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In vitro tribological and biocompatibility evaluation of sintered silicon nitride

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ABSTRACT

In the present work, dense silicon nitride (Si_3N_4) was developed using pressureless sintering for biomedical applications. The Si_3N_4 samples with 15 wt% sintering additives (Al_2O_3 + Y_2O_3) were sintered at 1700 °C for 2 h followed by characterization in terms of phase constituents, mechanical, *in vitro* tribological and biological properties. *In vitro* tribological tests in simulated body fluid (SBF) revealed that the wear rate and coefficient of friction of Si_3N_4 reduced by one order of magnitude in the presence of 10% fetal bovine serum (FBS). The *in vitro* biocompatibility evaluations using human osteoblast-like cells (MG63) confirmed that the sintered Si_3N_4 samples were non-cytotoxic.

1. Introduction

Now-a-days age-related degenerative and inflammatory diseases of hip and knee joints are becoming very common. In extreme situations, the dysfunctional joints are often replaced by artificial implants. A recent report showed that in the US alone the demand for primary total hip arthroplasty (THA) is estimated to increase by 174% to 572,000 by 2030 [1]. However, the longevity of current hip implants is limited and depends on the amount of wear debris generated from the articulating surfaces (femoral head and cup). The wear debris generated from these surfaces directly contributed toward the osteolysis of surrounding bones and subsequent aseptic loosening of the implants [2]. Modern hip implant bearing surfaces can be broadly divided into two groups, hard-on-soft and hard-on-hard type [3]. Sonntag et al. observed that the hard-on-hard bearing surfaces, specifically the ceramic-on-ceramic bearing surfaces, exhibit extremely low *in vitro* wear rate compared to other bearing surfaces [2]. Recent advances in terms of stringent control on processing techniques and microstructures of these ceramic bearings, per ISO 6474 for medical-grade total hip implant, significantly reduced the failure of ceramic heads (2 in 10,000 or less) [3,4]. In the last few decades, majority of the research emphasis has been on the oxide ceramics such as alumina and zirconia toughened alumina for THA [5]. However, non-oxide ceramics such as Si_3N_4 is also a promising material for orthopaedic applications due to its high strength, fracture toughness, wear resistance, low coefficient of friction and biocompatibility [6–11]. Interestingly, the Si-Y-Al-O-N phase on the surface of Si_3N_4 reduced the osteoclastic resorption in diseased bone and promoted osteoblastic activity for structural bone remodelling [8]. However, processing of Si_3N_4 is relatively difficult than oxide ceramics. Reaction bonding, hot pressing and hot isostatic pressing are the most common methods used for processing Si_3N_4 [6]. Considering the merits of this material, in the present article, we have made an attempt to fabricate dense Si_3N_4 samples using pressureless sintering and evaluated their mechanical, *in vitro* tribological and biocompatibility behaviour.

2. Experimental methods

Si_3N_4 (H.C. Starck) powder was used as matrix material. Yttrium oxide (Y_2O_3, H.C. Starck) and Alumina (Al_2O_3, A-16-SG, Almatis Alumina Pvt Ltd., India) powders were used as additives. Si_3N_4 powders and sintering additives (9 wt% Al_2O_3 + 6 wt% Y_2O_3) were attrition milled for 6 h in isopropyl alcohol. The dried powders were then cold isostatically pressed to form ∅15 mm pellets at 150 MPa pressure followed by sintering at 1700 °C under N_2 atmosphere for 2 h. The bulk density of sintered samples was determined by Archimedes principle. An X'Pert Pro MPD diffractometer (PANalytical) was used to identify the constituent phases. The Young's modulus of the sample was measured using ultrasonic

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wave technique (EPOCH4 Plus ultrasonic flaw detector, Olympus). The Vicker's micro-hardness (ESEWAY W-4303) measurements were performed at 98.1 N load applied for 10 s. The fracture toughness (K_{IC}) of the sintered Si_3N_4 samples was calculated from the indentation crack lengths using Nihara [12] and Antis equation [13].

The wettability of sintered samples was determined by measuring the contact angles of water using sessile drop method (DSA25S, Kruss GmbH). Ball-on-disc wear tests (NANOVEA, USA) were carried out in SBF and SBF+10% FBS at 37 °C under a normal load of 15 N, sliding speed of 40 mm/s for a sliding distance of 3000 m. A Si_3N_4 ball (∅3 mm) was used as counter body. The wear rate (mm^3/Nm) was calculated from the measured volume of the wear track using contact profilometer (Talysurf PGI 200S, Taylor Hobson, UK).

In vitro cytotoxicity of sintered Si_3N_4 was assessed by direct contact MTT assay using MG63 cells and the cell morphology was observed after cell fixation, following the procedure described elsewhere [11]. Statistical analysis was carried out using Student's *t*-test, with $p < .05$ being considered statistically significant.

3. Results and discussion

Table 1 shows theoretical density (TD) and relative density (RD) of pressureless sintered Si_3N_4 samples. After sintering at 1700 °C for 2 h a relative density of 93% was achieved in the present Si_3N_4 samples. The XRD analysis, shown in Fig. 1, indicates that the sintered samples are comprised of β-Si_3N_4 phase with no other impurity phases. All experimental peaks matched with standard JCPDS card number 82-0703 corresponding to β-Si_3N_4. The average hardness and Young's modulus of pressureless sintered Si_3N_4 samples, presented in Table 1, was 16.7 ± 0.1 GPa and 252 GPa, respectively. Although the sintered samples showed ~7% porosity, the small standard deviation in the hardness suggests the uniformity in terms of microstructure, composition and absence of gross defects in sintered Si_3N_4.

Fig. 1b shows the indentation fracture toughness measured using different indentation loads. According to Niihara et al., during indentation the crack system changes from palmqvist to median type as the indentation load increases [12]. At low loads (i.e. 3 and 5 kg) present Si_3N_4 samples exhibited palmqvist type cracks ($c/a < 2.5$) and therefore the fracture toughness was measured using Niihara's equation for palmqvist type cracks [12]. However, the indentation cracks became median type ($c/a > 2.5$) at 10 and 20 kg of indentation load. The fracture toughness estimated using Niihara (equation for median type crack) and Antis at 20 kg load was 5.3 ± 0.3 MPa $m^{1/2}$ and 3.6 ± 0.2 MPa $m^{1/2}$, respectively. One important consideration on the use of these equations is that they are based on empirical curve fitting rather than derived from physical models. Therefore, the local toughness of ceramics surfaces reported herein can be assumed to be within ±50% of the true values [14]. For example, the present fracture toughness of Si_3N_4 was close the value of 7.1 $MPam^{1/2}$ measured using Raman microprobe-assisted indentation [15].

Contact angle measurements were carried out on sintered Si_3N_4 and Ti6Al4V alloy using deionized water at ambient condition to assess their relative wettability, which is important in controlling the friction during articulation. The experimental results showed that contact angles of 59° ± 2 and 85° ± 2 for Ti6Al4V alloy and Si_3N_4, respectively. Such contact angle on Si_3N_4 is comparable to ZrO_2 and Al_2O_3-ZrO_2 solid surface [10].

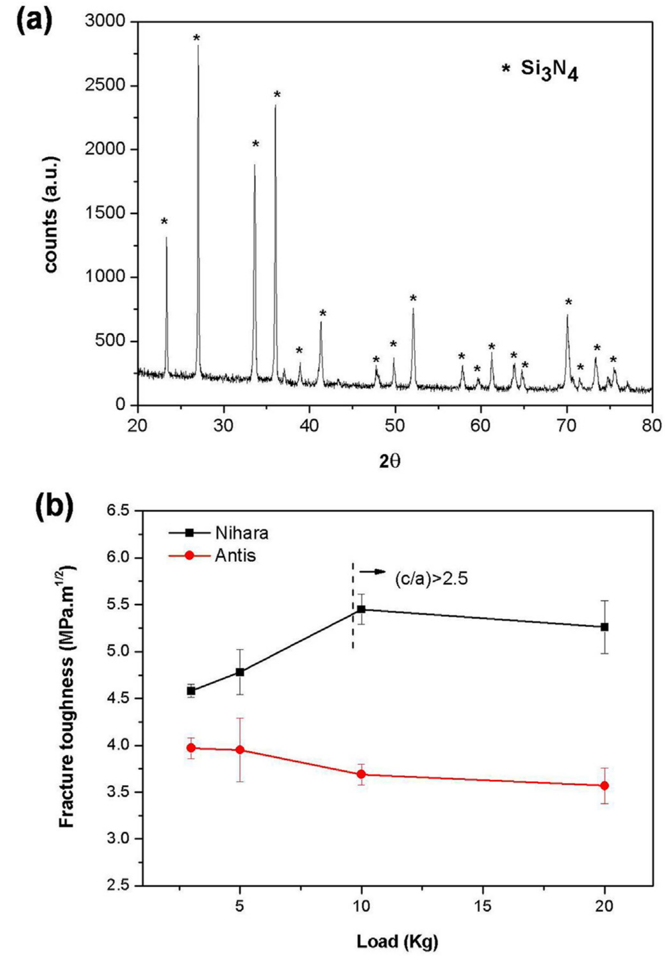

Fig. 1. (a) X-ray diffraction analysis of sintered Si_3N_4, (b) Indentation fracture toughness at different indentation loads.

The summary of ball-on-disk type rotating wear tests performed on sintered Si_3N_4 using Si_3N_4 balls, in SBF and SBF + 10% FBS, is presented in Table 1. The wear rate of sintered Si_3N_4 in SBF was 1.09×10^{-6} mm^3/Nm which is ~1000 times less than that of titanium (2.59×10^{-3} mm^3/Nm) against Si_3N_4 ball in SBF. When the identical tests were performed in the presence of 10% FBS in SBF, the wear rate of sintered Si_3N_4 was significantly reduced to 3.75×10^{-8} mm^3/Nm which is approximately two orders of magnitude less than that observed in SBF. Similarly, the wear rate of Ti6Al4V alloy was also decreased by one order of magnitude to 5.07×10^{-4} mm^3/Nm in presence of FBS. Similarly, the addition of FBS in SBF decreased the coefficient of friction (COF) from 0.366 to 0.021 i.e., a 10 times decrease. The decrease in the COF during

Table 1
Density, mechanical and tribological properties of pressureless sintered Si_3N_4 samples.

Density (g/cc), [RD (%)]	Hardness (GPa)	Young's modulus (GPa)	*In vitro* tribology		
			Lubricant	COF	Wear rate (mm^3/Nm)
3.21, [93%]	16.7 ± 0.1	252	SBF	0.366	$(1.09 \pm 0.5) \times 10^{-6}$
			SBF + 10%FBS	0.021	$(3.75 \pm 1.1) \times 10^{-8}$