spark (and/or plasma, if present) discharges in the gaps between powder particles at the beginning of the ON-OFF DC current pulses. It is supposed that the pulsed current propagates through the powder particles inside the SPS sintering die, as shown in Figure 1.6. The process inventor also claims that the ON-
OFF DC pulse energising method generates: 1) Spark plasma; 2) Spark impact pressure; 3) Joule heating; and 4) An electrical field promoting material transfer and diffusion\textsuperscript{61-65}.

However, in our case when sintering Si\textsubscript{3}N\textsubscript{4}-based ceramics, the mechanism as described above – the pulse current passing through the powder particles along their surface – is not applicable, since these ceramics are neither conducting nor semi-conducting. Whether spark plasma is generated is also doubtful, and the effect of the spark impact pressure on sintering Si\textsubscript{3}N\textsubscript{4}-based ceramics is therefore still debated. It is true, however, that the applied high-energy pulsed current generates a pulsed electric field during the entire sintering cycle. This pulsed electric field does eventually influence sintering process of Si\textsubscript{3}N\textsubscript{4}-based ceramics by promoting material transfer and diffusion of charged species in the liquid phase.

1.3.4 Features and applications of SPS
A unique feature of the SPS process is that it uses very fast heating rates (up to 600\textdegree{}C/min\textsuperscript{-1}); thus the consolidation rate is greatly enhanced (fully dense materials are obtained within minutes) and the sintering temperature can be a few hundred degrees lower than that typically used in conventional sintering processes such as HP and HIP. Four factors that contribute to the enhanced densification process can be discerned: (i) The use of rapid heating and cooling rates; (ii) Rapid transfer of heat because the die itself acts as a heating element; (iii) The application of a mechanical pressure exceeding that used in the conventional hot-pressing process; (iv) The use of a pulsed DC current to heat the sample, implying that samples are also exposed to a pulsed electric field during sintering. It is generally accepted that application of mechanical pressure promotes the removal of pores and enhances diffusion. However, it is frequently argued that the improved densification rates stem mostly from the use of direct current pulses of high energy.
Figure 1.7 Comparison of typical sintering profiles of sialon ceramics in conventional hot pressing and in spark plasma sintering (SPS).

Figure 1.8 SEM micrographs of (Yb+Y)-stabilised sialon specimens of composition A(Yb+Y)3512-07, prepared by: HP processing at 1800°C for 4hrs with a heating rate of 40°C·min⁻¹ (a) and SPS processing at 1700°C with a holding time of 14 min using a heating rate of 200°C·min⁻¹ (b).
Further advantages of SPS include ease of operation, accurate digital control of sintering profile as well as good reproducibility and reliability. Figure 1.7 shows two typical temperature-time profiles used in SPS and HP process, respectively, yielding fully densified Yb/Y-stabilised α-sialon ceramics with similar microstructures. SEM pictures of these samples are shown in Figure 1.8. A heating rate of $40^{\circ}\text{C} \cdot \text{min}^{-1}$ is frequently used in the HP experiment, and the entire sintering cycle takes more than 300 minutes. In the SPS experiment a high heating rate of $200^{\circ}\text{C}/\text{min}$ is used, and the entire sintering cycle takes less than 20 minutes. This shows that the densification takes place significantly much faster in the SPS than that in HP process.

SPS has been used to prepare many kinds of materials\textsuperscript{61,63,66-74}, such as advanced alloy materials, functional gradient materials (FGM), fine ceramics, amorphous materials, target materials, thermoelectric materials, nano-composites, and it has also been used for investigation of sintering kinetics. The interest in this sintering technique is steadily increasing, as manifested by the fact that the number of publications dealing with this topic has dramatically increased during the last few years\textsuperscript{75-83}.

### 1.4 Properties of Si$_3$N$_4$-based ceramics

The microstructure has a significant influence on the characteristic properties of a material. The microstructure of a material may be tailored by selecting: (i) An appropriate overall composition; (ii) The characteristics of the precursor powders; (iii) Type and amount of sintering additives; and (iv) Appropriate sintering parameters. In Si$_3$N$_4$-based ceramics, the amount, distribution, grain size and morphology of obtained α and β particles are the decisive factors that determine the properties of the product.
Table 1.1 Unit cell dimensions, morphologies and mechanical properties of Si₃N₄-based ceramics.

<table>
<thead>
<tr>
<th></th>
<th>Unit cell parameter (Å)</th>
<th>Morphology</th>
<th>Mechanical property</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
<td>Hᵥ₀ (GPa)</td>
</tr>
<tr>
<td>α-Si₃N₄</td>
<td>7.748(1)</td>
<td>5.617(1)</td>
<td>Equiaxed</td>
</tr>
<tr>
<td>β-Si₃N₄</td>
<td>7.617(1)</td>
<td>2.911(1)</td>
<td>Elongated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Elongated</td>
</tr>
<tr>
<td>β-sialon</td>
<td>7.610–7.716</td>
<td>2.911–3.007</td>
<td>Elongated</td>
</tr>
</tbody>
</table>

1.4.1 Mechanical properties

The hardness of Si₃N₄-based ceramics depends on the phase composition because different phases have different hardness values. As shown in Table 1.1, where the morphologies and mechanical properties of the major phases in silicon nitride-based ceramics are listed, the intrinsic hardness of α-sialon (up to 22GPa) is 40% higher than that of β-sialon and β-Si₃N₄. High fracture toughness values are found for ceramics that have interlocking microstructures; thus β-sialon ceramics consisting of interlocking elongated grains exhibit high fracture toughness, 5–7 MPa·m⁻¹/₂, whereas α-sialons with equiaxed morphology have low fracture toughness, between 3 and 3.5 MPa·m⁻¹/₂. The fracture toughness depends not only on the grain shape and size but also on the composition of the grain-boundary/amorphous phase.

1.4.2 Thermal-shock resistance

Thermal-shock resistance is one of the most important properties of a material assessing the resistance to weakening or fracture under a rapid change in temperature, particularly for high-temperature application of structural ceramics. In monolithic ceramics the thermal shock stems from the fact that the external surface of ceramic expands or contracts more rapidly than its interior, and this can lead to cracking or shattering.

Si₃N₄-based ceramics exhibit high thermal-shock resistance, withstanding quenching in cold water even from 800–1000°C, whereas other ceramics such as
ZrO₂ or Al₂O₃ ceramics can only withstand quenching from temperatures ranging from 200 to 400°C⁸⁷,⁸⁸. Various methods have been developed to determine thermal-shock behaviour. Here, a recently developed indentation-quench technique has been used to evaluate the thermal shock resistance of three representative sialon ceramics⁸⁹,⁹⁰. This thermal-shock resistance measurement involves four major steps: (i) Very carefully polishing the surfaces of specimens; (ii) Initiating well-defined cracks with a Vickers indenter; (iii) Heating the resultant specimens in a vertical tubular furnace to a pre-set temperature and subsequently quenching the specimens into a water bath; (iv) Measuring the crack growth and thereafter correlating it with the temperature difference.

1.4.3 Superplasticity of ceramics

Superplasticity refers to the capability of polycrystalline materials to undergo extensive deformation without any microstructural deterioration. Although superplastic forming is an established industrial process for many metals⁹¹, its applicability to brittle materials was not demonstrated until the late 1980s. In order to improve the super-plastic behaviour of a ceramic material, a prerequisite is a microstructure consisting of fine equiaxed grains, which is stable during the deformation. The common characteristics of materials with super-plastic behaviour may be summarised as follows:

i) Small grain size, typically less than approximately 1 μm.

ii) Equiaxed grain morphology. Large shear stresses across the grain boundaries are developed during deformation, and to the extent that the grains are non-spherical the grain boundary sliding mechanism becomes inefficient.

iii) High-energy grain boundaries. Diffusion and sliding proceeds faster along such high-energy boundaries. Nano- and/or submicron-sized grains have boundaries of higher energy than micron-sized grains.
iv) Presence of a second phase. At temperatures where grain-boundary diffusion and sliding are significant, grains frequently grow fast. A second phase might be necessary to inhibit grain growth.

v) An amorphous grain-boundary phase/liquid phase (if possible). The formation of an intergranular liquid/glassy phase, transient or permanent, is vital for super-plastic deformation in silicon nitride-based ceramics, because the liquid/glassy phase acts as a lubricant for particle rearrangement and sliding.

Super-plastic deformation of ceramics has attracted technical interest since around 1986, when it was reported that yttria-stabilised tetragonal zirconia polycrystals (Y-TZP) could be elongated over 100% in tension\textsuperscript{92-94}. Although polycrystalline tetragonal zirconia is the most intensively investigated material, new developments have been achieved in Si\textsubscript{3}N\textsubscript{4}- and SiC-based ceramics during recent years\textsuperscript{95}. By reducing the grain size, it turns out that the traditionally brittle ceramics become ductile\textsuperscript{96-98}. This provides a new method of obtaining ceramic objects with complex shape, and opens up for new applications of ceramics.

The super-plastic deformation of ceramics occurs mainly via sliding along grain boundaries; thus the presence of an intergranular glassy phase in conjunction with ultra-fine-grained microstructures improves the ductility\textsuperscript{95,99,100}. In Si\textsubscript{3}N\textsubscript{4}-based ceramics the deformation progresses very slowly when the coexisting glassy phase has a high softening temperature and occurs in low concentration\textsuperscript{97,101,102} and when the constituent grains possess a fibrous morphology\textsuperscript{103}. To enhance the ductility of Si\textsubscript{3}N\textsubscript{4}-based ceramics, in particular at lower temperatures, compacts that contain equiaxed submicron-sized grains have been prepared by: (i) Applying a low-temperature sintering procedure\textsuperscript{104}; (ii) Adding grain-growth inhibitors, e.g. SiC particles\textsuperscript{100}; (iii) Using β-Si\textsubscript{3}N\textsubscript{4} powder, because this precursor seems more resistant to grain growth\textsuperscript{101}. 
Si₃N₄-based ceramics with fine, equiaxed morphology show reduction in both fracture strength and fracture toughness at room temperature, but they are the ones that exhibit super-plastic behaviour at high temperature. The ductility of this type of ceramics is strongly temperature dependent; it increases with increasing temperature up to a certain critical temperature (Tc). Above Tc the ductility is hindered because the accelerated grain growth induces strain hardening. Strain rates of the order 10⁻⁴ s⁻¹ are thus obtained under a compressive stress of 40–50 MPa at temperatures around 1500°C. Attempts have been made to reduce the viscosity of the grain-boundary glassy phase even further via compositional adjustment in order to lower its softening temperature¹⁰². However, the resistance to creep and corrosion is thereby decreased, i.e. properties that are vital for materials intended for high-temperature applications are then sacrificed.
2. Aim of this thesis

The main work of this thesis has been focused on sintering and characterisation of sialon ceramics with different metal oxides as sintering additives. SPS is the principal sintering method that has been used to ensure full densification, while a conventional sintering process such as HP has also been applied for the sake of comparison. The main work includes the following aspects:

- The effect of sintering additives on sintering process during conventional HP processing, particularly their influence on grain growth.
- Introducing an extra liquid phase that is thermodynamically compatible with sialon phases by using a new approach, namely increasing the O/N ratio in the general formula $\text{RE}_{x}\text{Si}_{12-(3x+n)}\text{Al}_{3x+n}\text{O}_n\text{N}_{16-n}$ whilst keeping the RE, Si, and Al proportions constant.
- Investigation of sintering kinetics under SPS conditions, focusing on densification, phase transformation and grain growth, respectively.
- Tailoring the microstructures of sialon ceramics.
- Improving super-plastic properties of silicon nitride-based ceramics to yield complex shape components.
3. Experimental

3.1 Starting materials

The starting powders were commercial $\alpha$-Si$_3$N$_4$ (UBE, SN-10E), $\beta$-Si$_3$N$_4$ (SN P21FC), Al$_2$O$_3$ (Alcoa, SG30), AlN (HC Starck–Berlin, Grade C), Li$_2$CO$_3$ (in the Li-stabilised sialon system) and RE$_2$O$_3$ where RE = Y, Nd, Sm, Dy, and Yb (Johnson Matthey Chemicals Ltd.). When calculating the overall compositions, corrections were made for the small amounts of oxygen present in the Si$_3$N$_4$ and AlN raw mixtures. The starting materials, in batches of 50 g, were ball milled in water-free propanol for 24 hrs, using sialon milling media, and then dried in an oven at 80°C for 24 hrs. If not otherwise stated, $\alpha$-Si$_3$N$_4$ (UBE, SN-10E) was used as silicon nitride precursor in this work.

3.2 Composition design

3.2.1 Rare-earth stabilised $\alpha$-sialons

$\alpha$-sialon samples with two slightly different stoichiometric compositions were investigated, namely $x = 0.35$, $n = 1.2$ for RE = Y, Yb, Sm, Dy and an equimolar mixture of Y and Yb, and $x = 0.35$, $n = 1.0$ for RE = Nd in the general formula $\text{RE}_x\text{Si}_{12-(3x+n)}\text{Al}_{3x+n}\text{O}_n\text{N}_{16-n}$. The two compositions, referred to ARE3512 and ANd-3510 below, respectively, are located close to the oxygen-rich boundary of the $\alpha$-sialon phase region facing the $\beta$-sialon line.

The oxygen content of ARE3512 is 5.16 eq% in the starting overall composition. By fixing the cation ratio of this composition and increasing the oxygen content
from 5.16 to 15 eq%, a series of powder mixtures were prepared along the A–B line located slightly above the α-sialon plane in the Jänecke prism of the RE-Si-Al-O-N system, as shown in Figure 3.1.

Figure 3.1 A schematic representation of the Jänecke prism of RE-Si-Al-O-N systems. The compositions investigated in this thesis are located along the line A-B.

These compositions are named AY3512-ZZ, AYb3512-ZZ and A(Y+Yb)3512-ZZ below, where thus A(Y+Yb)3512-ZZ represents samples with Yb and Y in equal-molar proportions as stabilising agent, and with ZZ representing the oxygen content of the sample expressed in eq%. The ZZ value of the selected basic composition, \( \text{RE}_{0.35}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{1.20}\text{N}_{14.80} \) (ARE3512), is thus 5.16, and powder mixtures with ZZ = 07, 08, 09, 10, 11, 12, 13, and 15 were also prepared. Table 3.1 shows the systematic labels of the rare-earth stabilised samples prepared.

Table 3.1 Systematic labelling of the α- and β-sialons investigated based on a starting composition of \( \text{RE}_x\text{Si}_{12-(3x+n)}\text{Al}_{3x+n}\text{O}_n\text{N}_{16-n} \), where \( x = 0.35 \) and \( n = 1.2 \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>O eq%</th>
<th>Remarks</th>
<th>General formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARE3512(-05)</td>
<td>5.16</td>
<td>RE=Y, Yb, Y+Yb, DY, Sm</td>
<td>( \text{RE}<em>{0.35}\text{Si}</em>{9.75}\text{Al}<em>{2.25}\text{O}</em>{1.20}\text{N}_{14.80} )</td>
</tr>
<tr>
<td>ARE3512-07</td>
<td>7.0</td>
<td>RE=Y, Yb</td>
<td>( \text{RE}<em>{0.35}\text{Si}</em>{9.75}\text{Al}<em>{2.25}\text{O}</em>{1.64}\text{N}_{14.50} )</td>
</tr>
<tr>
<td>ARE3512-10</td>
<td>10.0</td>
<td>RE=Y, Yb</td>
<td>( \text{RE}<em>{0.35}\text{Si}</em>{9.75}\text{Al}<em>{2.25}\text{O}</em>{2.34}\text{N}_{14.04} )</td>
</tr>
<tr>
<td>ARE3512-15</td>
<td>15.0</td>
<td>RE=Y, Yb</td>
<td>( \text{RE}<em>{0.35}\text{Si}</em>{9.75}\text{Al}<em>{2.25}\text{O}</em>{3.51}\text{N}_{13.26} )</td>
</tr>
<tr>
<td>A(Yb+Y) 3512- ZZ</td>
<td>ZZ=07, 08, 09, 10, 11, 12, 13, and 15</td>
<td>Yb(<em>{0.175})Y(</em>{0.175})Si(<em>{9.75})Al(</em>{2.25})O(_{b})*</td>
<td></td>
</tr>
</tbody>
</table>

* a and b are calculated according to the O eq% by following the equations: \( 2a/(2a+3b) = \text{O eq}\% \) and \( 2a + 3b = 1.2 \cdot 2 + 14.8 \cdot 3 = 46.8 \).
3.2.2 Lithium stabilised monolithic α- and duplex α/β-sialon

Lithium-stabilised sialon samples with overall compositions either corresponding to an α/β-sialon composite with m = 0.5 and n = 2.0 or to a monophasic α-sialon with m = 1.0 and n = 2.5 in the general formula Li₈Si₁₂₋ₕAlₘ₋ₚOₜN₁₆₋ₚ were investigated. These two compositions are labelled Li0520 and ALi1025, respectively.

Both α-Si₃N₄ (UBE, SN-10E) and β-Si₃N₄ (SN P21FC) powders were used as precursors in connection with the preparation of the duplex composite α/β-sialon (Li0520). The resultant samples were labelled ALi0520 and BLi0520, with initial A and B representing α- and β-Si₃N₄ as precursors, respectively. The selected composition is located in the duplex α/β-sialon phase region, implying that the α- and β-sialon phases ought to form in conjunction with some glassy phase when thermodynamic equilibrium is approached.

Based on the monophasic α-sialon composition ALi1025, by slightly increasing the oxygen content to 17 eq% while keeping the cations constant, a duplex α/β-sialon with overall composition LiSi₈.₅Al₃.₅O₃.₉N₁₂.₆ was derived and labelled ALi1025-17. This composition yields a sialon composite containing ~54% α- and ~46% β-sialon.

3.2.3 Monolithic β-sialon

One monolithic β-sialon with composition Y₀.₀₁Si₁.₉₁Al₀.₂₁₅O₀.₁₆₆N₂.₆₆, labelled G20B06, was designed for comparison in investigating the grain growth kinetics and super-plastic behaviour.
3.3 Sintering methods

The precursor powder mixtures were consolidated using conventional hot pressing and/or SPS processing. The SPS process was used as principal sintering method for consolidating sialon ceramics in this work, and for comparison, the HP process was used to densify appropriate samples and to perform super-plastic deformation experiment.

3.3.1 Hot-press sintering (HP)

Hot pressing was performed in a graphite-heated furnace (Thermal technology, Germany) in protecting nitrogen atmosphere. The dried powders of RE-stabilised sialon ceramics were compacted to pellets with a diameter of 18 mm, which were then HPed at 32 MPa in nitrogen atmosphere in a graphite resistance furnace. A two-step sintering procedure was applied, i.e. the samples were first heated to 1500°C at a rate of 15°C·min⁻¹ and held there for one hour; they were then further heated to the final sintering temperature, 1800 or 1900°C, at a rate of 40°C·min⁻¹ and held there for 4 hrs. After sintering, the samples were allowed to cool inside the furnace at a rate of ~50°C·min⁻¹. To obtain fully dense sialon ceramics in HP, a prolonged dwelling time is necessary, making it difficult to control the morphology of obtained specimens.

3.3.2 Spark Plasma Sintering (SPS)

The SPS process was carried out in vacuum in a spark-plasma sintering apparatus, Dr. Sinter 2050 (Sumitomo Coal Mining Co. Ltd. Japan). The precursor powders were loaded in a cylindrical carbon die with an inner diameter of 20 mm. The samples were heated by passing a pulsed DC current through the pressurised die, i.e. using the die also as a heating source. The final sintering temperature was set between 1450 and 1830°C, with or without holding. The temperature was automatically raised to 600°C over a period of 3 min, and from this point it was then monitored and regulated by an optical pyrometer focussed on the surface of the die. If not otherwise stated, the heating rate was 200°C·min⁻¹ when sintering RE-
stabilised sialon, and 100°C·min⁻¹ in Li-stabilised systems; a pressure of 50 MPa was maintained throughout the sintering cycle. The set-up allows a cooling rate of > 350°C·min⁻¹ in the temperature range 1830–1000°C.

3.4 Characterisation techniques

3.4.1 X-ray powder diffraction

X-ray powder diffraction (XRD) was used for phase identification. The X-ray patterns were recorded in a Guinier–Hägg camera using monochromatic CuKα₁ radiation. Small amounts of Si were used as internal standard, and the patterns were evaluated by means of the SCANPI system. The unit cell parameters of the recognised crystalline phases were refined with the PIRUM computer software. The obtained cell parameters were used to calculate the x value of the α-sialon and the z value of the β-sialon in their general formulae according to the empirical expressions given by Shen et al. and Ekström et al.:

\[
a = 7.752 + 0.139x \quad c = 5.620 + 0.153x; \quad x = (x_a + x_b)/2
\]  
for the α phase;

\[
a = 7.603 + 0.0297z \quad c = 2.907 + 0.0255z; \quad z = (z_a + z_c)/2
\]  
for the β phase.

The amounts of α- and β-sialons in the obtained specimens were estimated by comparing the intensities of the two strongest peaks yielded by each phase, (102) and (210) for α-sialon and (110) and (210) for β-sialon.

3.4.2 SEM micrographs

Polished and/or fractured surfaces of all specimens were examined in a scanning electron microscope (SEM, Jeol JSM880), equipped with an energy-dispersive spectrometer (EDS, LINK ISIS). In order to obtain the best contrast between different phases, the micrographs were recorded in back-scattering electron mode (BSE) for polished surfaces. The α-sialon and RE-enriched intergranular phases
show medium grey and bright contrasts, respectively, while $\beta$-sialon and sialon polytypoids (if present) appear with dark black contrast. Fracture surfaces of the prepared samples of lithium-stabilised sialons were etched in a molten mixture of KOH and KNO$_3$ for 1–3 minutes before SEM examination.

The average size of the 10 largest grains that could be clearly distinguished in each SEM micrograph of the fractured or polished surfaces was measured. Five randomly selected, equally magnified areas of each sample were recorded and used for the grain size measurements. The sizes of selected grains were determined by means of an image analysis program (Image tool, UTHSCSA).

### 3.5 Property measurements

The bulk densities of the sintered samples were determined based upon the Archimedes principle. Before studying the mechanical properties and microstructures, the specimens were carefully polished by standard diamond polish technique down to 1 $\mu$m finish.

#### 3.5.1 Mechanical properties measurements

Hardness and fracture toughness were measured with a Vickers diamond pyramid indenter by applying a load of 98 N, and were calculated by both Anstis$^{109}$ and Evans$^{110}$ equations.

#### 3.5.2 Thermal-shock resistance measurements

The thermal shock resistance was examined in a vertical tubular furnace heated to a pre-set temperature, using fully dense cylindrical samples with a diameter of 12 mm and a thickness of $\sim$4 mm. Well-defined cracks were initiated with a Vickers indenter on the very carefully polished surfaces of samples. Four indents were made on each sample, each indent generating four cracks; a total of sixteen cracks were thus initiated on each sample. The sample was hoisted into the furnace and was
thermally equilibrated for 20 min and subsequently quenched into a 90°C water bath. Thereafter the crack growth at each temperature step was measured and correlated with the temperature difference.

3.5.3 Compressive deformation test
The compressive deformation tests were carried out both in the SPS apparatus and in a conventional hot-pressing chamber. Fully densified cylindrical samples with a diameter of 12 mm and a height of ~6 mm were loaded in a graphite die with inner diameter 20 mm, and were deformed under a uniaxial compressive stress applied \textit{via} the graphite punches of the pressure die. A constant heating rate of 40°C·min\textsuperscript{−1} was applied during the entire deformation cycle. A load corresponding to an initial stress of 40 MPa was applied at room temperature and was held constant during the entire deformation process.
4. Realising *in-situ* reinforced microstructure through a novel processing concept

4.1 Hot-pressed stoichiometric $\alpha$-sialons

Monophasic $\alpha$-sialon with stoichiometric composition ARE3512, *i.e.* $\text{RE}_{0.35}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{1.20}\text{N}_{14.80}$, where $\text{RE} = \text{Y, Yb, Dy, and Sm}$, or $\text{ANd3510}$, $\text{Nd}_{0.35}\text{Si}_{9.95}\text{Al}_{2.05}\text{O}_{1.00}\text{N}_{15.00}$, were prepared from $\alpha$-$\text{Si}_3\text{N}_4$ precursor powder using conventional hot pressing in protecting nitrogen atmosphere.

4.1.1 Crystalline phases present after hot pressing at 1500 °C

Crystalline phases present after hot pressing at 1500°C for 1 hr are listed in Table 4.1, which reveals that the reactions leading to the formation of $\alpha$-sialon are rather slow at this temperature, as manifested by the large amount of the nitride precursors, $\alpha$-$\text{Si}_3\text{N}_4$ and $\text{AlN}$ still remaining in the compacts. In addition, a nitrogen-rich melilite phase, $\text{RE}_2\text{Si}_3\text{Al}_{x}\text{O}_{3+x}\text{N}_{4-x}$ (labelled $M'$ below), formed in large amounts in the Nd-, Sm- and Dy-doped samples. In the Y-doped samples there appear small amounts of $M'$ together with larger amounts of the oxide phase, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG). No crystalline intermediate phase was observed in the Yb-doped sample. The $\alpha$-sialon/$\alpha$-$\text{Si}_3\text{N}_4$ ratio was found to be 0 and 0.10 in the Nd- and Sm-doped samples, respectively, whereas this ratio ranged from 0.20 to 0.30 for the other RE elements used. This confirms that the formation of $\alpha$-sialon is retarded in the Nd- and Sm-doped samples due to the formation of $M'$ phase.
4.1.2 Microstructure development

Fully dense compacts were obtained after hot pressing at 1800 and 1900°C for 4 hrs, and the only crystalline phase in these compacts was α-sialon, according to the X-ray powder patterns, with the exception of Nd- and Sm-doped samples where trace amounts of β-sialon grains were found. As shown in Figure 4.1, all samples contained a very small amount of a residual intergranular amorphous phase, confirming that the overall compositions of the present samples are indeed located on the oxygen-rich boundary of the single-phase α-sialon region.

Table 4.1 Crystalline phase assemblages in RE-doped α-sialons with stoichiometric composition after hot pressing for 1 hr at 1500°C

<table>
<thead>
<tr>
<th>Compositions</th>
<th>α-Si$_3$N$_4$</th>
<th>AlN</th>
<th>α sialon</th>
<th>Melilite</th>
<th>Garnet</th>
<th>α'/α#</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANd3510</td>
<td>vs</td>
<td>m</td>
<td>s</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>ASm3512</td>
<td>vs</td>
<td>m</td>
<td>vw</td>
<td>vs</td>
<td></td>
<td>0.10</td>
</tr>
<tr>
<td>AY3512</td>
<td>vs</td>
<td>m</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>0.17</td>
</tr>
<tr>
<td>ADy3512</td>
<td>vs</td>
<td>m</td>
<td>w</td>
<td>s</td>
<td></td>
<td>0.30</td>
</tr>
<tr>
<td>AYb3512</td>
<td>vs</td>
<td>m</td>
<td>w</td>
<td></td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>

* Intensity decreases in the order vs > s > m > w > vw. # Intensity ratio of (102) peaks from α-sialon /α-Si$_3$N$_4$.

Elongated α-sialon grains formed in large amounts in Nd- and Sm-doped samples, less abundantly in Y- and Dy-doped ones, and not at all in the Yb-doped one. The grain growth is obviously enhanced at the higher temperature, as coarser grains and/or grains with higher aspect ratios are formed at 1900 than at 1800°C, see Figure 4.1. The Nd- and Sm-doped samples prepared at 1900°C exhibit a clearly bimodal grain size distribution, i.e. they contain very large elongated grains up to a few tens of micrometers in length, embedded in a matrix consisting of sub-micrometer sized equi-axed grains. The Y- and Dy-doped samples prepared at 1900°C contain much coarser grains than found in compacts prepared at 1800°C, but most of these grains have equi-axed morphology. However, the Yb-doped
sample prepared at 1900°C still has a microstructure consisting of only small equi-axed grains with very narrow size distribution.

Figure 4.1 Back-scattered SEM micrographs of the samples with stoichiometric overall ARE3512 compositions, hot-pressed at 1800°C for 4 hours (a), and at 1900°C for 4 hours (b). The microstructure of the Y-doped sample resembles that of the Dy-doped one.
In the Nd-, Sm-, and Dy-doped $\alpha$-sialon systems, a number of intermediate phases form during heating, but they decompose near the final sintering temperature that provides the system with the transient liquid necessary for elongated grain growth. Because only a small amount of liquid forms at lower temperatures, the number of $\alpha$-sialon nuclei formed in this temperature region is limited, which explains why elongated $\alpha$-sialon grains are readily formed in these systems. In the Yb-doped system almost no transient phases are formed at intermediate temperatures, implying that more $\alpha$-sialon nuclei form in a narrow temperature interval and, accordingly, it becomes much more difficult to obtain elongated $\alpha$-sialon grains.

4.1.3 Strategy to obtain elongated morphology

Using conventional hot pressing, Y- and Yb-stabilised monophasic $\alpha$-sialons with stoichiometric composition, exemplified by AY5312 and AYb3512 (see Table 3.1), retain the equi-axed morphology even at a temperature as high as 1900°C. In such systems, due to the absence of the formation and subsequent decomposition of intermediate phases during sintering, conditions suitable for elongated grain growth has never been established. To obtain elongated morphology, a condition of higher temperature and/or extra liquid has to be satisfied. However, two facts are worth to consider: (i) Severe decomposition of Si$_3$N$_4$-based phases starts above 1900°C if an overpressure of N$_2$ is not applied; and (ii) Introducing too large amount of extra liquid that finally remains as a permanent glass phase at grain boundaries will deteriorate high-temperature properties of the formed ceramics.

Consequently, to resolve the difficulty in developing elongated grain morphology in monophasic $\alpha$-sialon ceramics, we propose two new concepts: (i) Developing a new method of introducing a small amount of liquid phase that is thermodynamically compatible with the $\alpha$-sialon phase; and (ii) Employing novel sintering techniques, which should provide possibilities to prevent exhausting the transient liquid during heating and momentarily promote the formation of a large concentration of a transient liquid at the temperature suitable for grain growth.
4.2 New method to introduce extra liquid phase

4.2.1 A new method to introduce liquid phase
Simply supplying one or more oxide additive(s) or a pre-designed liquid component to a monophasic $\alpha$-sialon composition will most probably shift the composition away from the $\alpha$-sialon forming region, implying that one or more crystalline phase(s), e.g. $\beta$-sialon, melilite or garnet, may be formed besides an amorphous intergranular phase$^{107}$. In the present work, a small amount of liquid phase that is thermodynamically compatible with $\alpha$-sialon was introduced by raising the oxygen content of an already oxygen-rich $\alpha$-sialon composition, i.e. by increasing the O/N ratio in $\text{RE}_n\text{Si}_{12-(3x+n)}\text{Al}_{3x+n}\text{O}_n\text{N}_{16-n}$ while keeping the RE, Si and Al contents unchanged, see §3.1. Thus, for instance, based on a stoichiometric composition of $\text{RE}_{0.35}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{1.20}\text{N}_{14.80}$, a series of sialons with varied oxygen equivalent percentages of 7 %, 8%, 9%, 10%, 11%, 12% and 15% were prepared, where RE represents Y and Yb in equi-molar proportion as seen in Table 3.1.

4.2.2 Effect of excess oxygen on the phase assemblages obtained
Densities, phase assemblages, and unit cell dimensions of $\alpha$- and $\beta$-sialon phases present in obtained specimens by hot-pressing at 1800°C for 4 hrs are listed in Table 4.2. It is evident that the crystalline phase assemblages in the compacts change from containing only the $\alpha$-sialon phase to containing mainly $\beta$-sialon via the formation of duplex $\alpha$/$\beta$-sialon compacts when the overall oxygen equivalent percentage of the samples increases from 5.16 eq% in $\text{RE}_{0.35}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{1.20}\text{N}_{14.80}$ to 15.0 eq% in $\text{RE}_{0.35}\text{Si}_{9.75}\text{Al}_{2.25}\text{O}_{3.51}\text{N}_{13.26}$. A detailed phase analysis study of the $\text{A(Y+Yb)3512-ZZ}$ sample series revealed that the upper limit of the oxygen content for obtaining monophasic $\alpha$-sialon is around 7.0 eq%. Compacts containing $\alpha$- and $\beta$-sialon phases were obtained between 7.0 and 12.5 eq% oxygen, and above 12.5 eq% the only crystalline phase present was $\beta$-sialon. It should be noted that the unit cell dimensions of the $\alpha$- and $\beta$-sialon phases are similar in all samples. Besides $\alpha$-sialon and $\beta$-sialon (if present) phases, no other crystalline phase was identified.
The amount of residual intergranular amorphous phase, which is expected to be liquid at the sintering temperature, increases with increasing overall content of oxygen, as revealed by the SEM pictures shown in Figure 4.2.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Phase content (%)</th>
<th>α-sialon</th>
<th>β-sialon</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-sialon</td>
<td>β-sialon</td>
<td>a(Å)</td>
<td>c(Å)</td>
</tr>
<tr>
<td>AY3512</td>
<td>100</td>
<td>0</td>
<td>7.8117</td>
<td>5.6918</td>
</tr>
<tr>
<td>AY3512-07</td>
<td>100</td>
<td>0</td>
<td>7.8051</td>
<td>5.6912</td>
</tr>
<tr>
<td>AY3512-10</td>
<td>35</td>
<td>65</td>
<td>7.8114</td>
<td>5.6941</td>
</tr>
<tr>
<td>AY3512-15</td>
<td>0</td>
<td>100</td>
<td>7.6338</td>
<td>2.9320</td>
</tr>
<tr>
<td>AYb3512</td>
<td>100</td>
<td>0</td>
<td>7.8115</td>
<td>5.6918</td>
</tr>
<tr>
<td>AYb3512-07</td>
<td>100</td>
<td>0</td>
<td>7.8115</td>
<td>5.6918</td>
</tr>
<tr>
<td>AYb3512-10</td>
<td>55</td>
<td>45</td>
<td>7.8115</td>
<td>5.6920</td>
</tr>
<tr>
<td>AYb3512-15</td>
<td>0</td>
<td>100</td>
<td>7.6351</td>
<td>2.9333</td>
</tr>
<tr>
<td>A(Yb+Y)3512</td>
<td>100</td>
<td>0</td>
<td>7.8098</td>
<td>5.6897</td>
</tr>
<tr>
<td>A(Yb+Y)3512-07</td>
<td>100</td>
<td>0</td>
<td>7.8095</td>
<td>5.6917</td>
</tr>
<tr>
<td>A(Yb+Y)3512-08</td>
<td>80</td>
<td>20</td>
<td>7.8076</td>
<td>5.6897</td>
</tr>
<tr>
<td>A(Yb+Y)3512-09</td>
<td>64</td>
<td>36</td>
<td>7.8105</td>
<td>5.6916</td>
</tr>
<tr>
<td>A(Yb+Y)3512-10</td>
<td>49</td>
<td>51</td>
<td>7.8112</td>
<td>5.6941</td>
</tr>
<tr>
<td>A(Yb+Y)3512-11</td>
<td>25</td>
<td>75</td>
<td>7.8099</td>
<td>5.6920</td>
</tr>
<tr>
<td>A(Yb+Y)3512-12</td>
<td>8</td>
<td>92</td>
<td>7.8086</td>
<td>5.6906</td>
</tr>
<tr>
<td>A(Yb+Y)3512-13</td>
<td>0</td>
<td>100</td>
<td>7.6338</td>
<td>2.9299</td>
</tr>
<tr>
<td>A(Yb+Y)3512-15</td>
<td>0</td>
<td>100</td>
<td>7.6338</td>
<td>2.9319</td>
</tr>
</tbody>
</table>

4.2.3 In-situ reinforced microstructures in samples with extra liquid phase

Without addition of an extra liquid phase, the α-sialon grains possess an equiaxed morphology with an average grain size around 1 μm when hot-pressed at 1800°C for 4 hrs, as shown in Figure 4.1 and Figure 4.2a. The Y-, Yb- or (Y+Yb)-doped specimens had very similar microstructures. In contrast, the presence of an extra liquid phase aids the formation of grains with elongated morphology, as revealed by
the SEM picture of (Yb+Y)-doped specimens shown in Figure 4.2b–d. There is a clear tendency for more elongated grains of both the α- and β-sialon phases to form with increasing overall oxygen content. One can also note that the average grain size decreases with increasing amount of liquid present, and that the elongated β-sialon grains are thinner than those of α-sialon.

![Figure 4.2 Backscattered SEM micrographs of (Y+Yb)-stabilised sialon ceramics based on the ARE3512-ZZ composition, hot pressed at 1800°C for 4 hrs and containing (a) 5.1 eq%, (b) 7 eq%, (c) 10 eq% and (c) 15 eq% oxygen.](image)

As revealed by Figure 4.2, a slight increase of the oxygen content from the stoichiometric value 5.16 eq% to the non-stoichiometric one 7.0 eq% caused a small amount of an extra liquid phase to be introduced while α-sialon still remains the only crystalline phase. The amount of liquid formed corresponds to ~3 vol% according the quantitative image analysis. An in-situ reinforced microstructure containing elongated grains (up to ten micrometers in length) embedded in a matrix consisting of sub-micron sized equiaxed grains was found in all specimens of this overall composition, whether or not Y, Yb, or a mixture of Y and Yb was used as stabilising agent. The number of elongated grains and their sizes vary with the type
of stabilising ion used. Thus, more elongated grains with wider cross-sections were formed in the (Y+Yb)-doped specimen than in those containing Y or Yb alone (see Figure 4.2b and Figure 4.3). A quantitative analysis reveals that the mean widths of the elongated grains are 1.3, 1.5, and 1.8 µm in the Y-, Yb-, and (Y+Yb)-doped specimens, respectively.

Figure 4.3 Backscattered SEM micrographs of monophasic α-sialon ceramics, hot pressed at 1800ºC for 4 hrs, with starting compositions AY3512-07 (a) and AYb3512-07 (b).

4.3 Employing a novel sintering technique to prepare sialon ceramics with tailored microstructures

4.3.1 Enhanced densification by SPS

The temperature dependence of the normalised shrinkage, the phase assemblages and the grain sizes of SPS consolidated specimens of composition AYb3512 are presented in Figure 4.4. The densification starts at ~1300ºC and is complete at ~1550ºC without holding. The entire densification takes less than 1.5 min, demonstrating the very rapid densification feature of the SPS process. As shown in Chapter 3, a transient liquid phase is formed at the intermediate sintering stage in samples of overall ARE3512 composition. This liquid phase is more or less totally consumed at the end of the sintering process, whereas approximately 3vol% of an extra liquid/glass remains after sintering samples based on overall composition ARE3512-07.
Figure 4.4 Shrinkage, grain size and phase content plotted versus temperature for SPS-consolidated samples based on the AYb3512 composition.

Figure 4.5 Normalised shrinkage curves recorded during SPS processing of specimens based on the compositions A(Yb+Y)3512 and A(Yb+Y)3512-07.

The corresponding normalised shrinkage curves of the specimens based on the stoichiometric composition A(Yb+Y)3512 and the non-stoichiometric composition A(Yb+Y)3512-07 are shown in Figure 4.5. In both cases the densification starts at ~1250°C but it completes at different temperatures, namely ~1550°C and ~1600 °C for compositions A(Yb+Y)3512-07 and A(Yb+Y)3512, respectively. It thus appears that the presence of an extra liquid phase improves the densification. Similar rapid
densifications were also observed in other RE-stabilised sialon ceramics, e.g. ADy3512, ASm3512 and ANd3510 (see Table 3.1) when the SPS process was applied. It can be noted that specimens hot-pressed at 1500°C for 1 hr did not become dense.

Figure 4.6 Normalised shrinkage recorded during SPS processing of the specimen based on the composition AY3512-10. Shown in the inset is the shrinkage rate versus the sintering temperature.

Figure 4.6 shows the shrinkage curve recorded for a α/β-sialon composite of overall composition AY3512-10, where the shrinkage starts at ~1200°C and ends at 1500°C, using a heating rate of 200°C·min⁻¹. Two shoulders are observed in this shrinkage curve. We interpret these two shoulders, marked by the arrows at ~1200 and ~1350°C, respectively, as onsets of the formation of two types of liquid phase. The insert shows the shrinkage rate during densification, and the curve comprises two peaks, which are assumed to correspond to these two types of liquid phase. The former signals the formation of an oxide-based liquid just above the lowest eutectic temperature in the Y₂O₃–SiO₂–Al₂O₃ system, and the latter implies formation of a nitrogen-containing liquid just above the lowest eutectic temperature in the Y–Al–Si–O–N system. The time difference between the formations of two liquid phases is less than 1 min. This implies that a non-equilibrium liquid is formed during the rapid sintering process, and its presence accelerates the densification, as the
viscosity of concomitant liquids is expected to be comparatively low. The densities, morphology and crystalline phase assemblages of the formed phase(s) in SPS consolidated specimens prepared in the temperature interval 1400°C to 1700°C are listed in Table 4.3. In this particular case, fully dense samples were obtained already at a temperature of ~1450°C, and the entire densification process was completed within 2 min.

Table 4.3 Densities, morphologies and crystalline phase assemblages for \( \alpha \)- and \( \beta \)-sialon phase formed in specimens of composition AY3512-10, SPS consolidated at different temperatures without holding.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g/cm(^3))</th>
<th>Morphology</th>
<th>Crystalline assemblages (%)</th>
<th>( \alpha )-S(_3)N(_4)*</th>
<th>( \beta )-sialon</th>
<th>( \alpha )-sialon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>2.95</td>
<td>Equiaxed</td>
<td></td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1450</td>
<td>3.28</td>
<td>Equiaxed</td>
<td></td>
<td>66</td>
<td>11</td>
<td>23</td>
</tr>
<tr>
<td>1500</td>
<td>3.26</td>
<td>Equiaxed</td>
<td></td>
<td>59</td>
<td>13</td>
<td>28</td>
</tr>
<tr>
<td>1600</td>
<td>3.25</td>
<td>Equiaxed</td>
<td></td>
<td>13</td>
<td>36</td>
<td>51</td>
</tr>
<tr>
<td>1650</td>
<td>3.25</td>
<td>Elongated</td>
<td></td>
<td>0</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>1700</td>
<td>3.24</td>
<td>Elongated</td>
<td></td>
<td>0</td>
<td>51</td>
<td>49</td>
</tr>
</tbody>
</table>

* Un-reacted \( \alpha \)-S\(_3\)N\(_4\)

Specimens of overall compositions ALi1025 and ALi1025-17 (see §3.2.2) were fully densified at \( T \geq 1450°C \) and 1400°C respectively, without holding and using a heating rate of 100°C·min\(^{-1}\), as seen in Figure 4.7. The sintering shrinkage starts at \( \sim 1100°C \) and stops at \( \sim 1450 \) and \( \sim 1400°C \) for compositions ALi1025 and ALi1025-17, respectively, implying that the entire densification process takes only 3–3.5 min. Two shoulders, marked by the arrows at \( \sim 1100 \) and \( \sim 1300°C \), were also observed in the shrinkage curves of these two compositions. This implies that the oxide-based liquid formed at the lowest eutectic in the Li\(_2\)O–SiO\(_2–\)Al\(_2\)O\(_3\) system, and the nitrogen-containing liquid formed at the lowest eutectic in the Li-Si-Al-O-N system. The ALi0520 and BLi0520 specimens (see §3.2.2) exhibit similar rapid densification, and fully dense samples were obtained at 1450 and 1500°C, respectively. The densities, crystalline phase assemblages and unit cell parameters of the \( \alpha/\beta \)-sialon phases formed in these two compacts are given in Table 4.4.
Figure 4.7 The shrinkages recorded in SPS apparatus during densification of the specimens based on compositions ALi1025 and ALi1025-17, plotted versus temperature.

Table 4.4 Densities, crystalline phase assemblages and unit cell parameters for α- and β-sialon phases formed in specimens ALi0520 and BLi0520 in the SPS apparatus at different temperatures, without holding.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>Phases (%)*</th>
<th>α- sialon</th>
<th>β- sialon</th>
<th>α/β</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>x_average</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>z_average</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALi0520</td>
<td>1450°C</td>
<td>3.14</td>
<td>19</td>
<td>0</td>
<td>81</td>
<td>7.8443</td>
<td>5.6898</td>
<td>0.48</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1600°C</td>
<td>3.13</td>
<td>100</td>
<td>0</td>
<td></td>
<td>7.8135</td>
<td>5.6775</td>
<td>0.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1650°C</td>
<td>3.13</td>
<td>76</td>
<td>24</td>
<td></td>
<td>7.8099</td>
<td>5.6769</td>
<td>0.40</td>
<td>7.6563</td>
<td>2.9403</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1700°C</td>
<td>3.04</td>
<td>47</td>
<td>53</td>
<td></td>
<td>7.8075</td>
<td>5.673</td>
<td>0.38</td>
<td>7.6586</td>
<td>2.9407</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>BLi0520</td>
<td>1500°C</td>
<td>3.14</td>
<td>15</td>
<td>0</td>
<td>85</td>
<td>7.8277</td>
<td>5.6913</td>
<td>0.51</td>
<td>7.6694</td>
<td>2.944</td>
<td>1.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1600°C</td>
<td>3.13</td>
<td>41</td>
<td>25</td>
<td>34</td>
<td>7.8212</td>
<td>5.6878</td>
<td>0.48</td>
<td>7.6588</td>
<td>2.9435</td>
<td>1.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1700°C</td>
<td>3.06</td>
<td>41</td>
<td>59</td>
<td>0</td>
<td>7.8125</td>
<td>5.6736</td>
<td>0.40</td>
<td>7.6528</td>
<td>2.9400</td>
<td>1.47</td>
<td></td>
</tr>
</tbody>
</table>

*α’ and β’ represent α- and β-sialon, respectively; α/β are the remained α- and β-Si₃N₄ in ALi0520 and BLi0520, respectively.

The shrinkage curves given in Figures 4.4-4.7 show a similar trend during the densification process, i.e. shrinkage is very rapid as soon as it is thermally activated. Two shoulders were observed in the shrinkage curve and these two shoulders signal two types of liquid phase appearing during the densification process.
Table 4.5 Preparation conditions, phase assemblages, unit cell dimensions and mechanical properties of specimens obtained in the SPS apparatus at different temperatures, without holding.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperatures (°C)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>α (%)*</th>
<th>$H_{\nu 10}$ (GPa)</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AYb3512</td>
<td>1550</td>
<td>7.8175</td>
<td>5.6972</td>
<td>76.4</td>
<td>20.2±0.2</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>7.8137</td>
<td>5.6875</td>
<td>90.0</td>
<td>20.4±0.2</td>
<td>3.6±0.2</td>
</tr>
<tr>
<td></td>
<td>1650</td>
<td>7.8078</td>
<td>5.6833</td>
<td>100</td>
<td>20.6±0.2</td>
<td>3.8±0.2</td>
</tr>
<tr>
<td></td>
<td>1700</td>
<td>7.8062</td>
<td>5.6826</td>
<td>100</td>
<td>19.7±0.2</td>
<td>4.2±0.1</td>
</tr>
<tr>
<td></td>
<td>1750</td>
<td>7.8083</td>
<td>5.6846</td>
<td>100</td>
<td>19.9±0.2</td>
<td>5.2±0.3</td>
</tr>
<tr>
<td></td>
<td>1830</td>
<td>7.8085</td>
<td>5.6865</td>
<td>100</td>
<td>19.6±0.2</td>
<td>5.3±0.2</td>
</tr>
<tr>
<td>AYb3512-07</td>
<td>1500</td>
<td>7.8352</td>
<td>5.7124</td>
<td>72.7</td>
<td>19.9±0.2</td>
<td>3.5±0.2</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>7.8113</td>
<td>5.6978</td>
<td>92.0</td>
<td>19.8±0.2</td>
<td>3.7±0.1</td>
</tr>
<tr>
<td></td>
<td>1650</td>
<td>7.8079</td>
<td>5.6883</td>
<td>100</td>
<td>20.2±0.2</td>
<td>3.9±0.2</td>
</tr>
<tr>
<td></td>
<td>1700</td>
<td>7.8065</td>
<td>5.6896</td>
<td>100</td>
<td>20.1±0.2</td>
<td>4.4±0.1</td>
</tr>
<tr>
<td></td>
<td>1750</td>
<td>100</td>
<td>19.6±0.2</td>
<td>6.3±0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1800</td>
<td>100</td>
<td>20.0±0.2</td>
<td>6.2±0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A(Yb+Y) 3512-07</td>
<td>1550</td>
<td>7.8185</td>
<td>5.6986</td>
<td>79.4</td>
<td>18.7±0.2</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td></td>
<td>1600</td>
<td>7.8152</td>
<td>5.6913</td>
<td>100</td>
<td>19.6±0.1</td>
<td>3.6±0.2</td>
</tr>
<tr>
<td></td>
<td>1700</td>
<td>7.8117</td>
<td>5.6887</td>
<td>100</td>
<td>20.3±0.2</td>
<td>4.3±0.2</td>
</tr>
<tr>
<td></td>
<td>1750</td>
<td>100</td>
<td>19.9±0.1</td>
<td>5.1±0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1830</td>
<td>100</td>
<td>20.1±0.2</td>
<td>5.4±0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The additional crystalline phase is un-reacted Si$_3$N$_4$.

4.3.2 Fast phase transformation

The temperature dependence of the α-sialon content in samples AYb3512, AYb3512-07 and A(Yb+Y)3512-07 is shown in Table 4.5. It is obvious that the α-sialon phase is the only crystalline phase when thermodynamic equilibrium is reached, while at the lowest sintering temperatures applied the transformation from α-Si$_3$N$_4$ to α-sialon is not complete even though full densification is achieved. Thus, at 1550°C the A(Yb+Y)3512-07 and AYb3512 samples are both fully densified, but contain, according to the X-ray analysis, ~20 % and ~23.4 % un-reacted α-Si$_3$N$_4$, respectively. The formation of α-sialon is not completed in fully
densified compacts until the sintering temperature is increased to 1600°C and 1650°C for compositions A(Yb+Y)3512-07 and AYb3512, respectively. Taking into account that the time spent in increasing the temperature from 1550 to 1650°C is approximately 0.5 min, it appears clearly that the phase transformation progress is also very fast in the SPS process. The unit cell dimensions of the α-sialon phase of the samples listed in Table 4.5 confirm that their compositions are very close to the oxygen-rich boundary of the α-sialon phase forming area; i.e. no matter if HP or SPS is employed for densification, the final phase constitutions of a given composition are the same, presumably representing thermodynamic equilibrium. A similarly rapid phase transformation has also been observed in SPS-consolidated rare earth-stabilised α-sialon samples with compositions ARE3512 (RE = Sm, Dy and Y) and ANd3510 (see Table 3.1), using fast heating rates (200°C⋅min⁻¹).

The crystalline phase content of the AY3512-10 composition is ~50 % α- and ~50 % β-sialon at equilibrium, as shown in Table 4.3. At ~1400°C, 90 % of the theoretical density is achieved, whereas the phase transformation from α-Si₃N₄ to α-sialon and/or β-sialon is restricted, as manifested by the fact that the dense compact contains 100 % un-reacted α-Si₃N₄. The phase transformation progresses in a fully dense compact, however, when the temperature is increased. At ~1650°C, an equilibrated α/β-sialon composite is obtained, containing ~50 % α- and ~50 % β-sialon. As a high heating rate 200°C⋅min⁻¹ is used in these experiments, the phase transformation completed within 1.25 min.

For the ALi0520 and BLi0520 compositions, the phase transformations and/or reaction sequences that occur in dense SPS consolidated samples at temperatures ranging from 1450 to 1750°C were investigated. The phase assemblages present, as revealed by XRD, are given in Table 4.4. At low temperatures, 1450 and 1500°C, the formation of α-sialon phase is favoured over β-sialon, no matter if α-Si₃N₄ or β-Si₃N₄ is used as precursor powder. Increasing the temperature to 1600°C, the amount of α-sialon phase formed increases and that of α-Si₃N₄ decreases. The
ALi0520 sample still does not contain any β-sialon phase, whereas BLi0520 is composed of a mixture of α- and β-sialon and remaining β-Si₃N₄ phases. When the temperature is increased to 1650°C, the β-sialon phase is also found in the ALi0520 sample, while BLi0520 still contains a mixture of α- and β-sialon and remaining β-Si₃N₄, but with higher content of β-sialon and lower content of α-sialon and β-Si₃N₄. Finally, when the temperature is increased to 1700°C for the ALi0520 and to 1750°C for the BLi0520 samples, the expected duplex α–β sialon ceramics are obtained.

![Graph showing the evolution of grain geometry and fracture toughness with sintering temperature.](image)

Figure 4.8 Evolution of grain geometry and fracture toughness with sintering temperature in SPS-consolidated samples, based on the AYb3512-07 composition.

4.3.3 Rapid anisotropic grain growth

The length and width of randomly selected equiaxed and elongated grains (when present) in samples of the AYb3512, AYb3512-07 and A(Yb+Y)3512-07 compositions are shown in Figure 4.4, Figure 4.8 and Figure 4.9, respectively. The fully dense compacts obtained at ~1550°C consist of nearly equiaxed grains of sub-micron size. Within less than 1 min, a microstructure consisting of fine equiaxed grains transformed into a tough interlocking one consisting of well facetted, elongated grains. This verifies that grain growth is strongly temperature-dependent but not directly associated with the phase transformation, because the onset
temperature of grain growth for both compositions AYb3512 and A(Yb+Y)3512-07 is \(~1650^\circ\text{C}\), while the transformation from \(\alpha\)-Si\(_3\)N\(_4\) to \(\alpha\)-sialon is completed already at 1600\(^{\circ}\text{C}\). Between 1650 and 1750\(^{\circ}\text{C}\), grains start to develop an elongated morphology, yielding an \textit{in-situ} reinforced microstructure. Obviously, above the temperature threshold for grain growth, very fast grain growth takes place, resulting in the formation of elongated grains with lengths ranging from a few to ten micrometers. Similar rapid anisotropic grain growth rates have also been observed in other RE-stabilised sialon samples as long as a transient liquid is formed or a permanent intergranular liquid phase is present. Such rapid anisotropic growth of \(\alpha\)-sialon grains is hard to interpret by the static Ostwald ripening mechanism\(^{43,88,111}\).

![Figure 4.9](image)

Figure 4.9 The evolution of grain geometry with sintering temperature during SPS processing of the samples based on the A(Yb+Y)3512-07 composition. The inset reveals that the fracture toughness increases with the formation of elongated grains.

SEM micrographs of fracture surfaces in specimens of compositions ARE3512 (RE= Sm, Dy, Y, Yb) and ANd3510, SPS consolidated at 1830\(^{\circ}\text{C}\) without holding are shown in Figure 4.10. In these experiments a heating rate of 200\(^{\circ}\text{C}/\text{min}\) was used, and the grain growth process, once activated, progressed very rapidly, and the resulting specimens contain elongated \(\alpha\)-sialon grains of the same or even larger size than those found in the Nd- and Sm-doped samples prepared by hot pressing at 1900\(^{\circ}\text{C}\) for 4 hrs. Applying similar sintering parameters, \textit{in-situ} reinforced microstructures were obtained even for Y- and Yb-doped \(\alpha\)-sialon samples, whereas
the very same compositions hot-pressed at 1900°C for 4 hrs yielded microstructures containing only large equiaxed grains.

Figure 4.10 SEM micrographs of fracture surfaces in samples, based on the composition ARE3512 (RE=Dy, Sm, Yb and Y) and ANd3510, after SPSing at 1830°C without holding, showing the in-situ reinforced microstructure formed in all systems investigated. The microstructure of the Y-doped sample resembles that of the Dy-doped one.

4.4 Concluding remarks

By selecting appropriate compositions and sintering parameters via the use of a new processing concept, fully dense ceramics with tailored microstructures can be obtained, which consist of either submicron-sized grains with equiaxed morphology or well faceted grains with elongated morphology. This opens up new possibilities for further materials development. It has been demonstrated that SPS is an efficient technique to implement this new concept.
5. Sintering kinetics

The densification, phase transformation/reaction and grain growth processes are most often observed to occur simultaneously during conventional sintering of \( \text{Si}_3\text{N}_4 \)-based ceramics, which implies that it is difficult to study the kinetics of each process separately. Using SPS, however, the densification process can be accomplished at such a low temperature that the kinetics of grain growth is retarded, and so are the phase transformation/reactions. Furthermore, the phase transformations/reactions can be accomplished before the grain growth process is initiated. This therefore provides us with a unique opportunity to monitor the kinetics of densification, phase transformation/reactions and grain growth separately.

5.1 Densification mechanism

Typical shrinkage data recorded during densification of \( \text{Si}_3\text{N}_4 \)-based ceramics by SPS are given in Figures 4.4-4.7. It is difficult to interpret these data on the basis of the classical sintering theories discussed above. The fact that full density can be achieved with very limited involvement of phase transformation and grain growth suggests that densification is accomplished mainly via particle rearrangement assisted by the presence of a liquid phase. Table 5.1 summarises the main densification characteristics of the prepared specimens. In the RE-doped sialon system the densification started at 1200–1300°C and ended at 1480–1600°C when a constant heating rate of 200°C-min\(^{-1}\) and a compressive stress of 50 MPa were applied. The recorded maximum shrinkage rate is in the range of 8.5 to 13 \( \times \) 10\(^{-3}\) sec\(^{-1}\). Full density was achieved when heating up to \( \sim \)1450°C, where the transformation of \( \alpha \)-Si\(_3\)N\(_4\) to \( \alpha \)- and/or \( \beta \)-sialon was of minor importance (see § 4.3).
Table 5.1 Densification characteristics of specimens heated in the SPS apparatus to 1700°C.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>T&lt;sub&gt;start&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;end&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; (°C)</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt; (s&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AYb3512</td>
<td>~ 1300</td>
<td>~ 1550</td>
<td>~ 1460</td>
<td>9.0×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>AYb3512-07</td>
<td>~ 1250</td>
<td>~ 1500</td>
<td>~ 1451</td>
<td>9.4×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>AY3512-10</td>
<td>~ 1200</td>
<td>~ 1480</td>
<td>~ 1407</td>
<td>9.6×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>A(Y+Yb) 3512</td>
<td>~ 1250</td>
<td>~ 1600</td>
<td>~ 1470</td>
<td>8.5×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>A(Y+Yb) 3512-07</td>
<td>~ 1250</td>
<td>~ 1550</td>
<td>~ 1430</td>
<td>1.3×10&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>ALi1025&lt;sup&gt;*&lt;/sup&gt;</td>
<td>~ 1100</td>
<td>~ 1450</td>
<td>~ 1420</td>
<td>4.8×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>ALi1025-17&lt;sup&gt;*&lt;/sup&gt;</td>
<td>~ 1100</td>
<td>~ 1400</td>
<td>~ 1360</td>
<td>4.6×10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

* In these cases the applied heating rate was 100°C·min<sup>-1</sup>.

Obviously, the rapid densification process observed in SPS differs from that in conventional hot pressing. Figure 5.1 shows the shrinkage data recorded during SPS processing of α-sialon based on the A(Yb+Y)3512-07 composition, when a heating rate of 100°C·min<sup>-1</sup> was used. In this particular case full density was approached after holding at 1350°C for only 1.5 min. Three stages can be distinguished, namely stage I) Initial particle rearrangement initiated when an oxygen-rich liquid forms; stage II) Extensive particle rearrangement effected by grain boundary sliding; and stage III) The final elimination of closed pores.

![Figure 5.1](image-url)  
Figure 5.1 The density plotted versus time, recorded during SPS processing of a specimen based on the A(Yb+Y)3512-07 composition. The applied heating rate and uniaxial pressure are 100°C·min<sup>-1</sup> and 50 MPa, respectively. Three densification stages are clearly revealed: I) Initial particle rearrangement; II) Extensive particle rearrangements; and III) The elimination of the closed pores.
For SPS, the most intriguing feature is the extensive second-stage particle rearrangement that occurs dramatically fast, once activated above a critical temperature. To determine the kinetics of this stage, Kingery’s theory was used to simulate the relation between shrinkage and holding time. As reviewed in Chapter 1, if the densification is mainly controlled by viscous flow, the shrinkage \( \frac{\Delta L}{L_0} \) data should be fitted by Equation (1-1) (see §1.2.3), \( \Delta L/L_0 = k \cdot t^{1+y} \), with the exponent \( 1+y \) slightly larger than one. Figure 5.2a shows the linear correlation of log (\( \Delta L/L_0 \)) with log t for the sample based on the A(Yb+Y)3512-07 composition, when it was densified up to 90% theoretical density. The slope of these fitted lines at 1350 and 1400°C are \( \sim 0.59 \) and \( \sim 0.17 \), respectively. These exponent values are far less than 1, indicating that viscous flow is not a dominating mechanism in this case.

On the other hand, when the data were fitted using Kingery’s equation for a solution-precipitation step, \( \frac{\Delta L}{L_0} \propto t^{1/n} \), the time exponent \( 1/n \) values are \( \sim 0.59 \) and \( \sim 0.17 \), \( i.e., \) the measured \( n \) values are 1.7 and 5.9 at 1350°C and 1400°C, respectively, approximating 2 and 5. This implies that a grain boundary reaction is the rate-controlling step at 1350°C, and diffusion becomes the controlling step at 1400°C. This can be accounted for by the fact that the dissolution of AlN and Si\(_3\)N\(_4\) into an early-formed oxygen-rich liquid is restricted below a certain critical temperature (1350°C) and thus becomes the rate-controlling step. Above this temperature, \( e.g. \) at 1400°C, the diffusion process becomes rate-controlling step instead, because at this temperature the dissolution process takes place rapidly, and large amount of nitrogen-containing liquid is formed. Further investigation of this process is required in future work to determine the activation energy and reaction constant. Anyhow, the experimental data gathered so far convincingly demonstrate that particle rearrangement occurs very rapidly during the SPS process, whether or not the grain boundary sliding is accompanied with a diffusion-controlled or a reaction-controlled process in the liquid.
Figure 5.2 Logarithmic shrinkage versus logarithmic time, derived from shrinkage data recorded during isothermal SPS processing of samples based on the A(Yb+Y)$_3$512-07 (a) and ALi1025 compositions (b). In all cases, a pressure of 50 MPa and a heating rate of 100°C·min$^{-1}$ were applied.
A similar densification mechanism is reasonable in the lithium-doped sialon system. In this case, as shown in Figure 5.2b, the time exponent in the temperature range 1250–1400°C is \(~0.17\), implying that the \( n \) value is 5.9. This indicates that grain-boundary sliding accompanied by diffusion process always operates at these temperatures, because the temperature required for dissolving Si\(_3\)N\(_4\) and AlN particles is in this case much lower.

Another fact that contributes to enhancing densification during SPS processing of silicon nitride-based ceramics is the non-equilibrium nature of the formed liquid phase. Due to the high heating rate applied, a concentration gradient is built up in the liquid, so that the liquid formed close to the Si\(_3\)N\(_4\) particles is rich in nitrogen, as illustrated in Figure 5.3. When rapidly heated, the oxygen-rich part of the liquid is brought up to a high temperature where it has very low viscosity, thus enhancing the particle sliding under compressive stress.

![Figure 5.3](image_url)

Figure 5.3 A sketch map illustrating the compositional gradient in the liquid phase formed. The nitrogen concentration in the shell regions surrounding Si\(_3\)N\(_4\) particles, marked with dark grey contrast, is higher than in other parts marked with light grey contrast.
5.2 Reaction sequence in fully dense ceramics

For a given overall composition, the final thermodynamic equilibrium phase assemblies are independent of the process employed, whether conventional hot pressing or SPS. However, the rate and the sequence of phase transformations/reactions that will take place are strongly dependent on the precursors used, their compositions, and the sintering parameters applied. In conventional hot pressing the densification of Si$_3$N$_4$-based ceramics takes several hours, and the densification is accompanied by phase transformations/reactions and grain growth. In the SPS process the densification can be accomplished with very limited involvement of phase transformations/reactions, as described in §4.3.3. Therefore, the phase transformation/reaction sequence can be precisely followed and manipulated during further annealing after complete densification.

For the AY3512-10 composition, the equilibrated compact contained 50 % $\alpha$-sialon and 50 % $\beta$-sialon. The temperature dependence of the phase formation that occurs in the fully dense compact is summarised in Table 4.3, and the following reaction sequence can be deduced:

Green body containing $\alpha$-Si$_3$N$_4$, Al$_2$O$_3$, AlN, Y$_2$O$_3$ $\rightarrow$ Dense compact containing $\alpha$-Si$_3$N$_4$, AlN and an amorphous Y-Al-Si-O-N phase $\rightarrow$ Dense compact containing $\alpha$-Si$_3$N$_4$, $\alpha$-sialon and an amorphous Y-Al-Si-O-N phase $\rightarrow$ Dense compact containing $\alpha$-Si$_3$N$_4$, $\alpha$-sialon, $\beta$-sialon and an amorphous Y-Al-Si-O-N phase $\rightarrow$ Dense compact containing $\alpha$-sialon, $\beta$-sialon and an amorphous Y-Al-Si-O-N phase.

In the lithium-stabilised $\alpha/\beta$ sialon sample of the composition Li0520, an $\alpha$-sialon-rich compact is initially formed, and prolonging the heat treatment yields a compact containing equal percentages of the $\alpha$- and $\beta$-sialon phases, as seen in Table 4.4. The following schematic reaction sequence seems be valid, independent of the use of $\alpha$-Si$_3$N$_4$ or $\beta$-Si$_3$N$_4$ as starting precursor:
Green body containing Si₃N₄, Al₂O₃, AlN, Li₂CO₃ → Dense compact containing Si₃N₄, α-sialon, AlN and an amorphous Li-Al-Si-O-N phase → (Dense compact containing α-sialon, and an amorphous Li-Al-Si-O-N phase) → Dense compact containing α-sialon, β-sialon and an amorphous Li-Al-Si-O-N phase.

It appears clear that the α-sialon phase is initially formed, irrespective of whether α-Si₃N₄ or β-Si₃N₄ is used as starting powder. Further heat treatment then induces α to β phase transition at higher temperature.

It is worth noting that when β-Si₃N₄ or a coarse α-Si₃N₄ powder is used as starting precursor to prepare α/β-sialon, the phase transformation from α-Si₃N₄ and/or β-Si₃N₄ to α-sialon phase is significantly retarded. This can be interpreted in the following manner: (i) The dissolution of coarser grains requires higher temperature; and (ii) β-Si₃N₄ phase frequently contains fewer defects and less oxygen than α-Si₃N₄, which is expected to retard dissolution.

The phase transformations/reactions that occur in the SPS process are controlled by the same mechanism as in conventional hot pressing, i.e. a solution-diffusion-reprecipitation mechanism, but it progresses much faster. This can be ascribed to the dissolution and diffusion processes being accelerated by the pulsed electric field.

5.3 Grain growth mechanism

The fact that densification and phase transformation can be accomplished before any appreciable grain growth occurs allows us to investigate the grain growth kinetics in fully dense compacts, thus minimising the influence of porosity and phase transformation.
5.3.1 Static ripening

The static ripening mechanism has been extensively investigated and reported in the literature\textsuperscript{43,88,111-114}. It dominates the microstructure evolution of hot-pressed $\alpha$-sialon ceramics, as described in §4.1 and §4.2. Figure 5.4 illustrates schematically a typical static ripening mechanism when sintering Si$_3$N$_4$-based ceramics. It clarifies that the grain growth involves three stages: (i) Dissolution of small grains in a liquid that is close to equilibrium with solids present; (ii) Diffusion through the liquid; and (iii) Isotropic and/or anisotropic grain growth. The characteristic features of the static ripening process are: (i) The grain growth process is thermally activated; (ii) The presence of a small amount liquid assists the development of elongated grain morphology; and (iii) The grain growth occurs at a slow speed. The slow grain boundary diffusion in the absence of a sufficient amount of liquid often masks the diversity of interfacial reactions that determine the morphology of growing grains. Therefore, under the static conditions it is difficult to develop an \textit{in-situ} reinforced microstructure in $\alpha$-sialon ceramics with stoichiometric composition, as exemplified in Figure 5.5.
5.3.2 Dynamic ripening

A distinct temperature threshold for grain growth is observed in SPS-consolidated α-sialon ceramics, above which grain growth is activated and the development of grains with elongated morphology occurs very rapidly (within minutes), whether or not an extra liquid is involved, as shown in §4.3. This rapid grain growth occurs in fully dense compacts and cannot be interpreted by the static ripening mechanism.

By SPS fully dense compacts are typically obtained in the temperature range 1350–1550°C with only a few minutes of holding, as discussed in §4.3.1 and §5.1. These compacts consist of fine grains and usually have crystalline phase assemblies and glass/liquid phases with compositions far from thermodynamic equilibrium. Prolonged sintering or further annealing makes grain growth take place rapidly, within minutes. The microstructures of AYb3512, consolidated by SPS at two different heating rates, 200°C-min⁻¹ and 40°C-min⁻¹, verify that the use of fast heating rates is essential for obtaining the required elongated grains, see Figure 5.6. Using rapid heating rates (200°C-min⁻¹) yields a microstructure with interlocking morphology, whereas using a slow heating rate (40°C C-min⁻¹) does not produce...
elongated grains. A heating rate of 40°C·min⁻¹ is typically used in conventional hot pressing of Si₃N₄-based ceramics.

We ascribe the rapid grain growth described above to an anisotropic ripening process that takes place dynamically – abbreviated as *dynamic ripening*. Dynamic ripening only occurs when the liquid phase is grossly out of thermodynamic equilibrium with the main crystalline phase(s), *i.e.* is associated to a thermodynamic state that provides a strong chemical driving force pushing the system towards equilibrium, enhancing the dissolution of small grains and producing a momentarily supersaturated liquid that fertilises rapid anisotropic grain growth by a diversity of interfacial reactions.

Figure 5.6 SEM photos of fractured surfaces in an α-sialon ceramic with a stoichiometric composition of AYb₃5₁₂, heated to 1750°C: a) using a heating rate of 200°C·min⁻¹; b) using a heating rate of 40°C·min⁻¹.

### 5.4 Sintering kinetics

Up to now it has been commonly accepted that phase transformation and reactions leading to the formation of various sialon phases are beneficial to grain growth, whereas the formation of rigid structure prevents further densification at the final sintering stage. During the SPS process, full density is accomplished with very limited involvement of phase transformation and grain growth. This implies that there is no obvious correlation between densification, phase transformations/reactions and grain growth; instead, they are just three individual
temperature-dependent processes that happen to occur simultaneously in conventional sintering processes. In SPS, the kinetics of these processes can be more precisely determined and monitored, due to the fact that it is possible to discern a slight difference in the onset temperatures of densification ($T_d$), phase transformations/reactions ($T_t$) and grain growth ($T_g$).

In general, our observations have revealed that $T_g \geq T_t \geq T_d$ in silicon nitride-based ceramics, as illustrated in Figure 5.7. These critical temperatures are adjustable by varying the composition and processing parameters. Any adjustment of the composition and/or processing parameters that depresses the kinetics of the densification and/or transformation, e.g. the a and b curves are replaced by a’ and b’ in Figure 5.7, may thus make grain growth take place concurrently with densification and/or phase transformation. In order to enhance the densification process, high temperatures are applied in conventional sintering techniques, and these densification temperatures are often well above $T_t$ and $T_g$, as determined in the SPS process.

Figure 5.7 A schematic drawing illustrating the kinetics of three temperature-dependent processes: densification, transformation and grain growth, which often occur simultaneously in sintering of silicon nitride-based ceramics. See also text.
Below $T_g$ the fine-grained microstructures are obtained, no matter if they consist of equilibrium or non-equilibrium phase constituents. This type of fine-grained ceramic is ideal for super-plastic deformation at a temperature below $T_g$. The fine-grained structures can be converted to tough self-reinforced microstructures consisting of interlocking elongated grains by post-annealing the deformed sample above $T_g$, as discussed above.
6. Property Evaluation

By the introduction of an extra liquid phase and/or employing the new processing concept, α-sialon ceramics with pre-determined morphologies can be precisely and easily developed, *e.g.* yielding either equiaxed or elongated grain morphologies, as described in §4.1 to §4.3. The latter type of microstructure enhances fracture toughness by grain bridging, crack deflection, and grain pull-out mechanisms. On the other hand, the microstructures with fine, equiaxed grains offer a variety of opportunities to fabricate ceramics with complicated shapes by super-plastic deformation.

The influence of the microstructure of the obtained Si₃N₄-based ceramics on properties such as hardness, fracture toughness, thermal-shock resistance and super-plastic behaviour will be elucidated in this chapter.

6.1 Mechanical properties

The hardness and fracture toughness values of the prepared sialon specimens are presented in Table 4.5, Figure 4.8 and Figure 4.9. In summary: *(i)* Compacts containing elongated grains exhibit fracture toughness values in the range 5.0 to 6.5 MPa·m¹⁄², whereas those containing equiaxed grains have fracture toughness values in the range 3.5 to 4.0 MPa·m¹⁄², verifying that compacts with interlocking microstructures exhibit improved fracture toughness; *(ii)* All α-sialon compacts have hardness values ~20 GPa; *(iii)* The hardness of samples in the A(Yb+Y)₃512-ZZ series varies with the α/β content ratio from ~21 GPa to ~16 GPa, and the fracture toughness increases concurrently from ~3.5 to ~6.0 MPa·m¹⁄² when the crystalline
assemblages present in the compact vary from monolithic $\alpha$-sialon to monolithic $\beta$-sialon via compacts containing various proportions of the $\alpha$- and $\beta$-sialon phase components.

![Figure 6.1](image)

**Figure 6.1** The crack growth in percent, plotted *versus* the thermal-shock temperature difference for specimens based on the A(Yb+Y)3512 composition, SPS consolidated at 1700°C without holding (a), and on the A(Yb+Y)3512-07 composition, SPS consolidated at 1700°C without holding (b) and with 10 minutes holding(c).

### 6.2 Improved damage tolerance

The cracks extensions on surfaces of the A(Yb+Y)3512 and A(Yb+Y)3512-07 compositions are plotted versus temperature difference in Figure 6.1. It is obvious that the samples SPSed at 1700°C without holding are less resistant to thermal shock than those prepared with a holding time of 10 min, and the curves of the former ones resemble those reported for hot-pressed duplex $\alpha/\beta$-sialon composites, which are regarded as having comparatively bad thermal-shock properties$^{116}$. However, the A(Yb+Y)3512-07 samples SPSed at 1700°C with a holding time of 10 min exhibit excellent thermal-shock properties, which are quite comparable to those of self-reinforced $\beta$-sialon ceramics containing 20 vol% glass phase, prepared by hot pressing$^{117}$. 

60
The SEM investigation reveals that microstructures formed in the stoichiometric A(Yb+Y)3512 composition SPSed at 1700°C without holding contains only equiaxed grains with diameters less than ~1 μm. When approximately 3 vol% of a liquid phase was added to this sample, the microstructure formed at 1700°C with 10 min holding time contained elongated grains with an average diameter of 1.2 μm and an aspect ratio of 4, distributed in a matrix of sub-micrometer-sized α-sialon grains. This clearly confirms that the improved thermal-shock resistance of this A(Yb+Y)3512-07 specimen can be attributed to the formation of an interlocking microstructure. It should be noted, however, that the presence of too large acicular grains will deteriorate the fracture strength and thus also the thermal-shock properties, because these grains act as crack initiation sites.

As a consequence, α-sialon ceramics that are inherently hard and contain acicular grains of appropriate sizes, formed in situ, exhibit improved fracture toughness values and excellent thermal-shock properties, which ought to widen their engineering application areas, especially as wear-resistant components and cutting-tool inserts.

6.3 Enhanced superplasticity

The rapid densification of sialon powders by the SPS process described above is interpreted in terms of the viscosity of the liquid/glassy phase present at the grain boundaries being reduced by the pulsed electric field. If this is correct, one expects a similar improvement in deformation rate. We have accordingly performed deformation tests for a variety of Si₃N₄-based ceramics with sub-micron sized microstructures in the SPS apparatus and, for comparison, in a conventional hot-pressing (HP) furnace. We have observed a radical improvement of the deformation rate when the SPS procedure is used. Below we will present some representative examples.
6.3.1 Lithium-stabilised monolithic $\alpha$-sialon and duplex $\alpha/\beta$-composite

The compressive strain in two lithium-stabilised sialons, of compositions ALi1025 and ALi1025-17 (see §3.2.2), has been recorded during super-plastic deformation in the SPS apparatus and is shown in Figure 6.2. The specimens used in the deformation experiment were compacted at 1450°C, using a holding time of 2 min and a pressure of 50 MPa. For comparison of mechanism, the densification curves of these compositions are also given in Figure 6.2. A maximum shrinkage rate of $4.8 \times 10^{-3}$ s$^{-1}$ during densification was recorded for the ALi1025 composition at 1420°C, and corresponding value for the ALi1025-17 composition at 1360°C is $4.6 \times 10^{-3}$ s$^{-1}$.

![Figure 6.2](image)

Figure 6.2 The shrinkages ($a_0$ and $b_0$) and compressive strains ($a_1$ and $b_1$) recorded during densification and super-plastic deformation, plotted versus temperature. $a$ and $b$ represent the specimens based on the ALi1025 and ALi1025-17 compositions, respectively.

Super-plastic deformation occurs surprisingly fast in the SPS apparatus as soon as the softening temperature of the intergranular glass phases is reached. The compressive deformation rates reached at $\sim$1420°C and $\sim$1380°C for the ALi1025 and ALi1025-17 compositions, respectively, are both in the range $\sim 5.0 \times 10^{-3}$ s$^{-1}$, i.e. comparable to the observed densification rates. This indicates that both processes depend on the same mechanism; i.e. the low-viscosity liquid allows a rapid flow of the sub-micron sized grains along the grain boundary under compressive stress.
The fact that no deformation occurs in the fully densified specimens at \( \sim 1100^\circ C \) – the eutectic temperature in the Li-Si-Al-O system – indicates that it is an oxynitride liquid/glassy phase that remains at the grain boundaries in the pre-prepared fully densified specimens. The observed difference between the super-plastic onset temperatures, \( \sim 1380 \) and \( \sim 1300^\circ C \) for the ALi1025 and ALi1025-17 compositions respectively, suggests that the amount of liquid is less and its viscosity presumably higher in ALi1025 than in ALi1025-17.

![Figure 6.3 SEM photos of the fracture surfaces in SPS consolidated specimens based on the ALi1025 (a) and ALi1025-17 compositions (b), and after deformation up to 1490^\circ C for a specimen based on ALi1025 (c) and up to 1450^\circ C for a specimen based on ALi1025-17 (d).](image)

The microstructures of these specimens are very similar before and after the deformation, as seen in Figure 6.3. Accordingly, there is no noticeable strain hardening, a process that has often been observed during super-plastic deformation of silicon nitride-based ceramics by more conventional methods. We ascribe the absence of strain hardening to the fact that the compacts used in the deformation experiments contain non-equilibrated phase assemblages, and that the reactions
leading to thermodynamic equilibrium are retarded at the temperatures where the compaction and deformation experiments were performed.

6.3.2 Y-/Yb-doped monophasic α-sialon and β-sialon

The two compositions A(Yb+Y)3512-07 and G20B06 (see §3.2.3) were first consolidated to full density by the SPS process at 1500°C for 2 min and 1550°C for 4 min, respectively. Their super-plastic behaviour was then tested in the SPS apparatus. These two dense compacts could be deformed dramatically rapidly above 1450°C and 1500°C, respectively, and strains of ~50% were achieved within ~2 minutes, as seen in Figure 6.4a. For comparison, the very same experiment was carried out with the HP equipment, but in this case the A(Yb+Y)3512-07 and G20B06 specimens could not be deformed until the temperature reached 1700 and 1800°C, respectively, and then with much lower strain rates. Compressive strain rates in the order of $10^{-2}$ s$^{-1}$ can easily be achieved at $T \geq 1500°C$ in the SPS apparatus. This rate is 2 orders of magnitude higher than has ever been achieved in conventional HP deformation experiments.

![Figure 6.4](image)

(a) Rapid deformation of α- and β-sialon ceramics recorded in the presence of an electric field. α and β represent the A(Yb+Y)3512-07 and G20B06 compositions, respectively. The $\alpha_1$ and $\beta_1$ samples exhibited ultra-fine-grained microstructures, whereas $\alpha_2$ and $\beta_2$ samples possessed tough interlocking microstructures consisting of fibrous grains. a) The obtained compressive strain data plotted *versus* temperature for samples deformed in an SPS apparatus and in a conventional HP furnace, respectively; b) Isothermal compressive strain data for α and β-sialon samples, recorded as functions of time at 1500°C.
The microstructures of these two sialon compacts, before and after the compressive SPS deformation, were examined by scanning electronic microscopy (SEM). The SPS pre-consolidated compacts, A(Yb+Y)3512-07 and G20B06, consisted of fine equiaxed grains with average sizes of 210 and 350 nm, respectively, and both compacts contained only very small amounts of grain-boundary glassy phase (less than 5 vol % as estimated from SEM micrographs). The deformed samples did not contain any elongated grains, and no grain growth was found in the G20B06 sample, whereas the average grain size in the A(Yb+Y)3512-07 sample increased from 210 nm to 490 nm.

Isothermal compressive-strain data for the same compositions, A(Yb+Y)3512-07 and G20B06, recorded at 1500°C are plotted versus time in Figure 6.4b. The graph brings out a strong correlation between ductility and microstructural features. The \( \alpha_1 \) and \( \beta_1 \) specimens, with ultra-fine equiaxed morphology, exhibit much faster super-plastic deformation than the \( \alpha_2 \) and \( \beta_2 \) specimens, which have tough and interlocking microstructures. The very same \( \alpha_1 \) and \( \beta_1 \) specimens were also isothermally deformed in HP at 1600°C for 30 min, using a pressure of 40 MPa, yielding compressive-strain rates of \( 1.4 \times 10^{-4} \text{ s}^{-1} \) and \( 2.0 \times 10^{-5} \text{ s}^{-1} \) for \( \alpha_1 \) and \( \beta_1 \), respectively. These values are two orders of magnitude lower than obtained with SPS at 1500°C.

It should be noted that the experimental conditions are identical in the SPS and HP deformation tests. The main difference between the two experiments is that in the SPS apparatus the samples are exposed to a pulsed electric field. We interpret our findings in terms of the electric field lowering the viscosity of the grain-boundary glassy/liquid phase, thus facilitating the motion of charged species at the grain boundary and thus yielding an increased deformation rate. The use of a pulsed direct current (electric field) seems essential, for the application of a static electric field may give rise to permanent charge separation in the glassy phase.
Additionally, owing to the rapid deformation in an electric field at low temperature, the grain growth is suppressed during the deformation process. After the compressive deformation the specimens still retain the submicron-sized equiaxed morphology, which can easily transform to an interlocking microstructure by further annealing/post-heating at a temperature above $T_g$, where dynamic ripening can take place. Materials with this type of microstructure exhibit compressive strain rates of the order $10^{-4}$ s$^{-1}$, even in the presence of pulsed electric field. This confirms that the formation of fine equiaxed grains is essential for super-plastic behaviour of ceramics. In conjunction with the formation of interlocking microstructures, the fracture toughness increases from typically below $\sim 3$ MPa·m$^{\frac{1}{2}}$ to above $\sim 5$ MPa·m$^{\frac{1}{2}}$.

![Figure 6.5](image.png)

Figure 6.5 A photograph of a component formed by super-plastic deformation of an $\alpha$-sialon ceramic in a graphite die at 1600°C for 2 min, in the presence of an electric field in the SPS apparatus.

6.3.3 Near net-shape forming

The enhanced super-plastic deformation rates discussed above make it possible to prepare components of complex shape, as exemplified in Figure 6.5. This $\alpha$-sialon component was deformed into its final shape at 1600°C within 2 min and contained a minor amount of grain boundary liquid phase. The deformed component is of complicated shape, with sharp edges and excellent surface finish, indicating that hard-to-machine Si$_3$N$_4$-based ceramic objects with complex shape can be prepared in near net-shape forms.
These achievements demonstrate the unique possibility to achieve super-plastic deformation of Si₃N₄-based ceramics containing very little glassy phase, which are suitable for high-temperature applications. The present finding implies that cost-effective industrial production of Si₃N₄-based components with complex shape is feasible via super-plastic deformation. This concept should also be applicable to other materials that are obtained by liquid-phase sintering.
7. Present understanding of the SPS process for enhancing the liquid phase sintering

7.1 Phenomena observed with the SPS apparatus

The common phenomena so far observed during the SPS processing of Si$_3$N$_4$-based ceramics may be summarised as follows: 

(i) Densification, phase transformation and grain growth processes are accelerated and take place sequentially, providing e.g. the possibility to separate grain growth from phase transformation and densification in monitoring the kinetics; 

(ii) Compressive deformation progresses much faster in the SPS apparatus than in conventional hot-pressing equipment, as verified by the observation that the strain rate of the very same sample in the former apparatus is two orders of magnitude larger than that in the latter; 

(iii) The microstructures of SPS consolidated materials can be precisely regulated, with better understanding and control of the sintering kinetics; and 

(iv) Dynamic ripening dominates the grain growth in a rapid SPS process.

The unique features of the SPS process provide the possibility of using very fast heating and cooling rates and very short holding times (in the order of minutes) to obtain fully dense ceramics. In addition, the pulsed electric field used for the SPS process may be expected to decrease the viscosity of the formed liquid phase due to the accelerated motion of the charged species in the liquid phase. The presence of this electric field thus seems to be another key factor in the SPS process.
7.2 Benefits of a rapid heating rate

The effect of heating rate on the microstructure of Si₃N₄-based ceramics is exemplified in Figure 5.6. The use of rapid heating rates appears to be essential in order to obtain fully dense Si₃N₄ ceramics with interlocking microstructures. The major advantages of using rapid sintering rates may be summarised as following: (i) The grain growth at the early stage of sintering is suppressed; (ii) The capillary force between particles increases throughout the densification cycle owing to very limited grain growth; (iii) The formation of undesirable intermediate phases is avoided; and (iv) The non-equilibrium nature of the liquid formed contributes to the enhancement of both densification and grain growth.

7.3 Benefits of pulsed DC heating

Pulsed DC heating has a unique effect on the sintering and the super-plastic deformation behaviour. During the entire sintering cycle, the sample is exposed to a pulsed electric field. Such a field exerts significant influence on the liquid-phase sintering. The major benefits may be summarised as follows: (i) The pulsed electric field most probably induces the process that enhances the densification rate, and therefore it ought to be operative only in the vicinity of the grain boundaries during the early stage of sintering; (ii) The pulsed electric field accelerates the homogenisation and the penetration of the liquid formed, and it therefore greatly promotes the diffusion and mass transfer processes during the densification period; (iii) The electric field lowers the viscosity of the grain-boundary glassy/liquid phase via promoting the motion of charged species, which in turn promotes grain boundary sliding and thus results in an increased densification and deformation rate.

7.4 Benefits of the use of high pressures

The possibility of applying high mechanical pressure in SPS process increases the possibility of manufacturing hard-to-make materials, e.g. of obtaining fully dense Si₃N₄-based ceramics within shorter time and at lower temperature than through a conventional hot-pressing process. High pressures have significant influence on the sintering process, especially in connection with liquid-phase sintering. The
following advantages of the use of high pressures can be discerned: (i) The density of the green body is greatly increased, and thus the distance of mass transfer and diffusion at intermediate sintering stages is reduced; (ii) The extent and rate of particle rearrangement is increased; (iii) The homogenisation and penetration of the liquid phase along grain boundaries may be expected to be enhanced.

7.4 Future work

Due to the inherent time limitation of a PhD thesis, I have not been able to explore the possibility of preparing truly nano-sized silicon nitride-based ceramics by SPS, or to consolidate other ceramics by applying this novel processing concept. I should therefore like to work along the following lines in the near future:

i) Preparing nano-structured silicon nitride ceramics by SPSing truly nano-sized precursor powders;

ii) Manufacturing ceramic components of complex shape by super-plastic deformation of the fully dense nano-structured ceramics obtained;

iii) Reaching better understanding of the enhanced sintering kinetics;

iv) Fabricating laminated composites consisting of nano-/micro-sized Si$_3$N$_4$ and SiC layers with tailored microstructures by manipulating the grain growth rate;

v) Enlarging the application field of SPS, *e.g.* to sintering new materials that may be impossible to achieve by conventional sintering methods.

Some of this work can be regarded as a natural continuation of my PhD work, others parts will be more explorative.
8. Summary

Monophasic $\alpha$-sialons with both stoichiometric and non-stoichiometric overall starting compositions have been consolidated by the SPS process and subsequently investigated with respect to their microstructures and mechanical properties. For comparison, appropriate experiments have also been performed by means of conventional hot pressing (HP). Although it is very difficult to achieve elongated grain morphology in monophasic $\alpha$-sialon with stoichiometric composition by means of the HP process, it is possible to obtain an interlocking microstructure, consisting of elongated grains, in the presence of extra liquid introduced.

A liquid phase, thermodynamically compatible with $\alpha$-sialon, was introduced by a new method, *i.e.* slightly increasing the O/N ratio of an already oxygen-rich $\alpha$-sialon composition, while keeping the cation ratios of the sialon phase, $\text{RE}_{x}\text{Si}_{12-(3x+n)}\text{Al}_{3x+n}\text{O}_{n}\text{N}_{16-n}$, constant. Reinforced microstructures were developed *in situ* in Y-, Yb-, and (Y+Yb)-stabilised $\alpha$-sialon ceramics containing ~3 vol% liquid phase, by means of a HP process at 1800°C for 4 hrs.

The SPS process is a promising technique that allows a better understanding of sintering kinetics and therefore makes it possible to obtain $\text{Si}_3\text{N}_4$-based ceramics with tailored microstructures, consisting of either fine, equiaxed or elongated grain morphology via manipulation of the sintering kinetics.

Densification, phase transformation/reactions and grain growth are three individual temperature-dependent processes that can be studied separately in most sialon systems by applying the SPS process, because the onset temperatures of
densification \( (T_d) \), phase transformations/reactions \( (T_i) \) and grain growth \( (T_g) \) are sufficiently different. In general, our observations reveal \( T_g \geq T_i \geq T_d \) in silicon nitride-based ceramics. These critical temperatures are adjustable by changing the composition and by selecting appropriate processing parameters.

Fully dense Si\textsubscript{3}N\textsubscript{4}-based ceramics can be produced in the SPS process merely by enhanced particle rearrangement via grain boundary sliding accompanied by either diffusion- or reaction-controlled process in the liquid, without, or with very limited grain growth. The rapid densification is ascribed to the retention of a fine particle size throughout the densification cycle, and to the creation of a non-equilibrium liquid phase by rapid heating.

Rapid grain growth after complete densification and phase transformation is accomplished by heat treatment at temperatures above \( T_g \) and by the use of high heating rates; this growth is driven by the dynamic ripening mechanism. This mechanism acts only when the liquid phase is grossly out of thermodynamic equilibrium with the main crystalline phase(s) present. As the entire system approaches its thermodynamic equilibrium state, the grain growth mechanism changes from dynamic to static ripening.

The interlocking microstructure is responsible for improved mechanical properties, e.g. compacts containing elongated grains exhibiting fracture toughness values in a range from 5 to 6.5 MPa·m\(^{1/2}\), whereas those containing equiaxed grains exhibited corresponding values in the range from 3.5 to 4.0 MPa·m\(^{1/2}\). The refined interlocking microstructure of monophasic \( \alpha \)-sialon ceramics exhibits excellent thermal-shock properties, quite comparable to those of the best hot-pressed, self-reinforced \( \beta \)-sialon ceramics containing 20 vol% glass phase.

The possibility of producing ceramics with fine, equiaxed grain morphologies is a key factor in connection with the tailoring the super-plastic properties of the materials. Thus Si\textsubscript{3}N\textsubscript{4}-based ceramics with fine equi-axed grain morphologies
exhibit a formidable improvement of super-plastic behaviour in the presence of an electric field, whether or not a monophasic $\alpha$- and $\beta$- sialon or a duplex $\alpha/\beta$- sialon composite is involved. A compressive strain rate of the order $10^{-2}$ s$^{-1}$ is observed at temperatures exceeding 1500$^\circ$C, which is two orders of magnitude higher than that ever achieved by the HP process, confirming that the super-plastic deformation takes place very rapidly in the SPS process. The enhanced ductility is accounted for by enhanced grain boundary sliding in the presence of a pulsed electric field, which in turn decreases viscosity of the glassy/liquid phase and increases the diffusivity within this phase. The rapid super-plastic deformation observed in this work opens up possibilities of making ceramic components with complicated shapes, e.g. production of near net-shaped ceramic cutting tool blanks with special geometries seems to be feasible.
Acknowledgements

Finally, I wish to express my sincere thanks to all the people who, in different ways, have supported me and helped me to complete this thesis, and who have made my stay in Sweden comfortable and enjoyable. Especially, I would like to thank the following persons:

First of all, I wish to express my deepest gratitude to Doc Zhijian Shen, my supervisor, who introduced me to the field of Si$_3$N$_4$ ceramics and who has guided my doctoral studies all the way. I would like to thank you for supporting and encouraging me throughout these years. Your incredible enthusiasm and optimistic dedication to science has impressed me deeply. I am especially grateful for your great ability, not only to share your academic knowledge but also to help organise my research, which has contributed to making my thesis and publications comprehensive. Your door has always been open, and I have immeasurably treasured your advice and guidance, both in the scientific field and in daily life. Without your help and support, it would have been impossible for me to complete this thesis. Many thanks also to your family for the kindness and generosity that made the first year of my stay in Sweden much easier. The moments when you let me share delicious food and nice barbecues are highly appreciated and unforgettable.

I also thank Professor Mats Nygren, my co-supervisor, for inviting me to Sweden and accepting me as PhD student, for all the support and help from you whenever needed, and for creating a most stimulating working atmosphere of scientific freedom. I am also grateful for your great interest in my work and for taking time to correct my papers and my thesis.
Prof Sven Lidin, for creating a stimulating and pleasant scientific environment, and of course, for your interest in my work and thesis and for always being helpful.

Prof Osamu Terasaki, for your interest and concerns in my thesis, and also for your comments and encouragement.

Dr Kjell Jansson, for teaching me to use the scanning electronic microscope (SEM) and for always being available for endless questions about that technique.

Dr Pernilla Magnusson: you are so sweet and considerate, thank you so much for sharing your office with me, for nice coffee breaks, for your considerateness and help, and of course, for teaching me how to perform thermal-shock measurements and for our joint publication of one paper.

Mr Lars Göthe, for always cheerfully accepting my samples, for recording and developing innumerable Guinier–Hägg films, and also for finding my mislaid mobile phone.

Mrs Jaroslava Östberg, for you never-ending helpfulness with my SEM samples, and for valuable discussions on my visit to Prague, and of course for extensive help and for coaching my Swedish.

Per-Erik Persson and Rolf Eriksson, for being available and helpful in solving computer problems; you are real good virus-killers!

Mr Mats Carlsson, for valuable tips and discussions about my thesis; also for lending me the first Swedish children’s book I ever read, for coaching my Swedish, and for all your wonderful help and coffee breaks.
Ms Hillevi Isaksson, for always being helpful with literature searches and for installing the search-engine program, and also for nice conversations and laughs during lunches and coffee breaks.

Dr Zhe Zhao, for all valuable discussions and help, both in and out of the lab. Special thanks to you for solving tough computer problems when I got my first new computer!

Mss Eva Pettersson and Ann-Britt Rönell – you are so nice and warm-hearted; thank you so much for all your help. I wish to thank Ann-Britt especially for considerateness and understanding; and of course, your help and advice on organising my disputation party are highly appreciated. You are so helpful whenever I have a problem.

Doc Sven Westman for language revision of my articles and thesis.

Everyone at KÖL–Thank you! Prof Ingrid Bryntse, Dr Monica Lundberg, Mss Yvonne Djurberg, Åsa Borin, Maria Petersson, Mr Arne Sjödin & Mr Victor Bravo Vicuna. Many thanks to Ingrid, my ex-roommate, for sharing your office with me and for all concerning and help specially during my first year in Sweden. Your help and kindness are highly appreciated.

Dr Martin Valldor is greatly thanked for supervising my project “Metal Substitution in the spin-glass YBaCo$_4$O$_7$” when I attended the Materials chemistry course, and for introducing me into a different world; I am very impressed by your enthusiasm for new structures and crystals.

Ms Emma Firman, whom I worked with when I was a teaching assistant for the first time, for being always kind and helpful. You are so good at pedagogy and teaching. Your help and encouragement are highly appreciated and unforgettable.
Dr Lars-Johan Norrby, for helpful advice and discussions during my teaching experience as a laboratory assistant, and of course also for your understanding and considerateness. Thank you!

Dr Annika Pohl, for those long and wonderful coffee breaks and summer excursions together, and for being a good friend. You are so sweet and considerate. I miss you so much since you moved to Uppsala University.

Mr Andreas Flemström, for being such a wonderful and constantly cheerful friend. I would like to thank you for showing me Stockholm, guiding me to nice restaurants, and teaching me how to use the microscope. Of course, thank you also for all joyful coffee break and jokes and laughs. “Tack så mycket! Min första svenska lärare, men tyvärr, jag är fortfarande jätte dålig på uttalet av “r”. Tack för träning ändå!”

Mr Henrik Rundgren, you are so open, nice and easy to talk with. “Tack så jätte mycket för otroligt goda kakor och buller. Framför allt för de goda tiderna när vi har fikat och skrattat åt! ”

Many thanks also go to my ex- and present-roommates, Dr Göran Nilsson, Ms Hanna Lind and Mr Richard Becker for spending a number of years with me, always willing to help and sharing a problem and for creating a stimulating and pleasant atmosphere to work in. Thank you so much!

All Chinese colleagues and friends within the department: Doc Xiaodong, Dr Ye Zhou, Dr Tuping, Dr Yiqiu, Zheng Weng, Dr Yaoquan, Joan Liu, Suying, Juanfang, Hong Zhang, Dr Zhen Liu, Yanbing, Drs Weikang & Yafeng – you all are so warm-hearted and helpful, both in and out of the lab. Your help and advice are treasured. Special thanks to Dr Yezhou for being my witness in obtaining an ID card, and for all the help I desperately needed when newly arrived in Sweden.
To friends outside the lab

All my friends out of the lab are of great importance to me. All of you enrich my life and make it more colourful and joyful, with parties, playing, games, fishing and trips together, big as well as small events. All those wonderful times are unforgettable and highly appreciated. I wish to thank all of you as much as I can. I cherish your friendship and your considerateness. I wish to thank the following persons especially:


Ett stort tack går också till min franske vän Oliver, mina tyska vänner Thomas, Stephan och min italianske vän Fabio, för alla våra fester och vår glädje tillsammans.

Many thanks go to Wujiang, HuangZhen, Jiawei, Sunwei Zhu and Inger Jiang, for all the fun we have had together, for all kinds of trips and excursions together, and also for those long discussions about making food, playing badminton and planning parties (you know?). I wish those wonderful, good times will remain with me forever.

Wanjue and Lixin, for all weekend-shopping excursions, help, encouragement and consideration; and also for the summer activities in “our common garden”. Special
thanks to lovely Diandian, for your “lördagsgodis” and the gladness you bring to me. I miss you so much since you left.

I wish to express great gratitude to Yaodong, Chen Yan, Huang Fang, Lingwan Wang for all joy, encouragement and help. Special thanks to Yaodong, for your guidance in planting flowers and also for sharing DVD films. Without you guys, my life would have been monotonous and boring.

Roger Ericsson, Kaihong and Kaimei, my ski coaches: thank you so much for your instruction, patience, and encouragement, for skiing and for friendship. I had such a fantastic a ski-trip; a wonderful experience that I will never forget. I already long for the next trip with you.

I wish to thank Liuwei, who is the “leader” of MBA (you know) and always positive and glad, and all MBA members during my first year in Sweden. All our activities together relieved my homesick feelings and made my life colourful and meaningful.

Here I would like to thank my closest friend Xinchun Tan from high school in China, for always helping me to remember things in China, and for helping and caring for my family.

…… to everyone who has contributed to the thesis in any way, even if you are not mentioned, you are definitely not forgotten!

To my family

Thanks you so much, Mama; you are always so strong and brave, struggling with all difficult situations by yourself so that I can concentrate on my work and smoothly finish my studies abroad. Your endless support and understanding are my driving
force. Finally, your daughter has grown up – she can handle anything. Believe in
her! Please enjoy your life and relax. I owe you so much, Mama!

I also want thank my brother and my sister-in-law for taking care of mother and
keeping her company when I am abroad. Of course, I would also like to thank my
favourite nephew for all his laughs and the happiness he brings to our family.

Last but not least, I would like to express my deepest gratitude to my life partner,
Liqiu, who is the light of my life. Thank you so much for ten-year journey together,
for all tears and happiness we have had together, and also for your endless support,
encouragement and love. With you, life will never be boring.
References


