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ORIGINAL ARTICLE

Perspectives of the Si_3N_4-TiN ceramic composite as a biomaterial and manufacturing of complex-shaped implantable devices by electrical discharge machining (EDM)

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ABSTRACT: ***Purpose:*** **In this work we investigated the suitability of electroconductive silicon nitride/titanium nitride composite for biomedical implantable devices with particular attention on the processing route that allows the net-shaping of complex components by electrical discharge machining (EDM).**
Methods: **The composite, constituted mainly of a β-Si_3N_4, dispersed TiN grains and a glassy grain boundary phase, exhibited a low density and high hardness, strength and toughness. Bulk, surface characteristics and properties of the Si_3N_4-TiN composite were analyzed. After the EDM process, the microstructure of the machined surface was examined.**
Results and Conclusions: **The obtained results showed that the Si_3N_4-TiN ceramic composite together with the EDM manufacturing process might potentially play a key role in implantable load-bearing prosthesis applications. (Journal of Applied Biomaterials & Biomechanics 2010; 8: 28-32)**

Key words: Silicon nitride, Titanium nitride, Electrical discharge machining, Implantable devices, Ceramic composite

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INTRODUCTION

Silicon nitride based composites are well recognized as engineering materials in high-temperature applications (1-3). In 1997 Zhou et al studied the possibilities of using silicon nitride and its composites as biomaterials (4). In particular, due to the high mechanical and tribological properties of the silicon nitride materials, in the last decades the scientific community has focused attention on the perspectives and potentials of these ceramics for use as permanent clinical devices, as articular prosthesis, for reconstructive bone surgery as fixture systems (5-7). Notwithstanding the excellent mechanical and physical properties of silicon nitride, there has been controversy concerning its biocompatibility. Recent results confirm the non-cytotoxicity of these materials (8, 9) and in vivo tests, implanting Si_3N_4 pieces into the femurs of rabbits (10), have demonstrated good bone/implant attachment, with no immuno-inflammatory or adverse cell reactions. Moreover, in detail, investigations on the influence of different qualities of commercial silicon nitride-based materials revealed no correlations between cell behavior and chemical composition (11). Unfortunately, owing to the high hardness, the production of complex shapes from simple pieces of silicon nitride through conventional mechanical machining, for example, using diamond tools is difficult and expensive. A possible solution to this problem is by incorporating electrically conductive reinforcement, such as particles of TiN, TiC, TiB_2, ZrB_2, in the Si_3N_4 matrix. These composites are expected to have excellent properties for wear and structural applications (12, 13), but mainly, the addition of the above-mentioned reinforcement phases in correct amounts (over about 30 vol%) makes the Si_3N_4 an electrically conductive composite, suitable to be conveniently manufactured even in complex shapes by electrical discharge machining (EDM) (14). To achieve electroconductivity TiN was introduced, producing a reinforced silicon nitride composite with high strength, low density, good electric conductivity and with no cell toxicity ascertained (15). The aim of this work was to study microstructural, mechanical and toxicological properties of the silicon nitride-titanium nitride ceramic composite; the processing route of EDM, to realize complex shapes, suitable for fixation devices in clinical applications, and for load bearing articular surfaces in prosthetic replacements have been explored and evaluated.

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MATERIALS AND METHODS

The selected composition consisted of a mixture of commercial raw powders, as described below and reported elsewhere (16):

– Si_3N_4 (SN-E10, UBE Ltd), (α-Si_3N_4, 95% vol) was the main constituent.
– Y_2O_3 (grade C, HC Starck Ltd) and Al_2O_3 (Ultra-High Purity, Baikowski Chemie SA) intended as sintering aids.
– TiN (grade C, HC Starck Ltd) as 35% in volume, added to obtain the electroconductivity and to increase the mechanical properties, especially in terms of fracture toughness (12) and tribological performances of surfaces, with a low wear rate (15).

The starting powders were mixed and treated according to optimized laboratory procedures. The densification process of the powder mixture was carried out by uniaxial hot pressing, under vacuum in an induction heated graphite die. After checking several densification routines, a pressure of 30 MPa at 1800 °C for 10 min was considered suitable to achieve the best characteristics in the ceramic composites yielded (16).

The densities of the sintered composites were measured by the Archimedes method. Microstructural characterizations by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) were carried out on cross-sections of different sintered billets after polishing (diamond pastes <1 µm) and plasma etching (CF_4, 15-30 sec).

The mechanical and physical properties of the Si_3N_4-TiN composite were analyzed according to the following methodologies (12):

– X-ray diffraction analysis, XRD (Rigaku Miniflex, using a Cu-Kα radiation), for the mineralogical phase composition.
– Vickers micro-hardness, using a Zwick 3212 tester with a 9.81 N load.
– Young's modulus, by resonant frequency method, on 28.0×8.0×0.8 mm specimens, using an H&P gain-phase analyzer.
– 4-point bending flexural strength test (Instron mod. 6025 testing machine, 0.5 mm/min crosshead speed), carried out on chamfered bars of 25.0×2.5×2.0 mm, with a SiC semi-articulated 4-pts. jig with a lower span of 20 mm and an upper span of 10 mm.
– Electrical conductivity, 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.

EDM tests were carried out with a maximal current intensity of 50 A, for wire EDM, until 60 A using die-sink EDM apparatus.

The microstructure of the surface and cross-sections of the machined samples were evaluated by SEM-EDS and XRD. The thickness of the surface scale formed during EDM and the roughness of the carved surfaces were measured both by SEM and a profilometer (Taylor Hobson Form-Talisurf 120; tip radius 2 µm and max resol. 10 nm).

RESULTS AND DISCUSSION

The microstructure of the Si_3N_4-TiN composite consists of elongated β-silicon nitride and titanium nitride grains, which are coarser than the matrix (Fig. 1). The presence of TiN grains (35 vol%) in the Si_3N_4 in the matrix forms an electroconductive network throughout the material: the electrical resistivity of this composite decreases down to 10^{-4} Ω·cm, so that EDM can be effective for machining (17). In addition, the presence of TiN grains induces a toughening and stiffening effect by hindering the crack propagation, much better than as occurs in other ceramics, commonly used for implantable devices.

By comparing (Tab. I) the physical and mechanical properties of the silicon nitride-titanium nitride composite with the those of other ceramics used in the biomedical field, such as zirconia and alumina, it is possible to argue that the Si_3N_4-TiN composite exhibits a series of positive functional characteristics, such as a low density, high hardness, strength and toughness, satisfying the requirements to produce effective articular load bearing surfaces prostheses. Moreover, with such a low electrical resistivity, it can be easily machined until it results in complex shapes with semi-finished surfaces (12). A previous work (12) reported that the properties of Si_3N_4-TiN composites

TABLE I - MECHANICAL AND PHYSICAL PROPERTIES: COMPARISON BETWEEN SI3N4-TIN AND OTHER BIOCERAMICS FOR PROSTHETIC IMPLANTS

Material	Composition	Density, (g/cm^3)	Hardness Vickers (1kg), (GPa)	Flexural Strength, (MPa)	Young's Modulus, (GPa)	Fracture Toughness K_Ic (MPa $m^{1/2}$)	Electrical Resistivity (Ωcm)
Si_3N_4-TiN	Si_3N_4 + 35% vol TiN	3.97	14.70±0.70	835±116.0	354	5.67±0.28	$5.88 \cdot 10^{-4}$
Al_2O_3	99.99% Al_2O_3	>3.97	14-16	300-500	400-450	4-5	$>1.00 \cdot 10^{13}$
Y-TZP	ZrO_2 + 3% mol Y_2O_3	6.05	12-14	1000-1500	200-250	6-12	$1.00 \cdot 10^{9}$
ZTA	$Al2O_3$ + 20% vol ZrO_2	4.40	12-15	700-1000	300-350	6-10	$>1.00 \cdot 10^{14}$

TABLE II - WORKING PARAMETERS FOR WIRE AND SINKER EDM APPLIED IN THE REALISATION OF THE DIFFERENT CERAMIC PROTOTYPE DEVICES

Wire EDM	Sinker EDM
V = 100 V	V = 60 V
I = 2 A	I = 1.3 A
Work Time: 7.5 sec	Off Time: 15 sec

may vary depending on TiN content and particle size: strength and toughness generally increase up to a threshold of about 30% vol of TiN content.

These features evidence the possibility to tailor the final properties of the ceramics, depending on the intended application, by properly selecting the amount and the particle size distribution of the secondary phase. For instance, the quantity of 35% vol TiN was found as the minimum (12) to allow the formation of electroconductive particle chains necessary to exploit EDM in Si_3N_4; on the other hand, the amount introduced was evaluated so as not to lower significantly other important biofunctional characteristics, for example, the wettability of the surface with aqueous fluids, concerning the intended use, comparable to those of other ceramics (Al_2O_3 and ZrO_2) in implanted prostheses for articular surfaces (15).

Due to the unique combination of mechanical properties, particularly of hardness, the machining of sintered silicon nitride based composites is usually carried out by hard grinding with diamond tools, likewise in the case of oxide ceramics. This method is very expensive, time consuming and it shows some limits concerning the geometry which could be realized. The electroconductive Si_3N_4-TiN offers the advantage to exploit a new machining route, through EDM. EDM is a machining process, already widely used in the field of electroconductive ceramics, which allows complex shapes to be obtained in a single processing step from dense bulks, obtaining accurate semi-finished surfaces, which may be even used as they are, or finished by diamond pastes. It must be stressed that this process is efficient only for bulks with high densification, in which the electroconductive network is quite homogeneous: this allows a higher efficiency in the process and, by applying the correct electrical parameters, a consequent very limited scaled layer produced by the ablation mechanism (16).

In this work, different complex shapes were described as prototypes realized at the laboratory level, using sinker and wire EDM: screws and plates for minifixation system (Fig. 2) (18, 19), basal thumb implants (Fig. 3) and radial implants (Fig. 4).

Moreover, prototypes of large bearing surfaces with complex topographies (eg total or monocompartmental

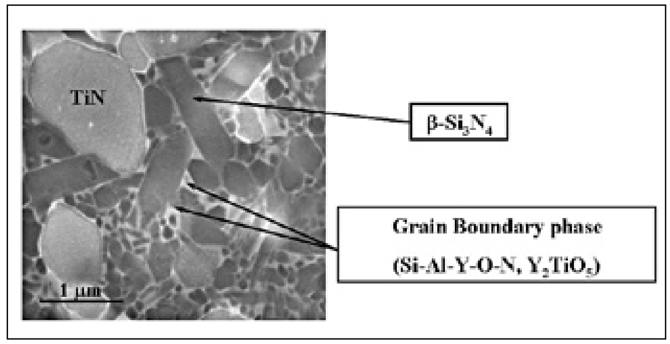

Fig. 1 - *Microstructure of hot pressed Si_3N_4-TiN ceramic composite.*

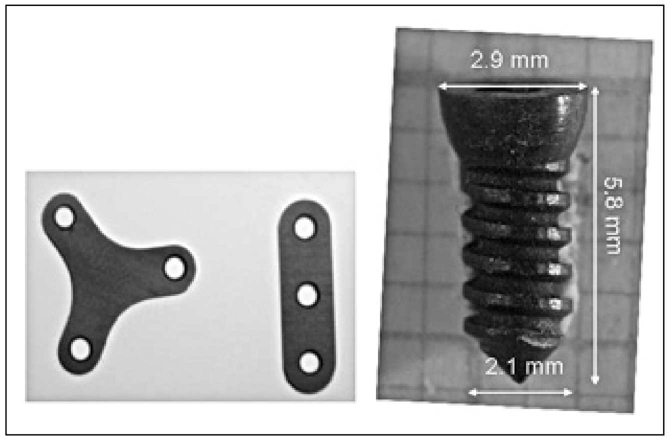

Fig. 2 - *Screw and plate prototype for minifixation system produced by EDM from hot pressed Si_3N_4-TiN billet.*

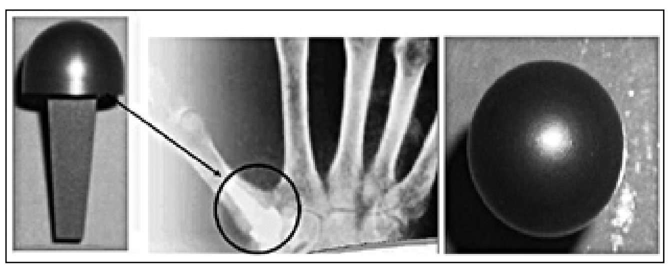

Fig. 3 - *Basal thumb implant produced by EDM from hot pressed Si_3N_4-TiN.*

knee joint surfaces) including the underlying abutments are in progress to be realized through CAD-CAM rendering.

The working parameters (wire EDM: 100 V; 2 A; sinker EDM 60 V and 1.3 A) were optimized to fit Si_3N_4-TiN characteristics using a copper electrode. Correct set-up of the process and optimization of working parameters (voltage or current intensity) is mandatory to avoid damage and the material bursting. Silicon nitride and titanium nitride exhibit different thermal expansion coefficients ($3.0{\cdot}10^{-6}{\cdot}°C^{-1}$

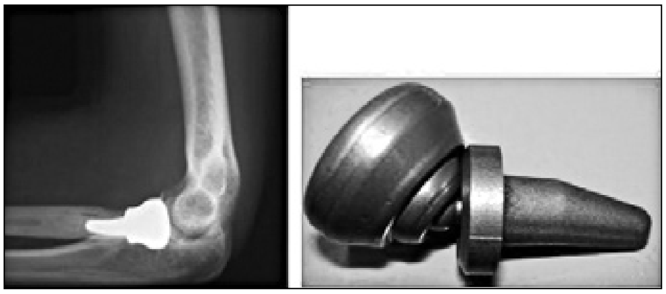

Fig. 4 - *Radial implant produced by EDM starting from a single-shaped piece.*

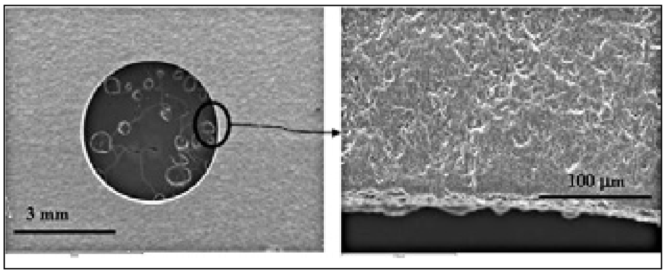

Fig. 5 - *Micrography of EDM machined surface and carved hole in Si_3N_4-TiN.*

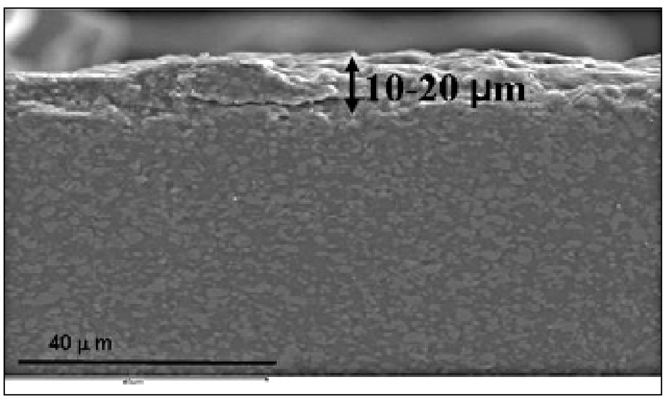

Fig. 6 - *Cross-section microstructure after EDM: the mean thickness of the surface scale is indicated.*

and $9.4 \cdot 10^{-6} \cdot °C^{-1}$, respectively) and this mismatch may generate a stress state in the material bulk, in particular at the grain boundaries. Considering this characteristic of the Si_3N_4-TiN composite, holes, undercuts and curved surfaces (see the examples in Fig. 2) have to be designed with great accuracy and their realization requires an optimized machining step-by-step strategy.

SEM observations of the machined surfaces demonstrated that no cracks formed around the carved holes and no evident huge scale defects were induced on the machined surfaces (Fig. 5), proving that the correct parameters were selected.

Ablation mechanism by EDM includes melting, evaporation and a subsequent local re-solidification; the volume of material involved that solidifies and adheres back to the surface depends on its composition: in this case, the re-solidified droplets are mainly TiN, as Si_3N_4 should be removed by evaporation. The thickness of the surface layer involved in melting and reprecipitation by EDM was found to be in the range of 10-20 µm (Fig. 6); for instance, total roughness (Rt) was found to be very variable, ranging from Ra value to those corresponding to the thickness of the involved layer. On flat and as-machined surfaces the material exhibited Ra=1.40 ± 0.15 µm.

Preliminary in vitro tests, performed by seeding epithelial cells on the surface altered by EDM, showed no relevant morphological modification of the cells and no apoptosis was observed after 24 hr (data not shown).

Further preliminary analyses concerning the biological performance of the composite and of the starting powders showed that both dense Si_3N_4, TiN and sintering aids are not cytotoxic, as already assessed by previous results (9).

This achievement encourages further activity and deeper investigations into the silicon nitride-titanium nitride as a biomaterial, and employing EDM for the fabrication of near-net-shapes devices.

CONCLUSION

Si_3N_4-TiN electroconductive ceramic composites were produced by hot pressing, to evaluate the potential of their application for load-bearing prosthesis and other implantable biocompatible devices. The microstructural and mechanical properties confirmed that silicon nitride may be a successful application as a biomaterial for functional substitution in load-bearing prosthesis. The evaluation of hardness, strength, toughness, Young's modulus and the tribological performances are comparable or higher than those of oxide ceramics commonly used for the fabrication of joint prostheses. These ceramics were assessed as non-cytotoxic: quantitative and more detailed biological tests including histochemistry (type I collagen; alkaline phosphatase; Von Kossa staining; osteocalcin) and histomorphometric parameters (cell attachment and spreading, proliferation and differentiation) on cells cultured onto the ceramic Si_3N_4-TiN composite material are currently still in progress, but the preliminary in vitro tests for cell interaction carried out to date are promising.

The main advantage of this non-oxidic ceramic electroconductive composite lies in the possibility to manufacture very complex near-net-shapes, even with undercuts, by EDM, from simple sintered billets. The silicon nitride-based materials may serve as affordable hard biomaterials for fixation, bone and articular substitutions, and be much better in load-bearing prosthesis.

Conflict of interest statement: None of the authors have any financial interest in the materials or equipment described in this study or in the companies that produce them.

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