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NANOSTRUCTURED TITANIUM – APPLICATION IN DENTAL IMPLANTS

NANOSTRUKTURNÍ TITAN – APLIKACE PRO DENTÁLNÍ IMPLANTÁTY

Abstrakt

Pro dentální náhrady jsou vyvíjeny nové materiály, lépe vyhovující požadavkům medicíny. Perspektivním materiálem je nanostrukturní titan (nTi). V práci je (nTi) porovnán s ostatními materiály pro dentální aplikace. nTi je bioinertní, neobsahuje žádné, ani jen potenciálně toxické ani alergenní přísady a má vyšší měrné pevnostní vlastnosti než jakýkoliv materiál používaný pro dentální implantáty. Z nTi byly vyrobeny šroubové implantáty Nanoimplant® o průměru 2.4 mm a délce intraosseální části 12 mm. Ty byly použity ve dvou klinických aplikacích. Průběh hojení i časného pooperačního období byl bez jakýchkoliv komplikací. Jedná se o ve světě prvou aplikaci nTi dentálního implantátu.

Abstract

New materials for dental substitutes are developed. Nanostructured titanium (nTi) is a perspective material for these purposes. This paper compares its properties with that of other materials used for the same purpose. nTi is bio inert, it contains neither even potentially toxic nor allergenetic additives and has significantly higher specific strength properties than any other material used for dental implants. Cylindrical threaded screw implants Nanoimplant® were made-up from nTi. Implants were used in two clinical applications. No complications were noticed during the early postoperative period and early loading. It was the first application of the nTi dental implant in the world reported.

1. INTRODUCTION

The material for dental implants is required to be biocompatible, mustn't be toxic and also shouldn't cause allergic reactions. It must have high ultimate strength *Rm* and yield point *Rp* with desirable low density ρ and low modulus of elasticity *E*.

Alloys of stainless steels, cobalt alloys, titanium and titanium alloys representing traditional metallic materials used for dental substitutes.

Titanium, in form of commercial pure Ti (cpTi) or Ti-based alloys, is used for medical and dental applications as a bioinert material from the second half of sixties of the 20th century [1 quoted in 2]. Nowadays, titanium is preferred to stainless steel and cobalt Ti alloys due to its excellent biocompatibility. Fig. 1. and Fig. 2., Tab. 1.

Consequently to the development of Ti alloys for aerospace and armament industry, there is wide range of alloys developed for medical applications.

At the beginning the purpose of the development was to take advantage of high strength of Ti alloys to cpTi. Typical material of this generation is $\alpha + \beta$ alloy Ti-6Al-4V.

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But later toxicity of vanadium (V) was proved [7, 8 quoted in 2] and also aluminium (Al) is considered to be potentially a toxic element.

Therefore in further development prevails effort to substitute toxic and potentially toxic elements in Ti alloys with nontoxic ones such as tantalum (Ta), molybdenum (Mo), niobium (Nb) or zirkonium (Zr). At the same time there are developed β Ti alloys that are characterized by low values of modulus of elasticity [9, many authors quoted also 2]. However, Ti alloys with elements of very different density and melting point require special production technologies that noticeably increase the production costs and the final price of a product.

Tab. 1 Biocompatibility of various materials assessed in accordance with a type of osteogenesis [6]

Type of osteogenesis	Biomaterials	
Intervene (distance) osteogenesis	Stainless steels, Vitallium (Co alloys), PMMA (polymethyl-methacrylate)	Biotolerant materials
Contact osteogenesis	cpTi, Ti alloys, C, Al, Zr, Titanium, TiN, Si_3N_4	Bioinert materials
Bonding osteogenesis (osteoinductivity)	Bioglass, Ceravital, Tricalcium phosphate, Hydroxylapatit, A-W ceramic	Bio-active materials

A problem in the course of the development of metallic biomaterials represents not only their actual or potential toxicity but also their allergenetic potential [10 quoted in 2].

Sensitivity of the population to allergenes dramatically increases. An allergy on metals is caused by metallic ions, which are released from metals by body liquids. Share of particular metals on origin of the allergies is different. Fig. 3. Ni, Co and Cr are the main alloying elements of stainless steels and cobalt alloys. Also some Ti-based alloys, e.g. Ti-20Cr-0.2Si, Ti-20Pd-5Cr and Ti-13Cu-4.5Ni, used in dental applications [2] contain elements classified as allergens.

Approximately 20% of European women and 5% of men up to 30 years were reported sensitive on Ni during the first half of the 20th century,. Sensitivity of continental population on Ni from the end of the last century is shown on Fig.4 [11 quoted in 2]. Ascending trend of this sensitivity surely develops even nowadays.

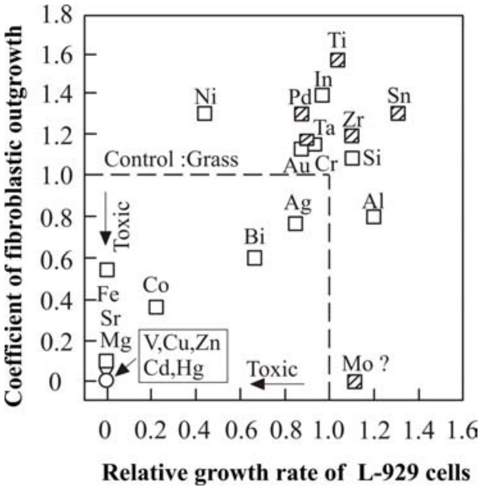

Fig. 1 Cytotoxicity of pure metals [3, 4 quoted in 2]

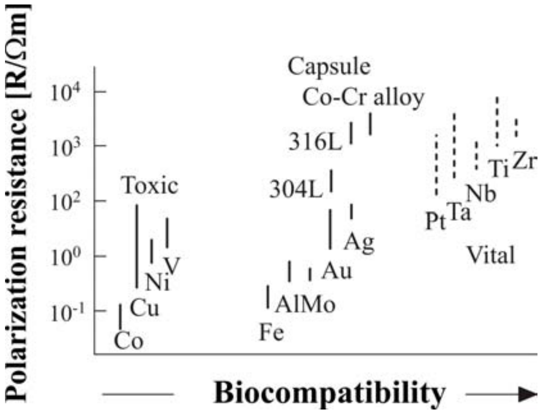

Fig. 2. Metal biocompatibility evaluated by corrosion resistance in accordance with polarizing resistance [5 quoted in 2]

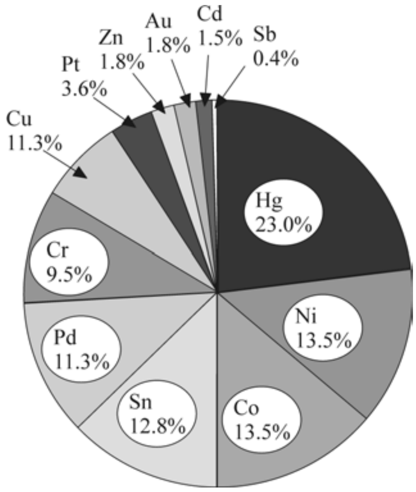

Fig. 3 Percentage share of particular elements
in allergy on metals. [10 quoted in 2]

Commercial pure cpTi stays the preferred material for dental applications. It is desirable to increase its other mechanical properties without using even potentially toxic or allergenic elements preserving its low value of modulus of elasticity. The use of nanostructured Ti is the possible way.

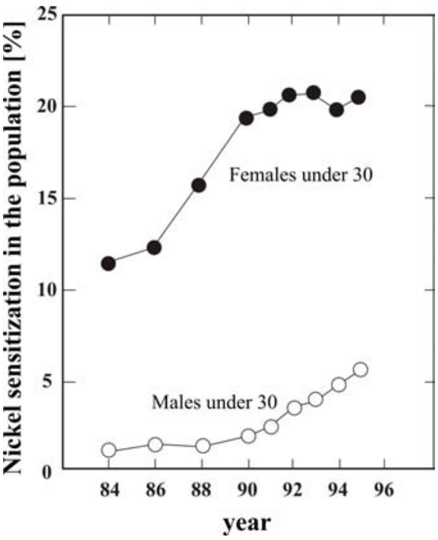

Fig. 4 Sensitivity of the European population on Ni

2 NANOSTRUCTURED MATERIALS

Nanomaterials are materials with structural elements of nanometer size, i.e. of 10^{-9} m. They stand for materials of the third millennium and its application extends many fields, including new developed medical products, going far beyond the borders of yesterday's science-fiction.

The replacement of tissues using so called *bulk nanostructured metals* as biomaterials is of interest. For such purpose, materials with very fine grain in dimensions about 1- 100 nm are regarded.

Underneath the size of some natural structures measured in nanometres to nTi is compared.

DNA	2,5 nm
Molecule of Aspirin	1 nm
Protein	5 – 50 nm
Virus	75 – 100 nm
Bacteria	1 000 – 10 000 nm
Red blood cell	7 000 nm
White blood cell	10 000 nm
Hair	50 000 nm
Grain of Ti	25 000 – 50 000 nm
Grain of nTi	100 – 300 nm

2.1 Nanostructured technically pure Ti (nTi)

Production technology

Various methods [12] for production of nanostructured materials have been developed, which can be classified into two categories based on their approach.

The first is the „bottom up“ approach, which builds material atom by atom or atom cluster by atom cluster. Methods in this category, they include inert gas condensation and other nano-powder production methods.

The second approach for nanostructured materials production is the "top down" approach, which refines coarse-grained metals through Severe Plastic Deformation (SPD).

The SPD techniques have significant advantages superior to the other synthesizing techniques. The nanostructured materials produced by SPD are 100% dense (this is an important issue for mechanical properties) and contamination free (important for biomedical properties).

Some important methods that are in this category include High Pressure Torsion (HPT), Accumulative Roll Bonding (ARB), Multipass Coin-Forging (MCF), Reppetitive Corrugation and Straightening (RCS), Conshearing process (CP) and Continuous Strip Shearing (C2S2). The most developed SPD technique is equal channel angular pressing (ECAP) [13] Fig. 5. Moreover SPD techniques have the capability of producing bulk nanostructured materials in size feat for dental applications.

Technology combines ECAP and rolling was used for production of nTi semi-product referred.

Properties

nTi properties suitable for dental implants are mentioned in Tab. 2 and Tab. 3 and in Fig. 7 and Fig. 8.

Bulk nanocrystalline materials are distinguished by exceptional mechanical properties, with high strength, high yield point and relatively low elastic limit being especially important for dental implants.

Mechanical properties of metallic substitute material are assessed related to its density as so called specific properties. Modulus of elasticity of nTi was measured by Three-point Bending Test on VSB-Technical University of Ostrava.

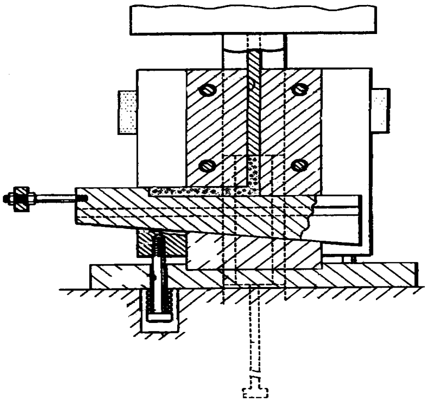

Fig. 5 ECAP – US Patent [13]

Tab. 2 Chemical composition of nTi

Grade ASTM F67-00	C [%]	Fe [%]	H [%]	N [%]	O [%]	Ti [%]
Grade 2	max. 0,08	max. 0,3	max. 0,015	max. 0,03	max 0,25	do 100
Grade 4	max. 0,08	max. 0,5	max. 0,015	max. 0,05	max 0,4	do 100

Tab. 3 Mechanical properties of nTi

Grade	Strength R_m [Mpa]	Yield point $R_{p\ 0,2}$ [Mpa]	Ductility A [%]	Contraction Z [%]	Modulus of elast. E [Gpa]
nTi Grade 2	1030	845	12.0	51.0	96
nTi Grade4	1235	1085	12.5	47.4	100

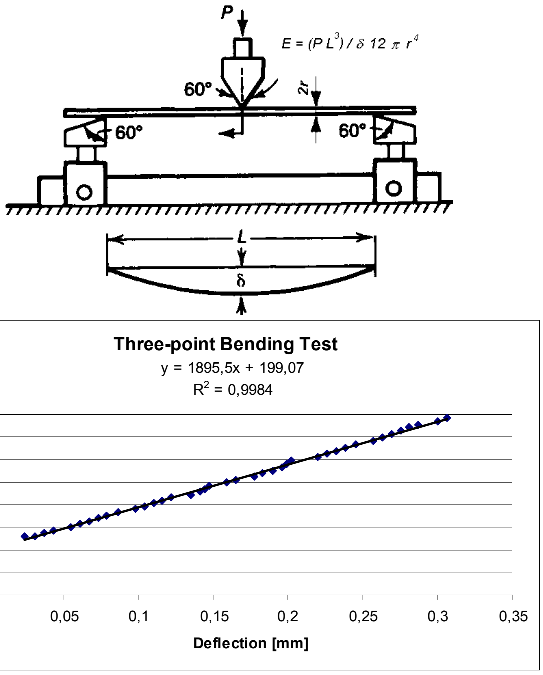

Fig. 6 Three-point Bending Test for nTi G4 –Schema and Results

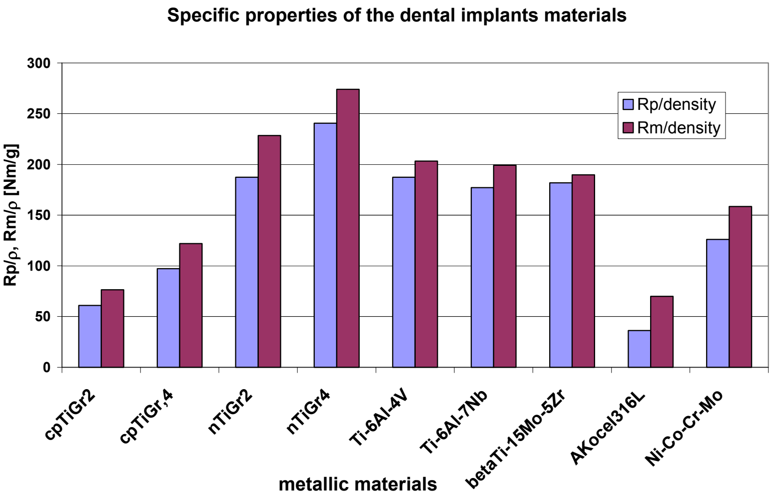

Fig. 7 Mechanical properties of materials for dental implants related to density of material

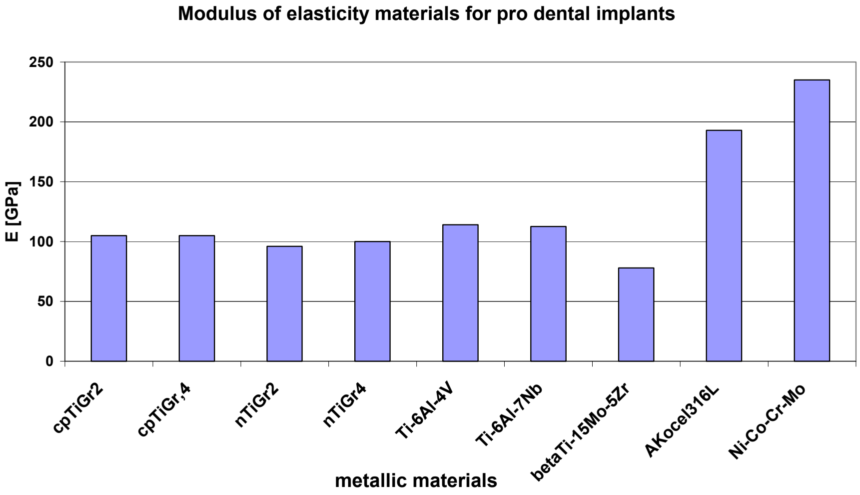

Fig. 8 Modulus of elasticity of materials for dental implants

Data about other mechanical properties of nTi were acquired with supplier and data about mechanical properties of other materials come from [14].

3 IMPLANT FROM nTi

The objective of our development was to produce an implant of smaller dimensions preserving the load capacity comparable to any ordinary 3.5 mm diameter titanium implant, which can be used as a pillar in indications of insufficient thickness of alveolar bone.

Material properties of mini-implants available on the market made from Ti-based alloys with diameter of 2 mm don't allow full loading and they are assigned rather for supportive function, most often for hybrid prosthesis or interstitial pillar. Certified system of quality Timplant® according to standard ČSN EN ISO 13485:2003 was respected during development of implant Nanoimplant®. The first set was produced from nTi GR 4. Optimal diameter of intraosseal part 2.4 mm was specified by calculation as an equivalent of strength of implant with thickness 3.5 mm. The lengths range of the spiral intraosseal parts varying from 10, 12, to 14 mm, followed by the polished gingival conic part, with the conic abutment ending enabling fixation of prosthetic part with screw, makes the unique and versatile design of the implant . Exposure of nanostructure surface of the implant was achieved by the etching the intraosseal part and concurrently sufficient roughness of surface is guaranteed, which is comparable to the surface of cpTi. An enlarged proportion of the screw thread diameter to the cylindrical part of the implant body (without screw thread), which is 1.29, contributes to primary stability. Mini-implants use to have this ratio up to 1.22, for implants with 3.5 mm diameter it is reported up to 1.18. Capacity calculation of implants was simulated in a plane of transition between intraosseal (echted) and gingival (burnished) part of implant Nanoimplant® in the Fig. 9 on the left and classical implant in the Fig.9 on the right.

4 APPLICATION

4.1 Case 1 Immediate treatment with implants in lower jaw [15]

Nanoimplants were used for the restoration of a frontal dentition defect in a 55 years old male. He lost all of his four lower incisors by severe parodontal disease, the teeth 32 and 31 were spontaneously eliminated at the beginning of 2005, teeth 42 and 41 were extracted with consequent surgical treatment without application of augmentative material. 7 months following the extractions 3 nanoimplants with diameter 2.4 mm were inserted to the frontal segment of the lower jaw. Fig.10. X-ray control of implant insertion.

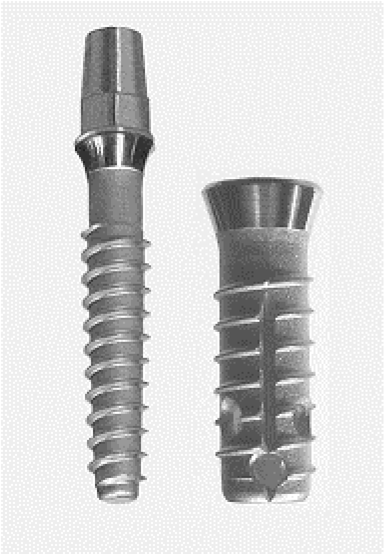

Fig. 9 On the left Nanoimplant® 2.4 mm, on the right implant Timplant® 3.5 mm

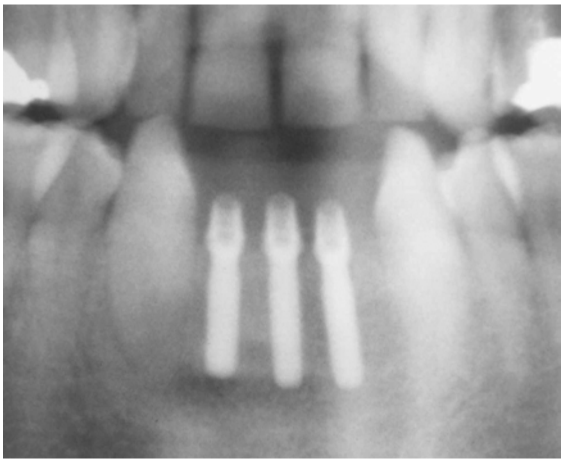

Fig. 10 X-ray control of implant insertion

No complications occurred either during immediate postoperative period or in subsequent healing period. At present, i.e. 5 months after implant insertion, all 3 implants are stable covered with a definite ceramic bridge and are clinically firm without signs of inflammation or resorption of the adjacent bone.

4.2 Case 2 Implant treatment in side segment of the lower jaw with alveolar split [16]

44 years old female with single-sided dental arc defect in the lower jaw as a consequence of previous parodontal disease. A very narrow alveolar ridge of the side segment excluded any application of ordinary implants.

Even for the placement of nanoimplants it was necessary to perform an alveolar split. Afterwards two nanoimplants of 14 mm length were inserted through the fissured alveolar split. The gap between both lamellas was filled with autolog bone acquired during implantation. On Fig.11 there are results of X-ray control of implant position are shown.

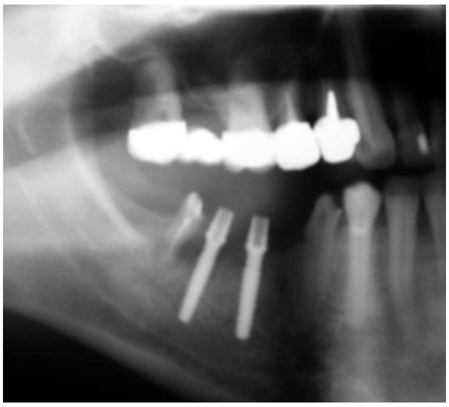

Fig.. 11 X-ray control of the position of implants inserted to alveolar split

Primary retention of the implants was very good, also healing of the operative wound passed without complications. At present the patient is treated with provisional fixed bridge, we are waiting on with definite treatment because of ongoing bony remodelation.

5 CONCLUSION

Nanostructured titanium preserves all of it is significant properties from the medical and biological point of view, because of which pure titanium became the preferred material not only for dental implants. At the same time, nTi surpasses other materials used for such applications due to its specific mechanical properties, important for long term secure function of the implant.

nTiGr4 material has 2,25 times higher tensile strength than cpTiGr4, 1,35 times higher ultimate strength than Ti-6Al-4V containing potentially toxic elements, 1,37 times and 1,44 times higher ultimate strength than Ti-based alloys Ti-6Al-7Nb and Ti-15Mo-5Zr.

Nanostructured implants were used for the first time in clinical practice for treatment of frontal dentition defect with immediate provisional bridge placement.

Currently, the high costs of nanostructured material affect the price of the implant necessarily. However, this increase is acceptable with its utility properties.

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