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Short communication

Spark plasma sintered β-phase silicon nitride with Sr and Ca as a sintering aid for load bearing medical applications

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Abstract

Due to its inherent good physical and chemical properties silicon nitride has high potential to be used for load bearing implants. However, the standard sintering additives alumina and rare earth oxides are limiting the biocompatibility of the material. The aim of the current project is to exchange the additives for more biologically beneficial additives. Spark plasma sintered silicon nitride was manufactured with strontium or calcium as sintering aids. The ability of forming high strength β-phase microstructure silicon nitride was investigated. Powders were prepared with 10 and 30 wt.% glass phase and sintered at 1600, 1650, 1700 and 1750 °C. X-ray diffraction demonstrated compositions with 10 wt.% glass phase with strontium as sintering aid to yield larger amount of β-phase. The highest amount of β-phase (96% of the crystalline structure) was obtained using SPS for strontium-doped silicon nitride at sintering temperature 1750 °C, resulting in the highest fracture toughness, 4.2 MPa $m^{1/2}$.

Keywords: Spark plasma sintering; Si_3N_4; Strontium; Calcium; Biomedical applications

1. Introduction

During the last decades silicon nitride (Si_3N_4) has been a subject of investigations for biomedical applications, especially for implants requiring high mechanical strength.[1–3] In load bearing applications such as hip and knee joints, the property profile that Si_3N_4 can offer, i.e. high wear resistance, low friction, high fracture toughness, low density and non-toxic chemical composition, has a great potential compared to current implant materials. In particular β-phase Si_3N_4 can obtain high fracture toughness, due to that it easily grows elongated grains, which can increase the material crack propagation resistance.[4,5] In addition to the mechanical properties, the chemical elements, silicon and nitrogen, are promising for use in biological applications.[6,7] Silicon nitride ceramics are today used as spinal implants, and recently a femoral head was implanted in a hip replacement.[3,8]

To obtain a dense Si_3N_4, sintering aids are used (to enable liquid phase sintering), since pure Si_3N_4 dissociates before complete densification.[4,9] Commonly, aluminum oxide and various rare earth or lanthanide oxides, such as yttrium oxide and magnesia, are used. In this study two combinations of sintering aids are investigated, Si_3N_4 plus strontium (Sr) and Si_3N_4 plus calcium (Ca). Both sintering aids are of interest for biomedical applications, Sr for its ability to increase bone formation, and decrease bone resorption[10,11] and Ca because it is the main element in hydroxyapatite and has successfully been used as a sintering aid for SiAlON previously.[12–14] A comparatively large amount of sintering aid was used, 10 and 30 wt.%, with the aim of acquiring some of the properties of bioglass, since bioglass has a high bone bioactivity.[15]

Spark plasma sintering (SPS) was used to densify the Si_3N_4 based materials. An advantage with SPS, compared to for example hot pressing, is the short sintering times. Another advantage with SPS compared to conventional sintering methods, is that lower temperatures can be used for sintering, which, in combination with the short sintering times, allow for smaller grain sizes.[16,17]

During the sintering process, sintering aids react with added silica (SiO_2) and creates an oxide melt. A transformation from α- to β-Si_3N_4 can take place, at high temperature α-phase dissolves

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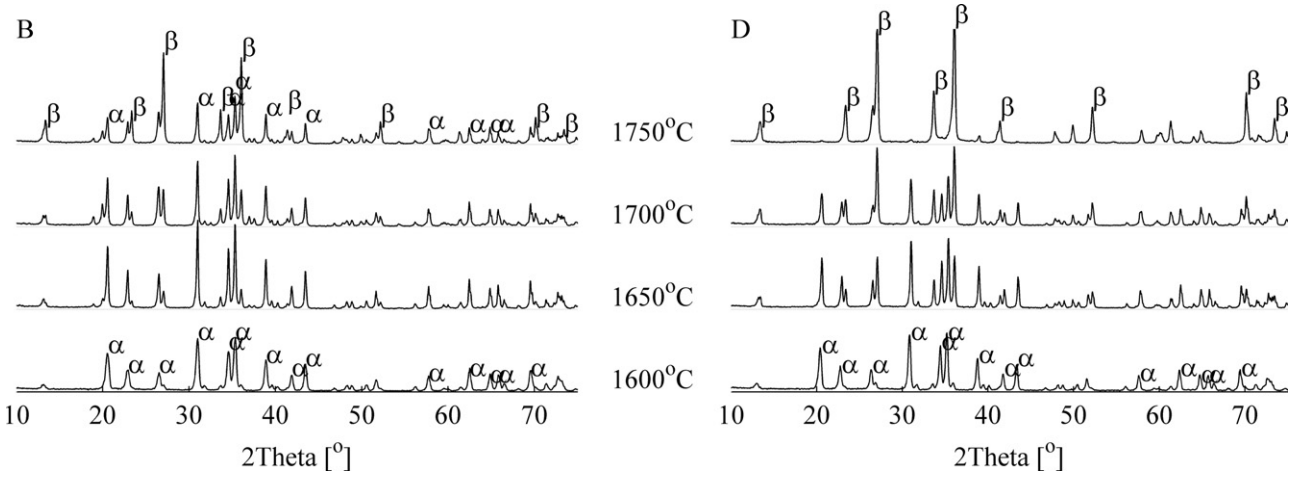

Fig. 1. XRD-spectra for sintered samples from powders B and D, at sintering temperatures 1600–1750 °C.

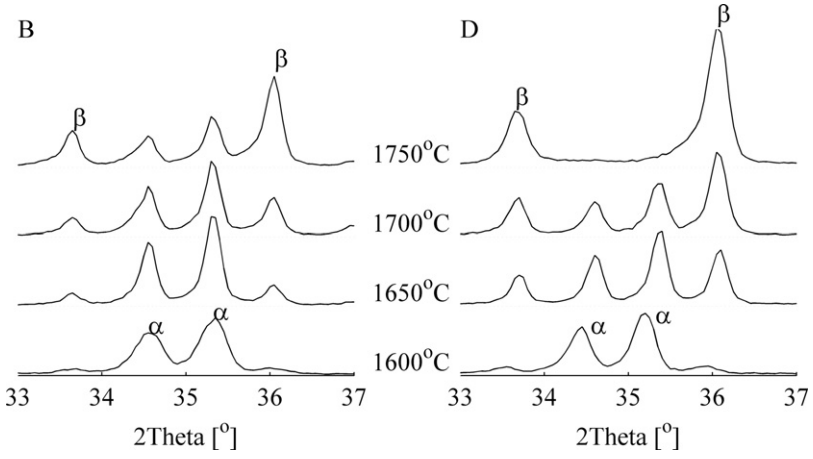

Fig. 2. XRD-spectra for sintered samples from powders B and D show more narrow spectra from Fig. 1. It demonstrates how the α- and β-phase changes with increased sintering temperatures, from 1600 °C to 1750 °C.

in the liquid phase, and β-phase grains are precipitated according to

$$[\alpha\text{-}Si_3N_4] + [SiO_2] + [M_xO_y] \rightarrow [\beta\text{-}Si_3N_4] + [M\text{–}Si\text{–}O\text{–}N], \quad (1)$$

where M is the metal used as sintering aid, here Sr or Ca. Around the β grains the liquid phase solidifies into M–Si–O–N glass phase.[18]

The aim in this study is to form dense β-Si_3N_4 with high fracture toughness using biologically resorbable sintering aids. In this short communication the microstructure and mechanical properties are investigated. The biocompatibility and bioactivity are subject for further research.

2. Experimental

Powders were prepared and evaluated according to the following procedure. A slurry of α-Si_3N_4 (>95%, SN-E10, UBE America Inc., USA), dispersing agent (Dispex A40), SiO_2 (Quartz, Carl Roth GmbH + Co. KG, Germany), $CaCO_3$ (Merck KGaA, Germany) or SrO_3 (Merck KGaA, Germany) and deionized water were milled in a vibration mill, with Si_3N_4 based milling media. After wet sieving, the slurries were freeze granulated. The slurry was sprayed into liquid nitrogen, and the

Table 1
Powder composition and theoretical amount of glass phase.

Powder	α-Si_3N_4 [wt.%]	SiO_2 [wt.%]	$CaCO_3$ [wt.%]	$SrCO_3$ [wt.%]	Glass phase [%]
A	69	26	5	0	30
B	89	9	2	0	10
C	65	21	0	14	30
D	89	7	0	4	10