

# On the possibility of silicon nitride as a ceramic for structural orthopaedic implants. Part I: processing, microstructure, mechanical properties, cytotoxicity

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**Abstract** Notwithstanding the good combination of mechanical and tribological properties, the suitability of silicon nitride for application as prosthesis in bone reconstruction or in articular joints replacements is still controversial. This study aims to design and produce three different silicon nitride-based ceramics and to test the materials. In this Part I the microstructure and mechanical properties evidence outstanding characteristics and the cytotoxicity studies confirm that all the materials are extremely inert and biocompatible. In Part II, the wear performance and the wettability and chemical stability against different aqueous media and physiological solutions are investigated and discussed.

## 1 Introduction

Silicon nitride-based ceramics constitute a class of structural materials characterized by high strength, fracture toughness, hardness, thermal shock resistance, wear resistance and low coefficient of friction. These key properties make silicon nitride suitable for high performance components in severe environments in different industrial applications including bearings, cutting tools, wear parts, valves and heat engine components. On the basis of the potentialities, silicon nitride attracts interest for orthopaedic and dental applications [1–10] in the human body, but is not yet established as a biomaterial in medicine. This is

related to some controversy in the literature about the biocompatibility [1, 4–6].

Among the components and devices for prosthetic implants, that can benefit from the properties of silicon nitride, possible applications concern:

- (i) *Total joint replacements*, that require material with low friction and wear rate. There is still a controversy about the suitability of silicon nitride for bearing surfaces in knee and hip-joint replacements. According to several studies [5, 11, 12], silicon nitride-silicon nitride coupling seems to satisfy this requirement because under some tests conditions the contact surface of silicon nitride becomes ultra-smooth due to tribochemical polishing and the friction becomes very low at increasing sliding distances. Therefore, from the tribological point of view, silicon nitride-silicon nitride should be a very good material for hip prostheses [2, 5]. Particularly if the surface is ultra-smooth by the fine machining or running-in, the tribological properties of silicon nitride against itself in water is excellent [2, 5]. The influence of material combination and lubricant on friction and wear for hip joint was studied in detail [13]. According to other studies [14], advanced non-oxide ceramics such as  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$ , should not be suitable for bearing surfaces in knee- and hip-joint replacement, consequently to the formation of surface  $\text{SiO}_2$ , which could chip off, inducing a catastrophic third body wear.
- (ii) *Mini-osteofixation systems* (plates, screws, etc.), e.g. in maxillofacial surgery [15, 16], in substitution of metallic implants which originate possible interaction with the surrounding tissue and may impair modern diagnostic imaging systems. In addition to widely proven alumina, silicon nitride ceramics with a nearly

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double flexural strength have to be taken into account [4].

- (iii) *Multiwell drug-release devices* [17], *microelectro-mechanical systems (Bio-MEMS)* [18], *3-d micro-electrode arrays (MEA)* [19], micro-machined neural probes, drug delivery micropumps, microfabricated immunoisolation biocapsules require materials that create interfaces compatible either with fabrication processing and biological systems [20].
- (iv) *Intervertebral spacers and spinal surgery*, reaction bonded silicon nitride resulted a successful implant material for spinal fusion, in terms of resistance to slippage, implant/bone fusion, resistance to subsidence, potential for reaction, decrease of pain [1].
- (v) *Implantations in otorhinolaryngology and traumatology*, ossicular chain reconstruction prostheses, disks for reconstruction of anterior or lateral skull base defects, and applications in traumatic damages, even under conditions of mucosal attachment and possible infections [15, 16].

Several works on biocompatibility and bioactivity of silicon nitride outline that silicon nitride-based ceramics can be used as materials for clinical applications in the field of hard tissues surgery. The absence of toxic behaviour was ascertained during toxicity tests [21]. In vivo tests, implanting  $\text{Si}_3\text{N}_4$  pieces into the femurs of rabbits [6] have demonstrated good bone/implant attachment, no immunoinflammatory reactions, no adverse cell reactions. These tests suggested that  $\text{Si}_3\text{N}_4$  has good biocompatibility and probably better osteointegration than alumina. Porous intramedullary  $\text{Si}_3\text{N}_4$  rods implanted in rabbit supported bony ingrowth [22]. Further investigations on the influence of different qualities of commercial silicon nitride-based materials revealed no correlations between cell yields and chemical composition [23]. Polished surfaces of silicon nitride seem to promote advanced biocompatibility [23] and have the ability to propagate human osteoblast cells in vitro [24]. After incubation of  $\text{Si}_3\text{N}_4$  (either bulk pieces or particles) in the culture media, nitrite did not leach out, suggesting that this ceramic does not induce nitric oxide production. It means that silicon nitride does not induce inflammation while promoting the proliferation of osteoblast cells [25]. It was reported that, in cells growth on polished silicon nitride surface, the parameters concerning viability and morphology are comparable to those of titanium [26].

In the application of silicon nitride as biomaterial a key aspect is the presence in this ceramic of grain boundary phases deriving from the necessary use of sintering aids. The grain boundary phases kind and amount depend on the selected additives, generally oxides of Mg, Al, rare earth, which, during sintering, react with the silica present on the

silicon nitride particles and other impurities, leading to the formation of a liquid phase. This allows the sintering of silicon nitride, but the final dense ceramics contains amorphous or partially crystalline grain boundary phases, basically silicates or oxynitrides, containing the cations constituting the starting oxide species. Therefore silicon nitride-based ceramics can be regarded as ceramic-glass composites. It has to be taken into account that the glassy phases may exhibit bioactivity different from silicon nitride crystalline phase. The fabrication of  $\text{Si}_3\text{N}_4$ -based composites containing bioactive glasses (in amount of 30 vol%) has been successfully tested [3].

This article examines the properties of three different silicon nitride-based materials produced by hot pressing process: (i) two monolithic materials sintered through the addition of two selected sintering aids: magnesium oxide (MgO) and a bioactive glass, (ii) an electroconductive composite material containing 35 vol% TiN plus some sintering aids oxides ( $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ ). This latter material has the advantage that can be machined by electrical discharge machining to obtain complex shapes, like screws, miniplates, etc.

Besides the analyses of microstructure, these materials have been tested under the point of view of the cytotoxicity, and mechanical properties, reported in Part I, wettability and interfacial interaction with different liquid lubricants, tribological behaviour and surface modification due to the contact with the liquid media and to the wear tests, described in Part II.

## 2 Materials and methods

### 2.1 Materials production

The dense silicon nitride-based materials were fabricated starting from the following powder mixtures (the amounts are expressed as volume%): A: 90.0  $\text{Si}_3\text{N}_4$  + 10.0 bioactive glass; B: 91.3  $\text{Si}_3\text{N}_4$  + 8.7 MgO; C: 65.0 (93 wt%  $\text{Si}_3\text{N}_4$  + 2 wt%  $\text{Al}_2\text{O}_3$  + 5 wt%  $\text{Y}_2\text{O}_3$ ) + 35.0 TiN.

Characteristics of the starting raw materials:

- (i)  $\text{Si}_3\text{N}_4$  (UBE Ltd., Type SN-E10)— $\alpha$ - $\text{Si}_3\text{N}_4$  phase 95 vol%, specific surface area:  $11.5 \text{ m}^2/\text{g}$  m. Mean particle size:  $0.19 \mu\text{m}$ . Impurities (wt%): O 1.4; Ca 0.05; Fe 0.010; Al 0.05; Cl 0.010. The powder has a narrow particle size distribution, and equiaxed globular-shaped particles. Usually silicon nitride surface is partially oxidized, due to its thermodynamic instability in air and consists of a layer with a composition corresponding to an intermediate state between silica and silicon oxynitride containing mainly silanol ( $\text{Si-OH}$ ) and secondary amine groups ( $\text{Si}_2\text{-NH}$ ). The

composition of the surface film depends on manufacturing method and treatments, so that it results in different relative amounts of amphoteric silanol and basic amine groups [27].

(ii) sintering additives:

- (1) The *bioactive glass* (selected to act as sintering aid for samples of A composition) is a well studied, widely experimented in-vitro and in-vivo bioactive glassy material, gifted of outstanding properties concerning osteoinduction and osteointegration, even in case of pathologic osteopenic bone [28, 29]. The composition of the glass is the following (wt%): SiO<sub>2</sub> 43.94; P<sub>2</sub>O<sub>5</sub> 10.27; CaO 31.93; Na<sub>2</sub>O 4.55; K<sub>2</sub>O 0.19; MgO 2.79; CaF<sub>2</sub> 4.94; Ta<sub>2</sub>O<sub>5</sub> 0.99; La<sub>2</sub>O<sub>3</sub> 0.50. The liquidus temperature is 1,290°C and the density is 2.80 g/cm<sup>3</sup>. The glass was prepared according to the procedure described in [30] and used in powder; its particles size was reduced by a prolonged milling to an average granular size of ~1 μm.
- (2) MgO (99.99% purity, Aldrich Ltd.) was used as sintering aid for sample B.
- (3) Y<sub>2</sub>O<sub>3</sub> (99.99% purity, H.C. Starck Ltd.) and Al<sub>2</sub>O<sub>3</sub> (Ultra-High Purity, Baikowski Chemie SA), were used as sintering aids for sample C.
- (4) TiN powder (grade C; H.C. Starck Ltd.) was introduced to obtain the electroconductive composite C.

The powders were mixed through a wet ball milling using Si<sub>3</sub>N<sub>4</sub> balls for 72 h in ethyl alcohol. Then each slurry was dried, under nitrogen atmosphere, using a rotary evaporator and the obtained dry powder was sieved through a metallic sieve at 400 μm.

The densification process of all the powder mixtures was carried out by uniaxial hot pressing, under vacuum in an induction heated graphite die using a pressure of 30 MPa at various temperatures: 1,750°C for composition A, 1,650°C for composition B and 1,800°C for composition C. The linear shrinkage of the samples was recorded during hot pressing process.

## 2.2 Materials characterization

### 2.2.1 Microstructure

The density of the hot pressed materials was measured using the Archimedes method. The microstructure was examined on polished and plasma etched surfaces (CF<sub>4</sub>, 15–30 s.) by scanning electron microscopy and microanalysis. Crystal-line phases were revealed by X-ray diffraction analyses.

Fracture surfaces were observed as well, particularly to identify the fracture origins.

### 2.2.2 Mechanical properties

Each kind of material was submitted to microhardness, Young's modulus and flexural strength tests.

Vickers hardness was measured using a Zwick 3212 tester with a 9.81 N load. Young's modulus was measured by resonant frequency on 28.0 × 8.0 × 0.8 mm<sup>3</sup> specimens using an H&P gain-phase analyser. The 4-pts flexural strength ( $\sigma$ ) was measured at room temperature on chamfered bars 25.0 × 2.5 × 2.0 mm<sup>3</sup>, using a semi-articulated SiC four-point jig with a lower span of 20 mm and an upper span of 10 mm on an universal screw-type testing machine Instron mod. 6025, using a crosshead speed of 0.5 mm/min.

### 2.2.3 Cytotoxicity

In-vitro cytotoxicity test was performed on the three hot pressed materials, on the starting powder mixtures and on the titanium nitride powder. The tests were performed according to the ISO 10093-part 5 normative [31]. The biocompatibility was assessed through either the (i) direct contact procedure, or the (ii) elution one, on bars of dense silicon nitride and on powder samples, which were preliminary sterilized in an autoclave.

- (i) Direct contact procedure: a cell culture NCTC L 929 was used. The sample to be tested was put in contact with a monolayer of the cell culture and incubated for 24 h at a temperature of 37°C, under CO<sub>2</sub> atmosphere. After 24 h, the cell culture has been analyzed to evaluate the biological reactivity.
- (ii) Elution procedure. The eluate was prepared using the culture medium (constituted by the cell culture NCTC L929). The extract was obtained under static conditions: the samples were immersed into the culture medium, considering a weight/volume ratio of 0.2 g/ml. The sample was incubated for 72 h at 37°C. An amount of 2 ml of extract of the test material has put in contact with the cell culture for 48 h, at 37°C under CO<sub>2</sub> atmosphere. After 24 and 48 h, the cultured cell monolayers were examined using inversion microscopy and scored on a relative scale of 0–4 based on the degree of cellular destruction to evaluate the biological reactivity.

In both tests, the same procedures were adopted to evaluate the positive and negative control tests using, respectively, extracts from latex and from USP Reference Standard negative control plastic [32].

### 2.2.4 Electrical conductivity and electrical discharge machining

The electrical resistivity of the composite  $\text{Si}_3\text{N}_4 + 35$  vol% TiN was measured by a four-probe method. The current intensity, supplied by a Keithley current source was held under 10 mA to avoid Joule effects. The potential was measured by a nanovoltmeter.

Electrical discharge machining (EDM) approaching tests on  $\text{Si}_3\text{N}_4 + 35$  vol% TiN were carried out either by wire EDM, using a brass wire and water as dielectric, and die-sink EDM equipment.

## 3 Results and discussion

### 3.1 Microstructure

The three hot pressed materials are nearly fully dense (Table 1). X-ray diffractometry (XRD) patterns show that the main crystalline phase is  $\beta$ - $\text{Si}_3\text{N}_4$ , traces of  $\alpha$ - $\text{Si}_3\text{N}_4$  are revealed in sample 2. Besides, sample B, produced with the addition of MgO, contains an amount (about 5 vol%) of crystalline magnesium silicate phase ( $\text{Mg}_2\text{SiO}_4$ ), detected by XRD. Instead, in sample A and C the grain boundary phases are completely amorphous. Sample A contains the bioactive glass used as sintering aid. Sample C, in addition to silicon nitride and titanium nitride, has a small amount (about 3 vol%) of amorphous silicates and/or oxinitrides of Y and Al.

Figures 1–3 show the microstructure of the three materials (A, B, C, respectively). The two monolithic ceramics evidence the typical microstructure of silicon nitride, constituted by elongated silicon nitride grains in a matrix of nearly equiaxed grains. In the electroconductive composite C, the TiN particles are coarser than the silicon nitride grains. Figure 4 highlights the microstructure of the  $\text{Si}_3\text{N}_4$  matrix of the composite material C: the Transmission Electron Microscope (TEM) picture represents a typical example of the microstructure of dense silicon nitride-based material, where the grain boundary phase locates preferentially at triple points, but a continuous film of

amorphous phase is present at the interfaces between the boundaries  $\text{Si}_3\text{N}_4$  grains. Energy dispersive X-ray (EDX) analyses confirmed that the grain boundary phase consists of silicates and oxinitrides of the cations contained in the sintering aids.

### 3.2 Mechanical properties

The mechanical properties of the three hot pressed silicon nitride-based ceramics are shown in Table 1. The *hardness* values are typical of the silicon nitride ceramic: the lower value measured in sample A compared to sample B is related to the higher volume of sintering aids: it means that a larger volume of grain boundary phase has consequently formed, which, moreover, is completely amorphous. The composite C contains TiN that is softer than the matrix [33]: the harness value recorded agrees reasonably with the presence of this phase in such composite material.

*Young's modulus* of material B well agrees with the value given in literature for fully dense silicon nitrides. As in the case of hardness, the Young's modulus of material A, produced with the addition of 10 vol% bioactive glass, is smaller due to the presence of amorphous phase. The modulus value of the  $\text{Si}_3\text{N}_4$ -TiN composite increases due to the presence of TiN, this phase being stiffer than the matrix [33, 34].

The value of room temperature *flexural strength* is in the range previously evaluated on several silicon nitride-based ceramics [34–36].

In all the cases the properties of the present materials are extremely higher than those reported in literature [3] relatively to  $\text{Si}_3\text{N}_4$ -30 vol% bioactive glass composites: it means that the materials design in terms of composition and selection of reinforcing phases supports the merit of the materials herewith studied. The developed ceramics represent a significant improvement in mechanical properties compared to other inert bioceramics like alumina and zirconia [3].

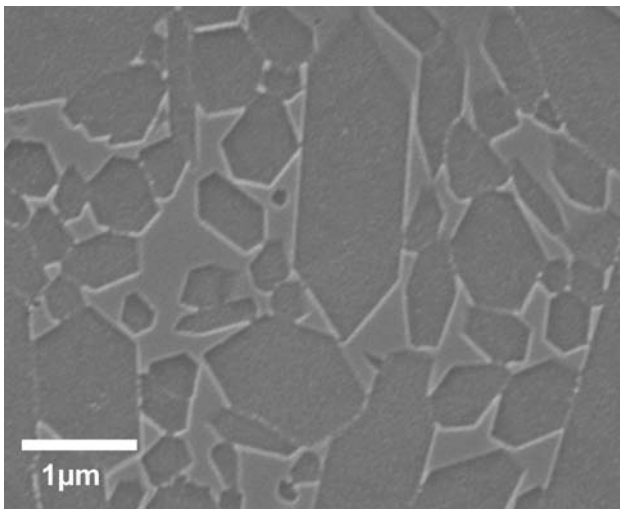
Strength is correlated with the probability of fracture: it is expected that the in-vivo reliability can be improved using silicon nitride-based materials for femoral heads and acetabular components in total hip replacements or other high load clinical applications.

**Table 1** Compositions, hot pressing parameters, and physico-mechanical properties of the three silicon nitride-based ceramics

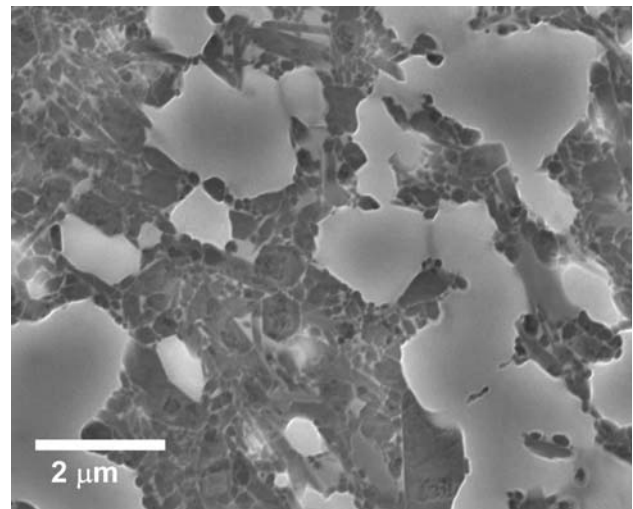
Material code	Composition	T (°C) <sup>a</sup>	t (min)	$\delta$ (g/cm <sup>3</sup> )	$\delta_r$ (%)	Hv (1 kg) (GPa)	Flexural strength (MPa)	Young's modulus (GPa)
A	$\text{Si}_3\text{N}_4 + 10\%$ vol. bioactive glass	1,750	20	3.14	99.4	15.29 ± 0.51	934 ± 215.5	276
B	$\text{Si}_3\text{N}_4 + 8.6\%$ vol. MgO	1,650	60	3.19	~100	18.70 ± 6.63	969 ± 149.2	316
C	$\text{Si}_3\text{N}_4 + (2\% \text{Y}_2\text{O}_3 + 5\% \text{Al}_2\text{O}_3) + 35\%$ vol. TiN	1,800	10	3.97	~100	14.70 ± 0.70	835 ± 116.0	354

<sup>a</sup> Hot Pressing parameters at 30 MPa

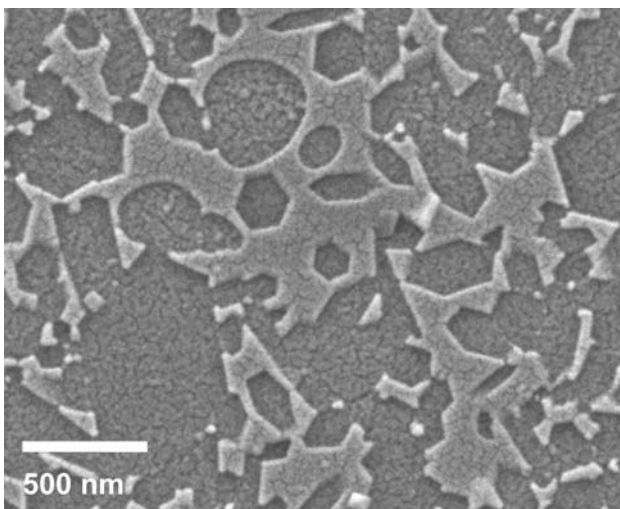




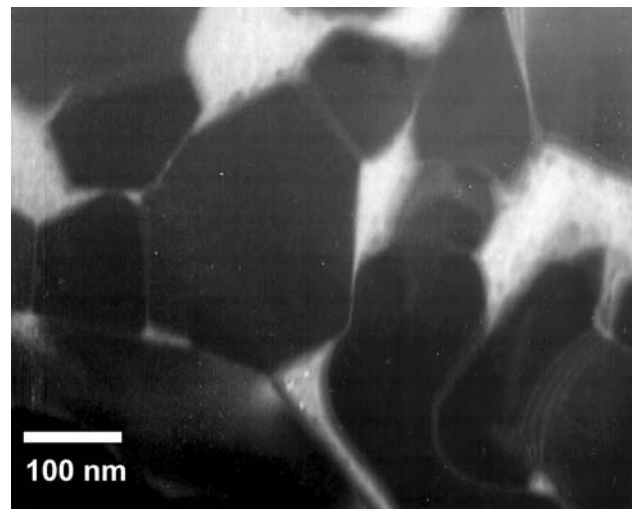
**Fig. 1** Sample A ( $\text{Si}_3\text{N}_4$  + bioactive glass). Surface polished and etched



**Fig. 3** Polished and etched surface of the composite  $\text{Si}_3\text{N}_4$ -TiN (composition C)



**Fig. 2** Sample B ( $\text{Si}_3\text{N}_4$  + MgO). Surface polished and etched



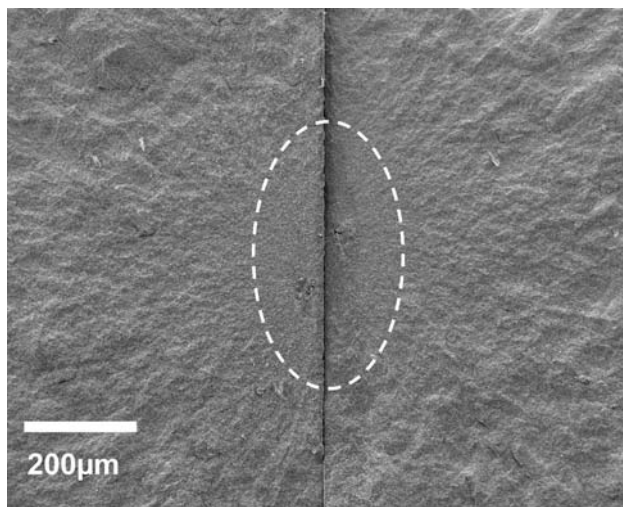
**Fig. 4** Dark field image of the  $\text{Si}_3\text{N}_4$ -TiN composite, highlighting the grain boundary phases (bright areas)

The large standard deviation of the flexural strength data shown in Table 1 indicated the presence of critical defects in the tested samples and the need to optimize the powder treatments, basically milling and mixing procedures. The fracture origin was investigated on fracture surfaces. Some examples of flaws that could act as critical defects, shown in Fig. 5, are mainly inhomogeneities in the microstructure, such as voids between macro-grains of TiN particles in the composite C or agglomerates of secondary phases in material A. The cause of the critical defects present into the material is mainly the inhomogeneous distribution of sintering aid in the starting powder mixture, probably because of the presence of hard agglomerates not disaggregated during ball milling.

### 3.3 Cytotoxicity

In vitro tests of cytotoxicity were performed to evaluate the toxicity of the three dense silicon nitride-based materials and of the raw materials, including, therefore, the  $\text{Si}_3\text{N}_4$  phases, the formed intergranular phases and the TiN electroconductive phase. In addition the tests include the analysis of the toxicity of possible contaminations from the different processing steps: powder mixing, drying, sieving, sintering, etc.

All the tests performed either on the dense materials and on the powders scored 0, while the negative and positive controls scored 0 and 4, respectively. The results stressed the non-cytotoxicity of the materials, either dense silicon nitride or  $\text{Si}_3\text{N}_4$ -sintering aids powder mixtures, in



**Fig. 5** Faced fracture surfaces in a bar-shaped sample for composition B, after flexural strength test. In all of three compositions samples inhomogeneities of the microstructures are revealed as the weakness points from which preferentially flaws take origin

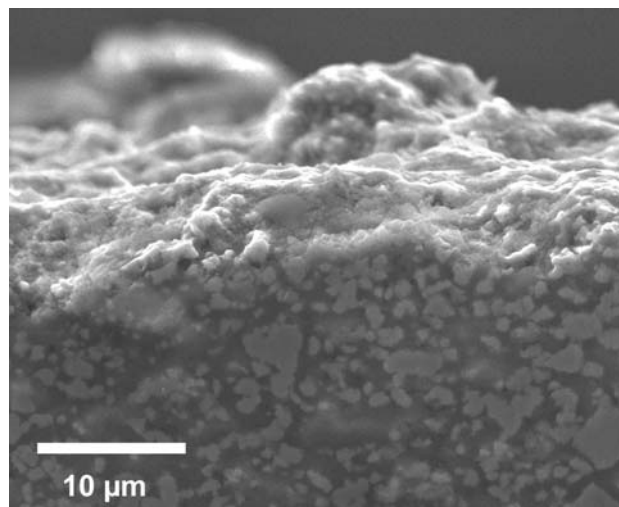
agreement with previous data from the literature [3, 4, 6, 18–23, 29]. Therefore neither the raw material powders:  $\text{Si}_3\text{N}_4$ , TiN and the sintering aids, nor possible contaminations from the processing affect the biocompatibility of the studied ceramics.

Regarding titanium nitride, this compound has been selected, among the possible electroconductive materials compatible with silicon nitride for the production of high strength ceramic-ceramic electroconductive, in view of the positive recent results and applications, where TiN has been used to produce hydroxyapatite-based composites [37–39]. These studies indicate the suitability of TiN either as second reinforcing phase for hydroxyapatite [37, 38] and outline its suitability for abrasion resistant implants or coatings [39, 40]. The present study confirms, therefore, that TiN is an extremely chemically inert and biocompatible compound.

#### 3.4 Electrical conductivity and electrical discharge machining

The electrical resistivity of the composite  $\text{Si}_3\text{N}_4$ -TiN was measured to be  $5.88 \times 10^{-4} \Omega \text{ cm}$ . The material is, therefore, electroconductive, because of the formation of chains of TiN electroconductive particles.

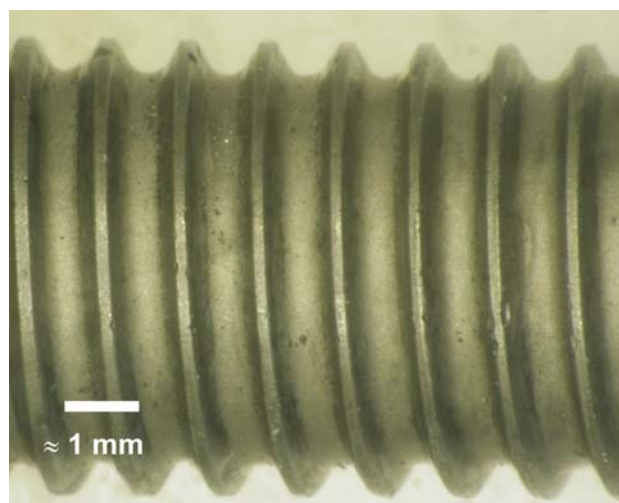
This properties allows the machinability through electrical discharge machining. The use of wire EDM equipment resulted in a cutting speed of about 1.5 mm/min, on flat samples 1 cm high. The microstructure of the EDM treated surface of the composite shows the formation of a surface layer of 10–20  $\mu\text{m}$  in thickness (Fig. 6), that evidences the superpositioning of craters with varying diameters and positions. This derives from the material removing mechanisms, which are linked to the interaction



**Fig. 6** Cross section of C composition ( $\text{Si}_3\text{N}_4$ -TiN) sample surface machined by EDM

between the materials characteristics and the parameters adopted during EDM. Two main mechanisms should be involved: melting and evaporation [34, 41]; therefore the surface is covered by layers of droplets deriving from melting and evaporation. The quantity of material that solidifies and adheres to the surface is a function of the composition and microstructure of the ceramic: in the present case, the resolidified droplets are almost entirely TiN as  $\text{Si}_3\text{N}_4$  should be removed by evaporation.

EDM offers a great potential in the manufacturing of complex-shaped components, through macro- and micro-machining of simple-shaped ceramics, for many applications, including clinical ones. A detail of a bone fixture prototype device, produced starting from the electroconductive composite  $\text{Si}_3\text{N}_4$ -TiN, is depicted in Fig. 7. The



**Fig. 7** EDM-machined feasibility prototype device (screw) on the  $\text{Si}_3\text{N}_4$ -TiN material

degradation of the surface properties due to EDM has to be evaluated relatively to the surface interaction with the environment during the application. In most of the potential clinical application of an electroconductive ceramic, the final polishing with abrasive tools or powder (alumina, silicon carbide, diamond) through mechanical routes can be considered a suitable procedure to remove the surface scales induced by EDM and, therefore to restore the properties of the bulk in the exposed surface.

#### 4 Conclusions

Silicon nitride-based ceramics with the choice of proper sintering aids or secondary phases are very promising candidates for high stress mechanical applications due to the high mechanical properties and the non existence of detrimental intergranular phases after processing and very good bonding between the constituents which ensures a good stress transfer.

The non-toxic behaviour of the studied  $\text{Si}_3\text{N}_4$ -based ceramics, combined with the mechanical properties, confirm the great potential of these materials for high stress medical applications.

In part II the results concerning the wear behaviour and the wettability and chemical interaction against water and physiological solution are reported.

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