MODERN PROBLEMS OF PHYSICS

NANOSTUCTURED and ULTRAFINE GRAINED BIOINERT METALS and ALLOYS and BIOACTIVE CaP COATINGS

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Tomsk, Russia - 2024

TOMSK SCENTIFIC CENTER of
SIBERIAN BRANCH of
RUSSIAN ACADEMY of SCIENCES
was founded in 1978
(http://www.tsc.ru).
At present there are five academic scientific institutes in TSC.

The total number of staff of Tomsk Scientific Center is ~2000.
700 scientists, 5 corresponding members and academicians of RAS,
490 doctors of sciences and Ph.Ds and 160 post-graduate students works in Scientific Center.

TOMSK SCIENTIFIC CENTER of SB RAS is located in Academtown near Tomsk

HCEI of SB RAS

ISPMS of SB RAS

IAO of SB RAS

IMCS of SB RAS

IPC of SB RAS

INSTITUTE of STRENGTH PHYSICS and MATERIALS SCIENCE, SIBERIAN BRANCH of RUSSIAN ACADEMY of SCIENCES (http://www.ispms.tsc.ru)

Institute of Strength Physics and Materials Science of the Siberian Branch of RAS (ISPMS of SB RAS) was founded in 1984. It is one of the leading research institutes in the Siberian region which deal with materials science, design and development of new materials, including nanomaterials and products on their basis.

Institute of Strength Physics and Materials Science of SB RAS

The main activities of ISPMS of RAS

- physical mesomechanics of heterogeneous media;
- nanostructured bulk and nanosized materials, nanostructured surface layers, thin films and coatings;
- nanotechnologies;
- advanced materials based on metals, ceramics and polymers;
- computer-aided design of new materials and technology of their production;
- fundamentals of hardening and surface treatment technology;
- non-destructive testing;
- ngineering of custom-made equipment and technology for research, diagnostics and industry;
- biomaterials.

INSTITUTE of STRENGTH PHYSICS and MATERIALS SCIENCE, SIBERIAN BRANCH of RUSSIAN ACADEMY of SCIENCES
(http://www.ispms.ru)

Evgeny A. Kolubaev
Doctor of Science (Engng)
Director of ISPMS of SB RAS

PaninV.E. was Academician of RAS

Founder of ISPMS of SB RAS

Laboratory «Physics of nanostructured biocomposites»

The main tasks

1. The development of the severe plastic deformation methods to produce the nanostructured and ultrafine grained state in bioinert metals: commercially pure titanium VT1-0 (Grade 2) and VT1-00 (Grade 1), alloys of zirconium-niobium and titanium-niobium systems.

2. The development of bioinert oxide and bioactive calcium-phosphate coatings on the bioinert metal surface.

3. The ion implantation and electron beam treatment of nanostructured metals to increase their fatigue life and endurance strength.

4. Theoretical modeling of the calcium-phosphate coatings growth on metallic substrate at microarc oxidation and computer calculation of stresses on interface “substrate – coating”.

5. The design of medical implants (dental implants) on the basis of nanostructured titanium and calcium-phosphate biocoating.

6. Development of physical and technical bases of producing of medical implants by laser sintering from low modulus bioinert alloys of titanium-niobium system

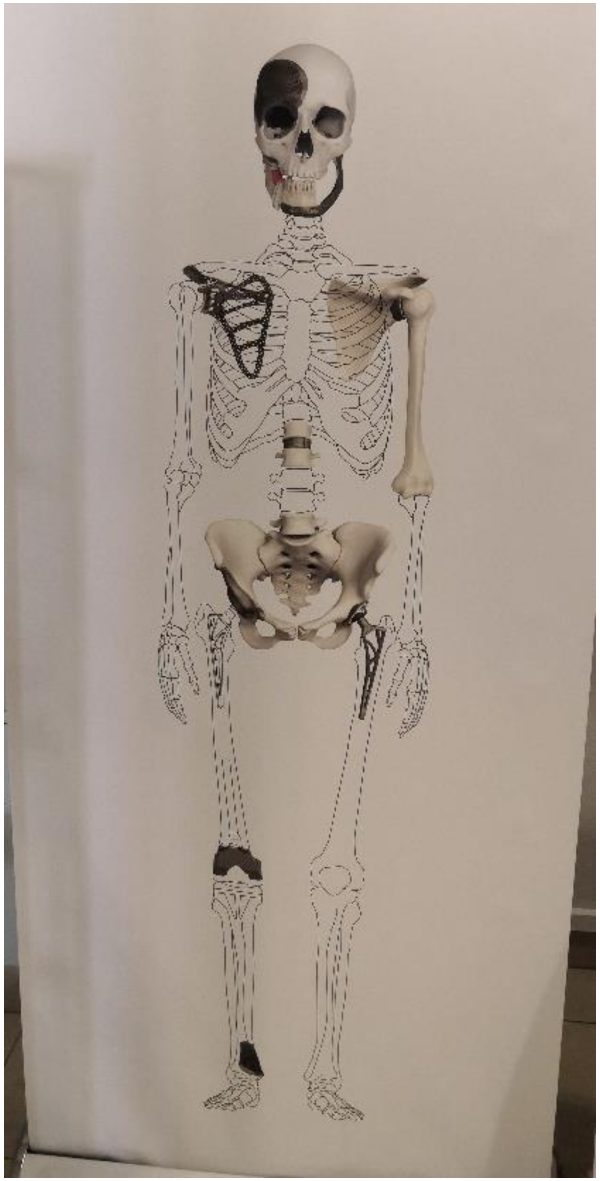
BIOMATERIALS

1. Metals and alloys
2. Bioceramic materials
3. Biopolymers
4. Carbon

1. Bulk biomaterials
2. Biocoatings and films
3. Nanomaterials
4. Biocomposities

All groups of biomaterials are intensively developed

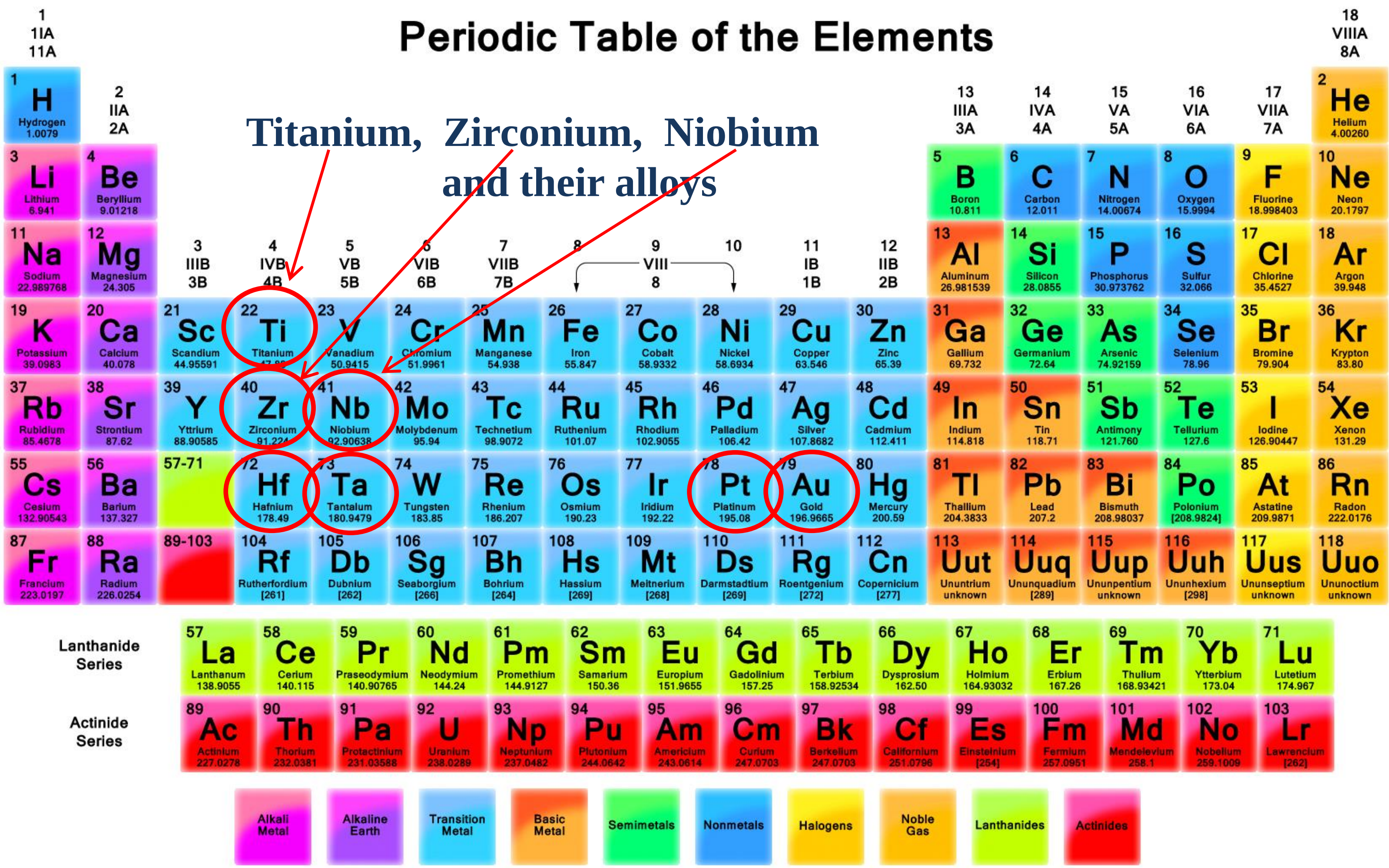
Any Part of Human Bone System Can Be Replaced with Bioinert Metal Implant!



Medical implants consisted of bioinert metals (titanium, zirconium, niobium) and their alloys and biocompatible coatings based on calcium phosphates are widely used in medical applications.

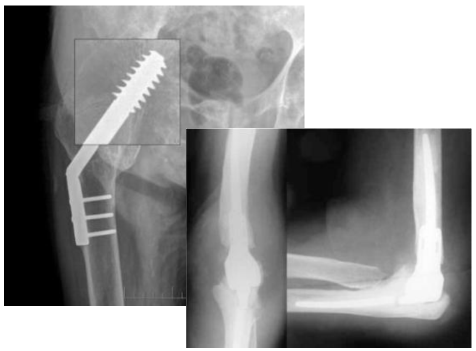
Bioinert metals

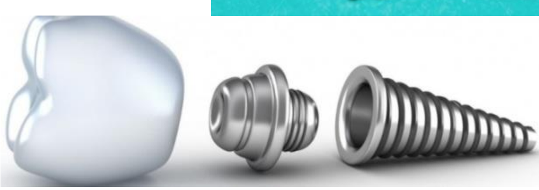
Titanium, Zirconium, Niobium and their alloys



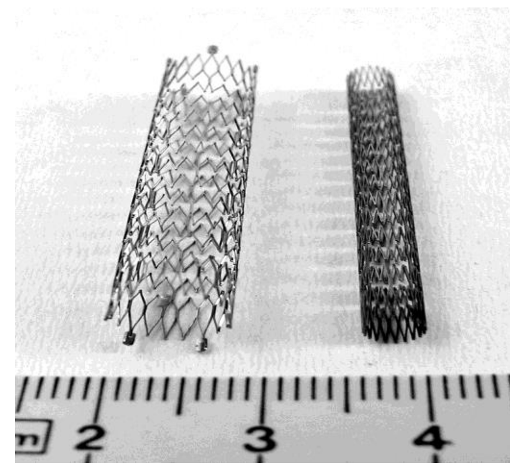
Metals and Alloys for substrates

Ti and Ti-Nb alloys
VT1-0
Ti-(40-45) Nb



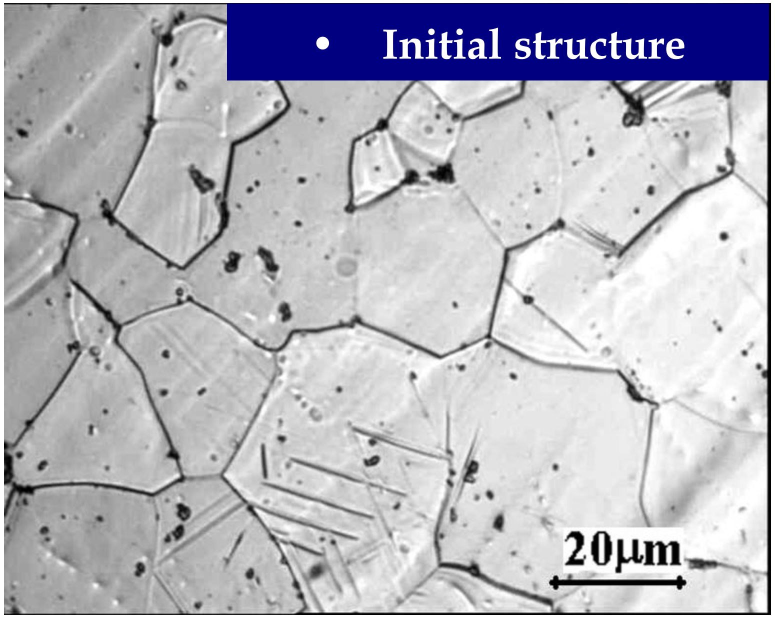


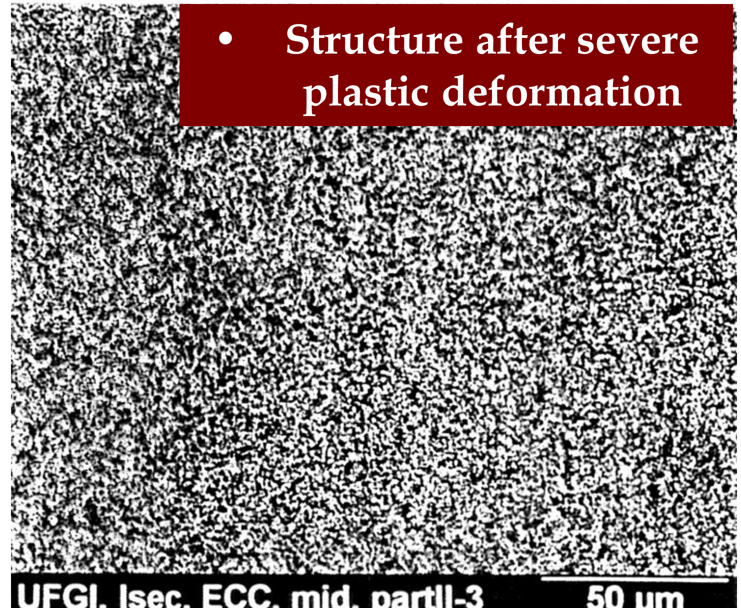
Mg alloys
Mg-0.8 Ca

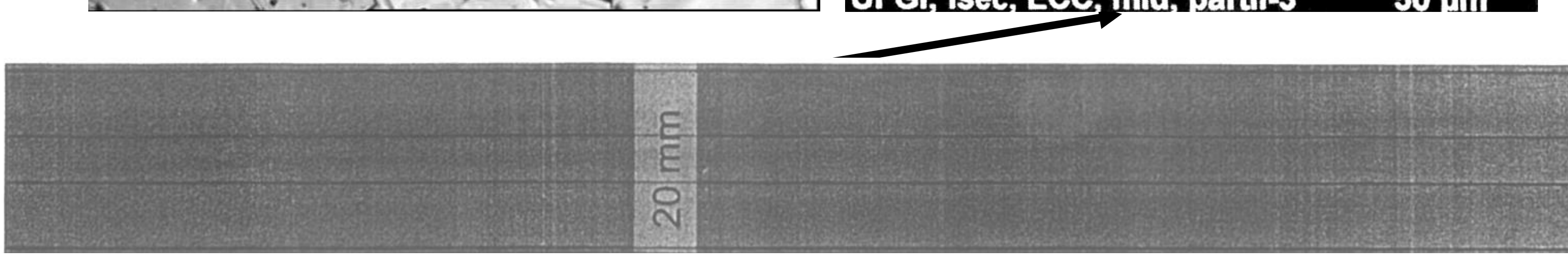


Zr-Nb alloy
Zr-1 Nb
(E110)

Ultrafine grained / nanostructured state in bulk of metal







The first paper reported about nanostructure formed in the bulk of metal (copper) with severe plastic deformation method

Ufa, Russia, 1991-1993

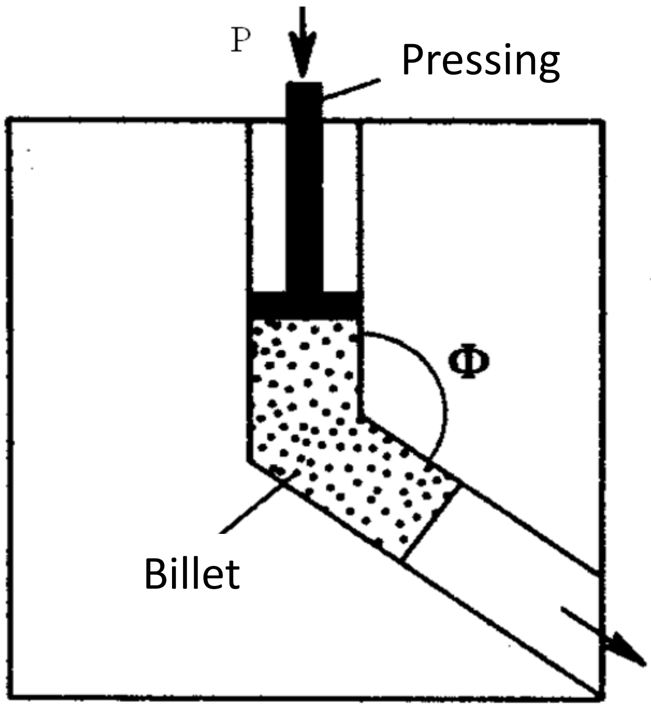
R.Z. Valiev, N.K. Tsenev, N.A. Krasilnikov, Mater. Sci. Eng., 1991

R.Z. Valiev, A.V. Korznikov, R.R. Mulyukov, Mater. Sci. Eng., 1993

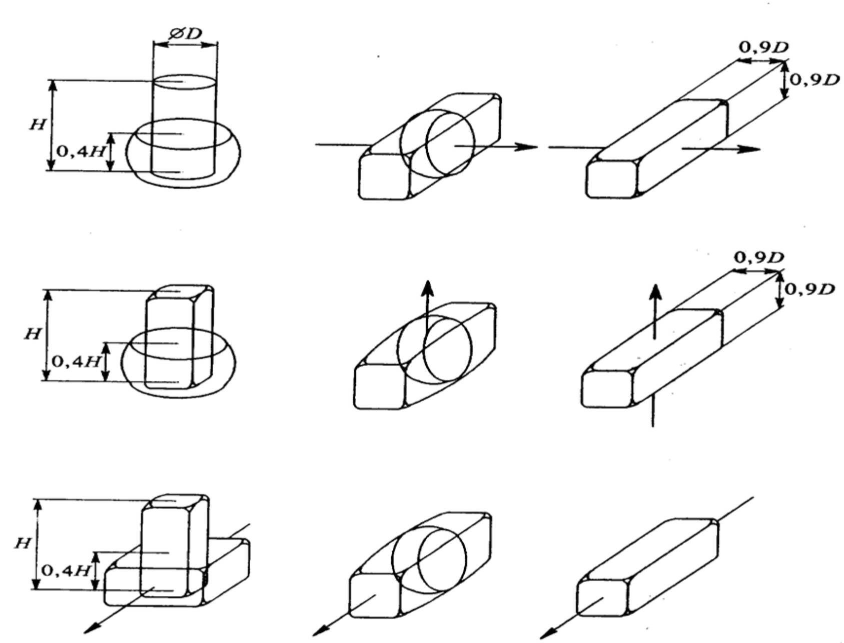
SEVERE PLASTIC DEFORMATION METHODS

Severe plastic deformation is plastic deformation of metals in conditions of high level of mechanical stresses. In this case the catastrophic decreasing of grain size takes place in the bulk of metals and alloys.

There are a set of severe plastic deformation methods.

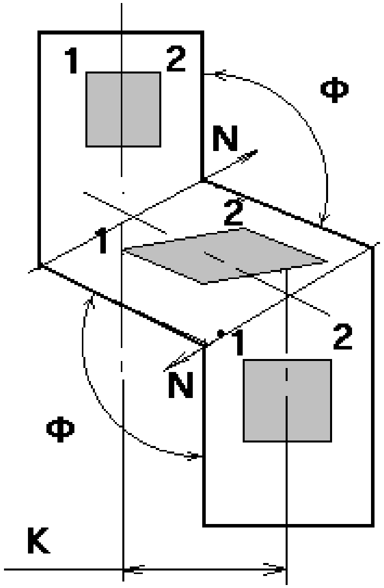


Equal channel angle pressing (ECAP)

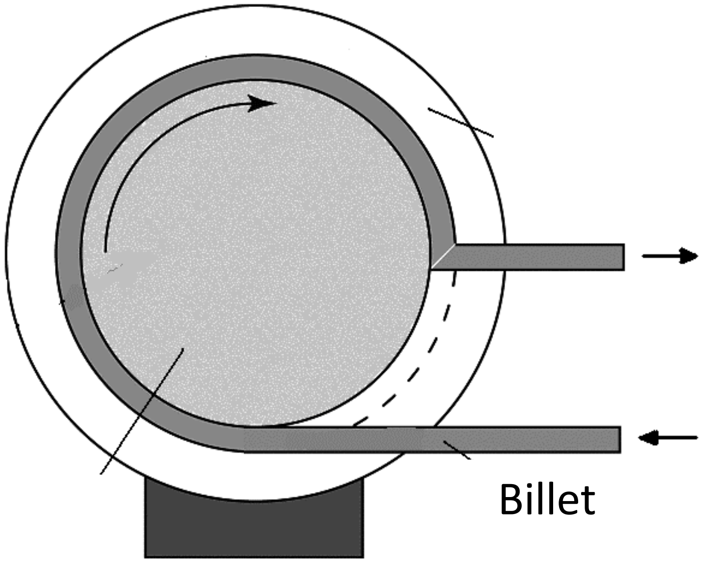


ABC - pressing

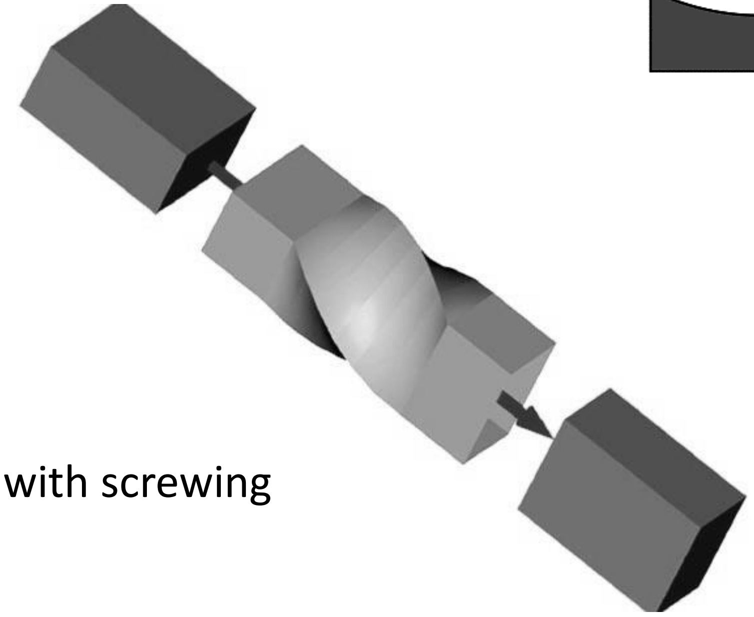
SEVERE PLASTIC DEFORMATION METHODS



Double ECAP



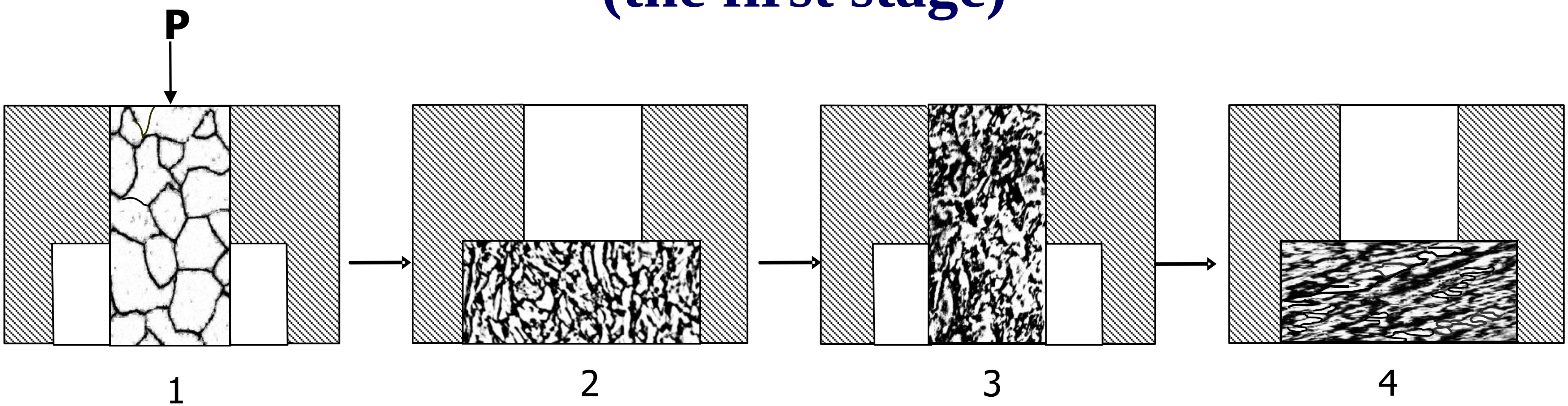
ECAP - conform



Extrusion with screwing

The SPD combined two stages method consisted of multistep abc-pressing in a press-mold and multipass rolling with subsequent annealing was suggested in ISPMS of SB RAS

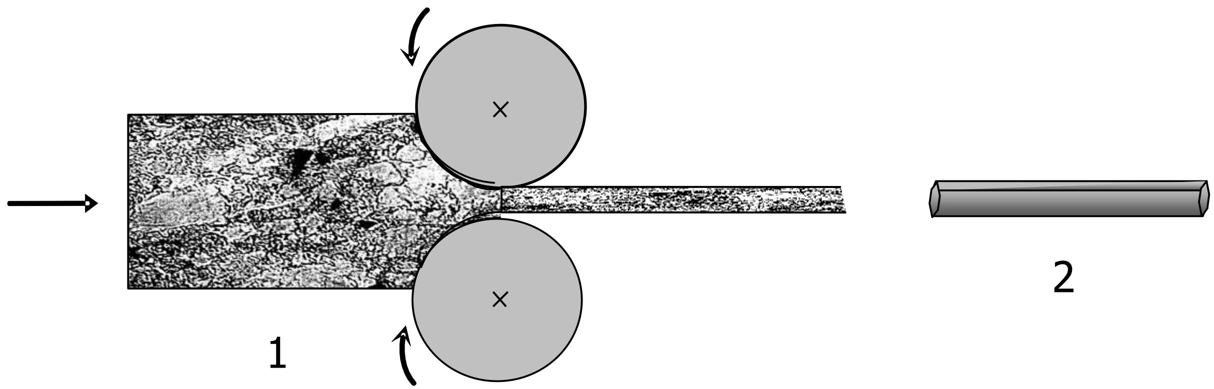
Production of submicrocrystalline titanium (the first stage)



1 – initial billet in press-mold, P – direction of pressing 2 – billet after the first step of pressing, 3, 4 – iteration of the next steps of pressing with the change in deformation axis

At the first stage the titanium billets were subjected to the multistep uniaxial pressing with the change in deformation axis. The first stage included successive, step-by-step decrease of temperature from 700°C to 400°C. Each cycle at predetermined temperature included triple or fourfold pressing in a press-mold with the change in deformation axis. A press-mold allowing to preserve the initial shape of the billet for the next stage of pressing was used for the intense grinding of grains in titanium.

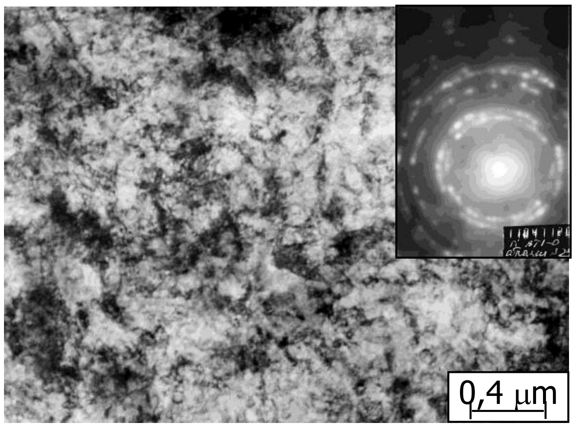
Production of ultrafine grained / nanostructured titanium (the second stage)

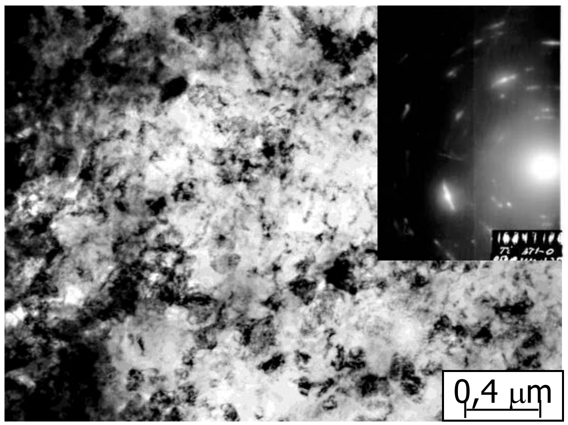


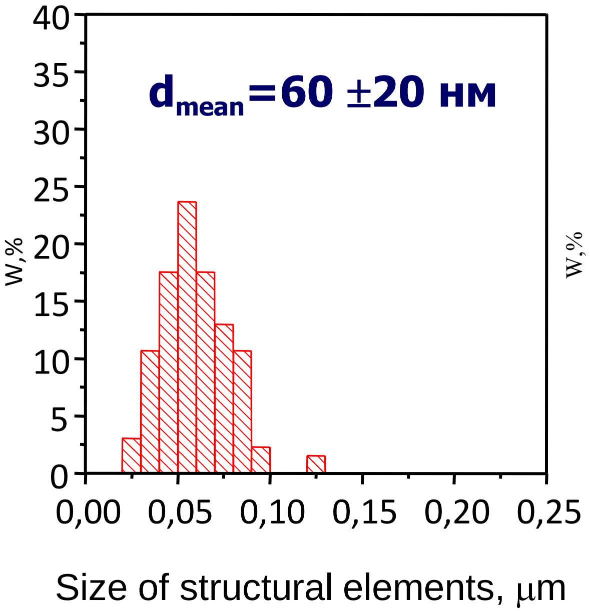
1 – process of rolling in grooved rollers, 2 – billet in the form of stick after pooling

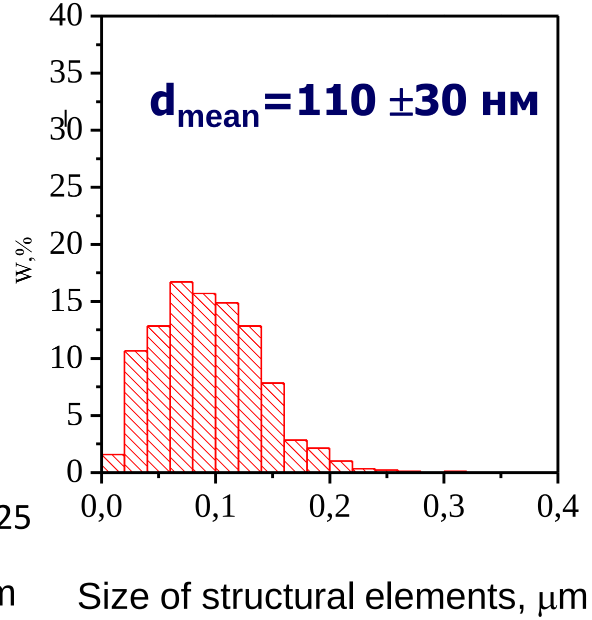
At the second stage the billets were deformed by rolling at room temperature. The value of the accumulated deformation during the rolling was 80 %. After the rolling the titanium billets were stick-shaped with the section of 6×6 mm^2 and the length of more than 500 mm. Then the sticks were annealed at the temperature of 250 and 300°C during 1 hour.

Microstructure of nanostructured titanium and histograms of the structural elements size







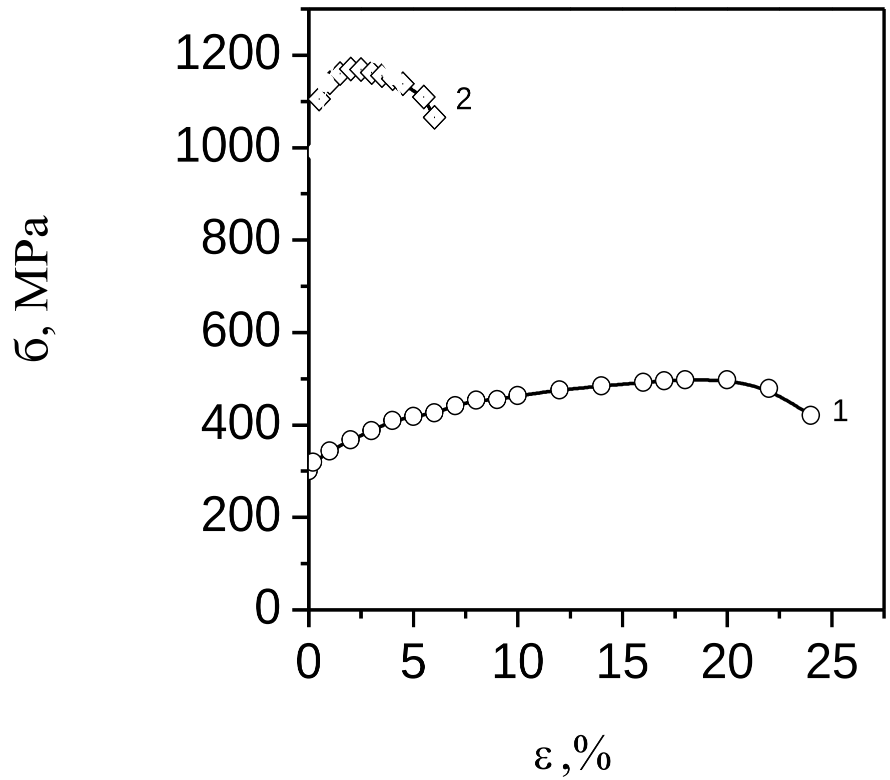


The microstructure of the samples was analyzed using transmission electron microscopy. The sizes of structural elements were measured in the TEM dark field images.

The rolling during the second stage moulds nanostructured state homogeneous by volume, with the average size of the structure elements equaling 60 nm.

The titanium billets with this micro-structure have low ductility under tension, not exceeding 1-2%. The annealing at the temperatures of 300°C increases the plasticity while preserving the type of titanium structure with the small increase in the size of the stuctural elements till 110 nm.

Mechanical behavior of nanostructured titanium at tension



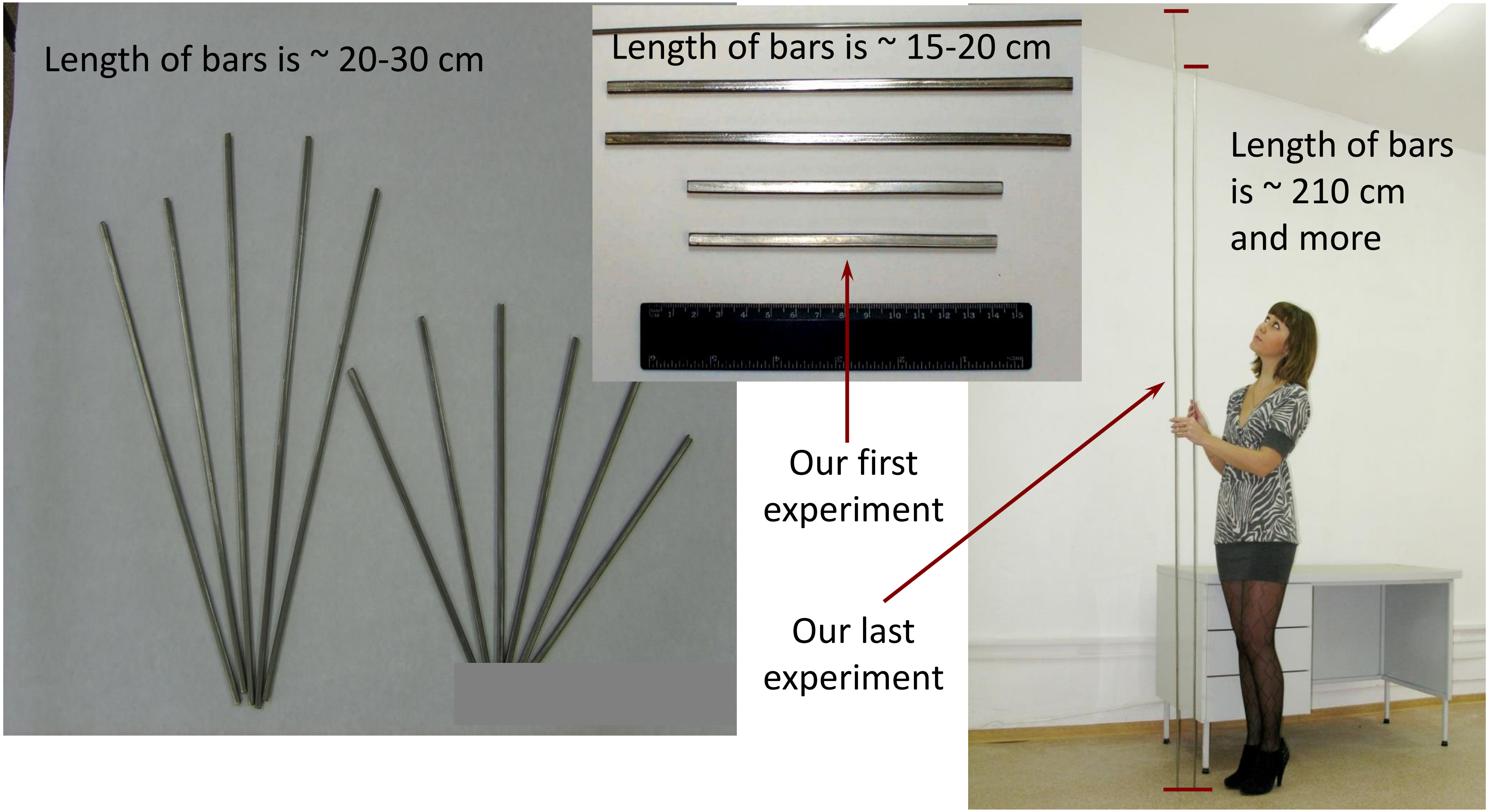
The results of uniaxial tension tests of nanostructural titanium samples are presented in the deformation diagram. The curve 1 is for the initial coarse-grained titanium (yield point is 270 MPa, ultimate strength is 400 MPa, plasticity is 25%). Formed nanostructured state (curve 2) ensures the considerable growth of the mechanical properties of titanium under satisfactory ductility (yield point is 1000-1100 MPa, ultimate strength is 1100-1200 MPa, plasticity is 6 %.

Mechanical characteristics of titanium (VT1-0) in different structural states, titanium Grade-4 and titanium alloys Ti-4Al-6V and Ti-2Al-5Mo-5V

Substrate	d_{mean}, μm	$\sigma_{0,2}$ MPa	σ_{B}, MPA	σ_{0}, MPa	δ, %	H_{μ}, MPa
Ti, coarse grained state	15	270	400	300	23	1700
Ti, ultrafine grained state	0,2	900	1000	-	6	2800
Ti, nanostructured state	0,1	1000 - 1100	1100 - 1200	580	6	3300
Ti (Grade 4)	25	≥480	≥550	-	15	2200
Alloy Ti-4Al-6V	10	1010	1100	570	>6	3500
Alloy Ti-2Al-5Mo-5V	-	1000	1050	-	>10	3400

Table presents the information on mechanical properties (yield point, ultimate strength, endurance limit under cyclic bend, plasticity up to fracture and microhardness) of titanium samples in different state, titanium alloys and Grade 4 titanium applied in medicine. It is clear that the mechanical properties of the nanostructural titanium correspond to the properties of the high-tensile titanium alloys.

Rods from Nanostructured / Ultrafine Grained Titanium



The images of nanostructured titanium billets are represented. Billets have the square or round section and length of 0.5 - 1 m and more.

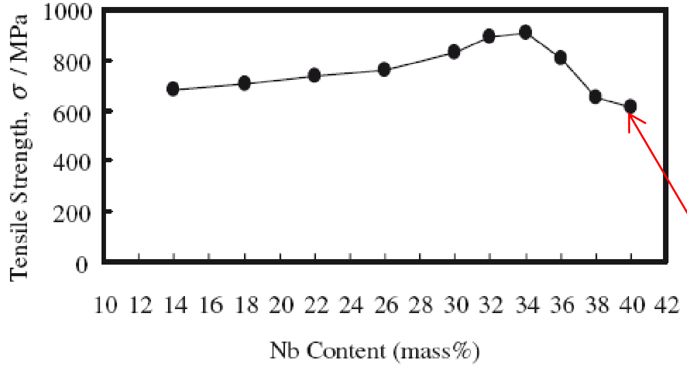
Low modulus β-type titanium alloys for biomedical applications β-type titanium alloys

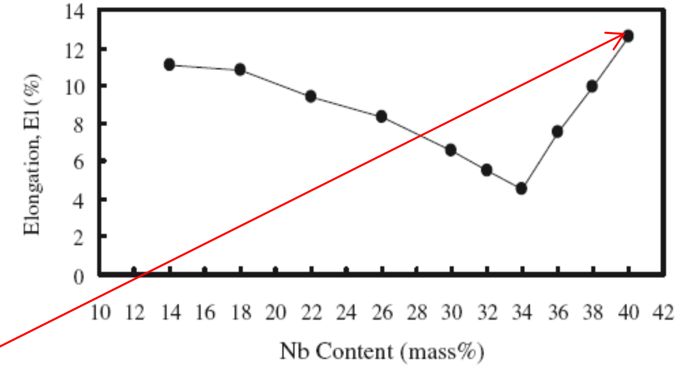
Ti–13Nb–13Zr ASTM F 1713
Ti–12Mo–6Zr–2Fe (TMZF) ASTM F 1813
Ti–12Mo–5Zr–5Sn
Ti–15Mo ASTM F 2066
Ti–16Nb–10Hf (Tiadyne 1610)
Ti–15Mo–2.8Nb–0.2Si
Ti–15Mo–5Zr–3Al
Ti–30Ta
Ti–45Nb AMS 4982
Ti–35Zr–10Nb
Ti–35Nb–7Zr–5Ta (TNZT)
Ti–29Nb–13Ta–4.6Zr (TNTZ)
Ti–35Nb–4Sn
Ti–50Ta

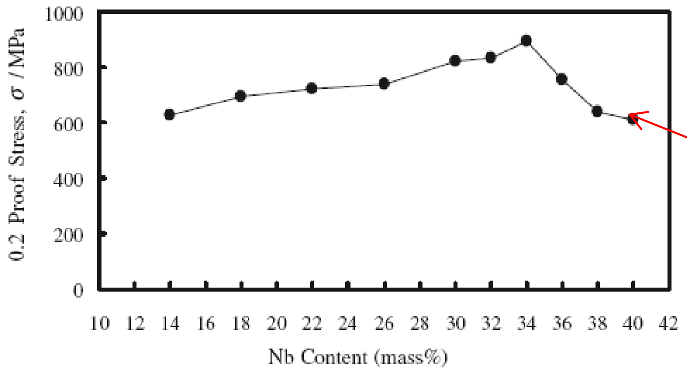
Ti–8Fe–8Ta
Ti–8Fe–8Ta–4Zr
Ti–35Nb–2Ta–3Zr
Ti–22.5Nb–0.7Zr–2Ta
Ti–23Nb–0.7Ta–2.0Zr–1.2O
Ti–28Nb–13Zr–0.5Fe (TNZF)
Ti–24Nb–4Zr–7.9Sn (Ti2448)
Ti–7.5Mo
Ti–12Mo–3Nb
Ti–12Mo–5Ta
Ti–12Cr
Ti–30Zr–7Mo
Ti–30Zr–3Mo–3Cr
TiNi

Development of new metallic alloys for biomedical applications. Mitsuo Niinomi ⇑, Masaaki Nakai, Junko Hieda. Acta Biomaterialia. 8 (2012), 3888 - 3903

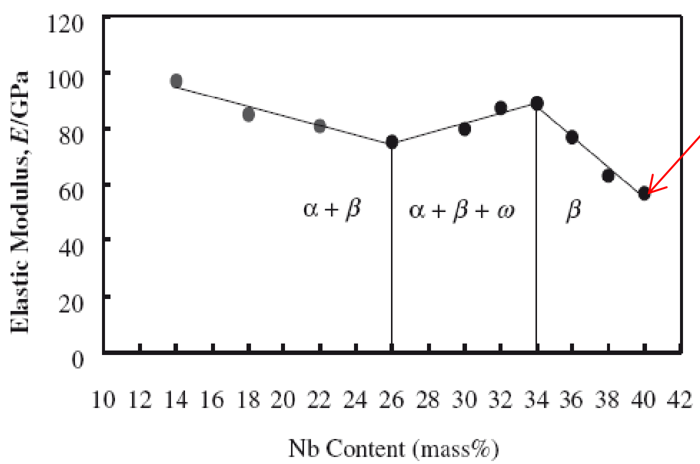
The **Ti-Nb** alloys with a relatively high Nb content are perspective alloys for medical applications







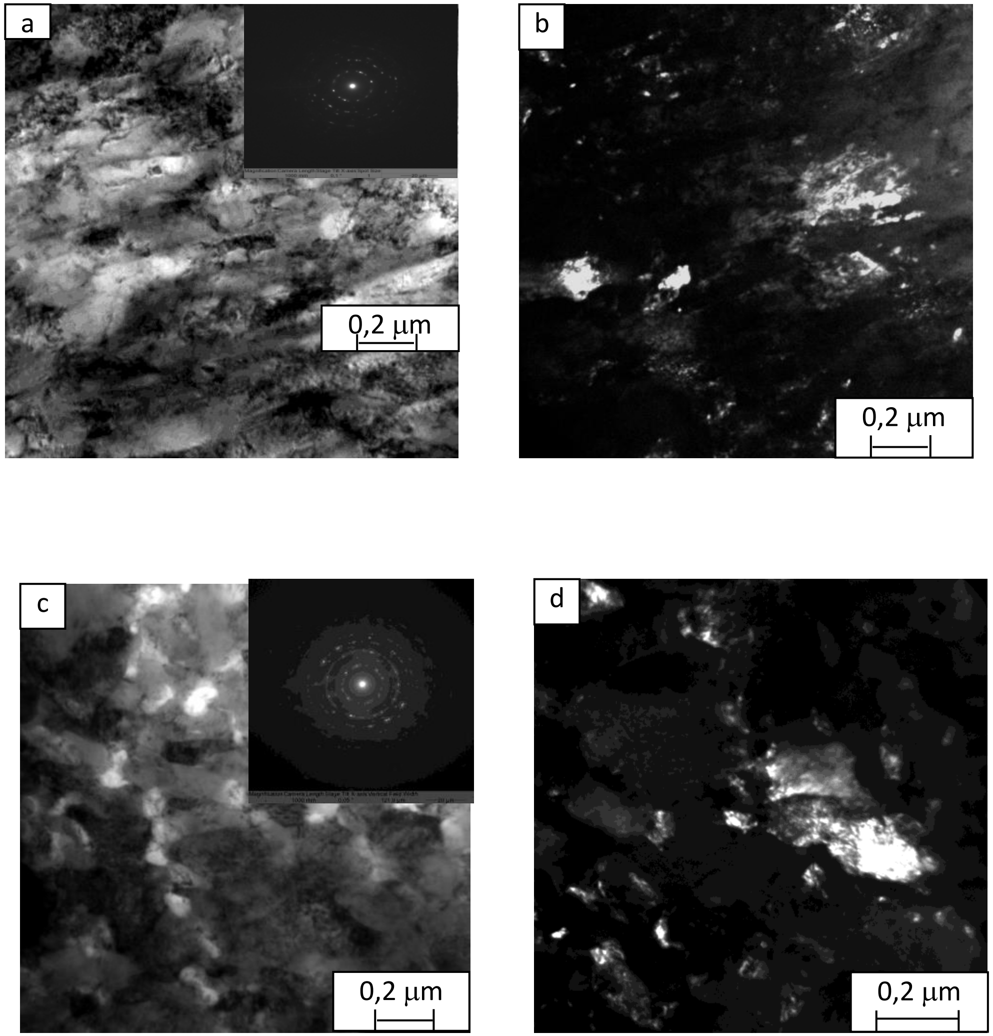
Ti-40 mass%Nb alloy

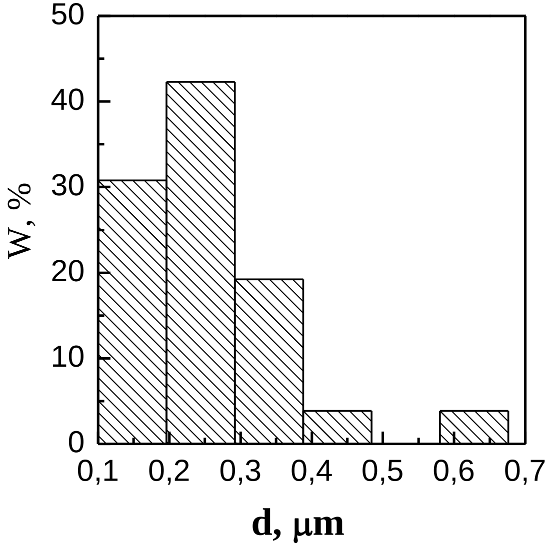


A Ti-Nb alloy with a relatively high Nb content (above 36 mass%) is preferable for use as medical implants and reducing stress shielding effect. The Ti-40 mass%Nb alloy has an elastic modulus of some 57 GPa, a reasonably high ductility (13% elongation), a moderate tensile strength (600 MPa) and essentially a ductile fracture nature.

Composition/Phase Structure and Properties of Titanium-Niobium Alloys. Yen-Huei Hon, Jian-Yih Wang, Yung-Ning Pan. Materials Transactions, Vol. 44, No. 11 (2003) pp. 2384 – 2390.

Titanium – 40 mass % niobium alloy





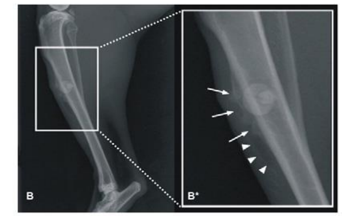
d_{mean} = 0.3 μm

H_{μ} = 2800 MPa

Mg alloys

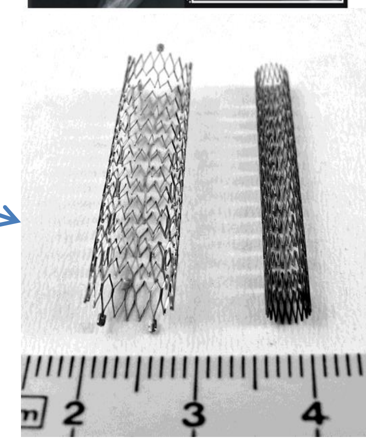
Feature of the magnesium alloys

- ✓ good biological compatibility
- ✓ good biomecanical properties - modulus of elasticity for magnesium alloys equal to about 45 GP
- ✓ ability to the bioresorption



Application

- ✓Traumatology and orthopedics (plates, screws, ties)
- ✓ Cardiology (stents)



Problem

- ✓High speed of the bioresorption,
- ✓H_2 emphasizing

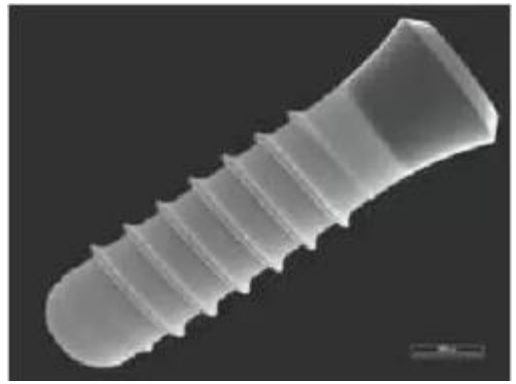
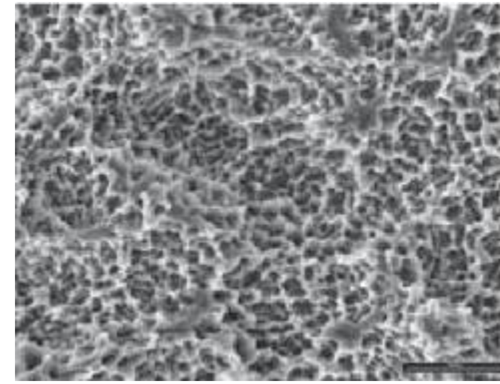
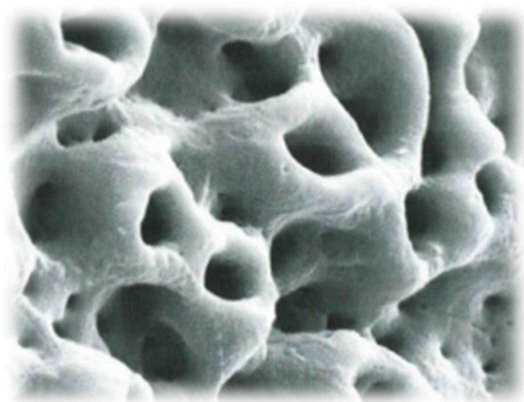
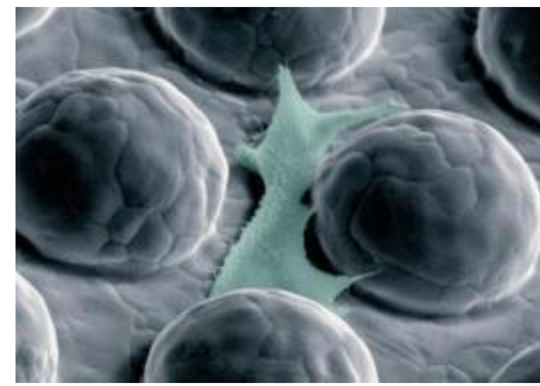
The way of solution

- ✓Formation of the calcium phosphate coatings with a controlled rate of bioresorption on the magnesium alloys surface

Calcium phosphate coatings have a high biocompatibility and allow regulating the process of bioresection of implants from magnesium alloys

Requirements for medical implants

- ✓ The presence of porous (rough) surface
- ✓ Low contact angle and good wettability
- ✓ High adhesion strength of the coating to the implant surface is not less than 15 MPa (ISO 13779-4)
- ✓ The absence of toxicity (toxic contaminants and materials)
- ✓ The biocompatibility of the implant material with the bone tissue


Hydroxyapatite

$Ca_{10}(PO_4)_6(OH)_2$

↓

$M_{10}(RO_4)_6X_2$

M: Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Cu^{2+}, Zn^{2+}, La^{3+}…;

RO_4: PO_4^{3-}, CO_3^{2-}, SO_4^{2-}, VO_4^{3-}, SiO_4^{4-}…;

X: $(OH)^-$, F^-, O^{2-}, Cl^-, CO_3^{2-} …

Monika Šupová, Substituted hydroxyapatites for biomedical applications: A review, Ceramics International 41(2015) 9203–9231

Advantages of Ca-P coatings

1. Ca-P coating is source of Ca and P

2. Ca-P coating improves osteointegration process

3. Ca-P coating protects metallic implants from corrosion

Hydroxyapatite is main component for coating deposition

Methods of Ca-P biocoating deposition

- Sol-gel method
- Rf-magnetron sputtering

  \- processes duration is long

- Plasma spraying
- Detonation gas spraying

  \- cost of the final product is higher

  (Sol-gel, Rf-magnetron sputtering, Plasma spraying, Detonation gas spraying):
  \+ identical phase compositions of spraying material (HAP) and coating
  \- absence of chemical bonds between the formed coating and a substrate surface

- Electrophoretic deposition method
- Electrolytic deposition method

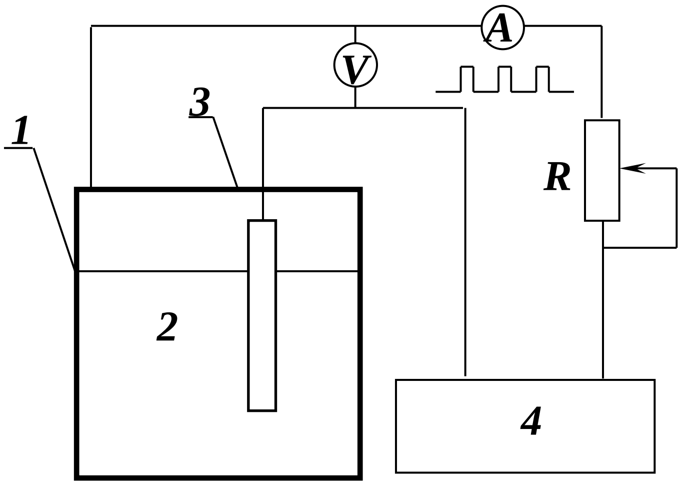
  \- low adhesion strength
  \+ simple process
  \+ lost cost

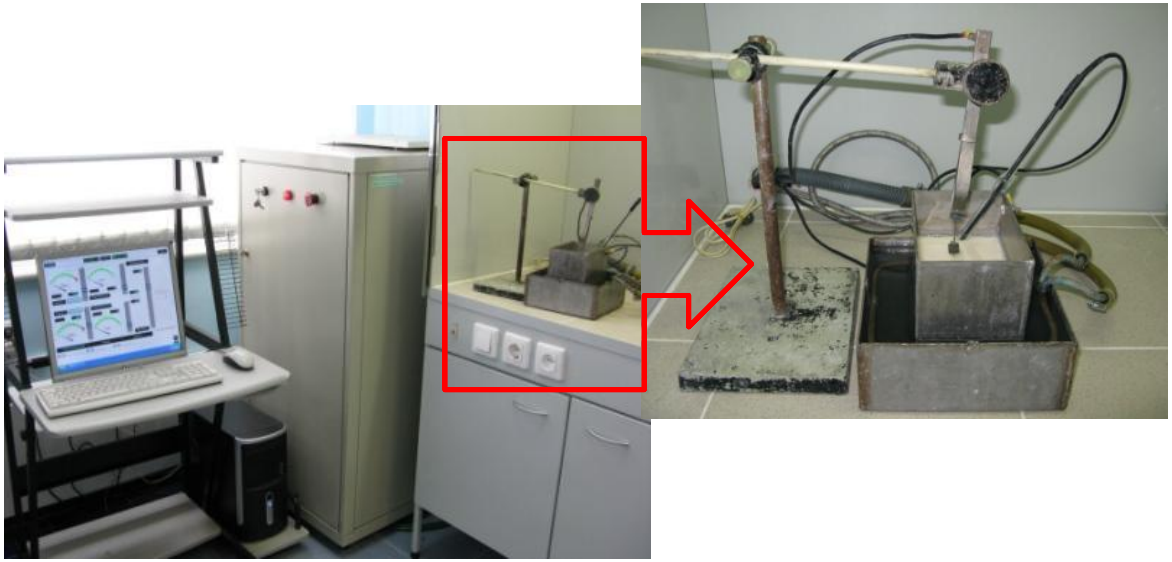
- Micro-arc oxidation

  \+ convenient and effective process to put calcium phosphate coatings on implants of complex shape with good physical and chemical properties

Micro-arc oxidation method

Configuration & schematic view of technological complex Microarc-3.0





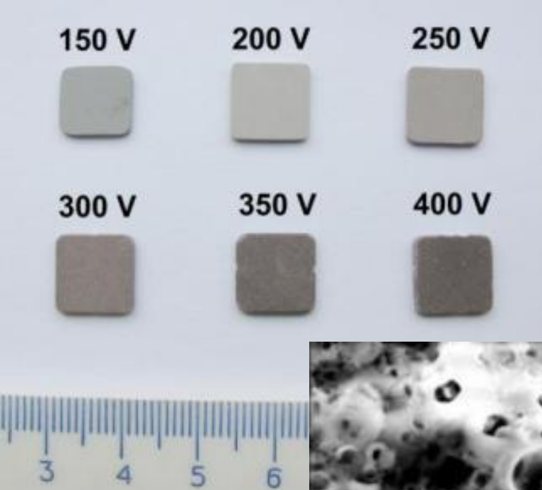
1 – galvanic bath (cathode);
2 – electrolyte;
3 – sample (anode);
4 – pulse electrical power source.

Electrolyte component	Quantity
H_3PO_4	10-30%
$Ca_{10}(PO_4)_6(OH)_2$	60-180 g/l
$CaCO_3$	90 -180 g/l
H_2O	1,5 l

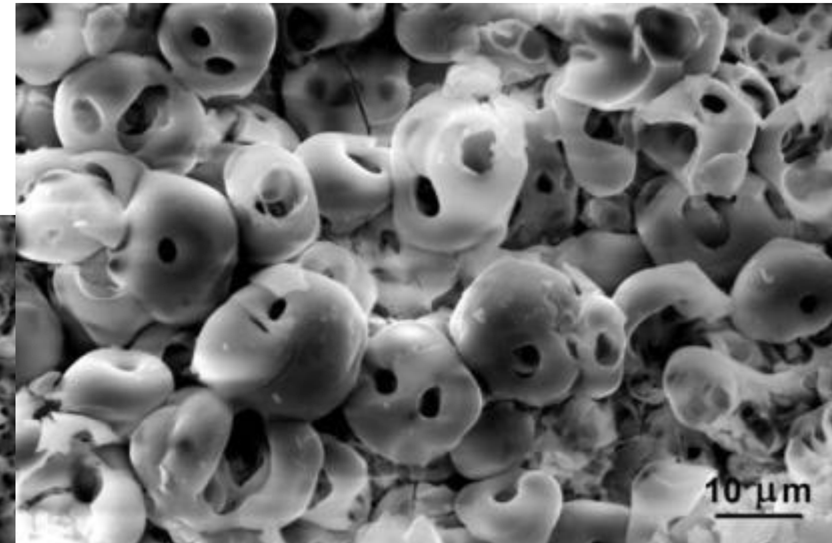
The technological complex operates in :

- Anode & anode-cathode regimes;
- pulse period is 50-500 μs;
- pulse frequency is 10-100 Hz;
- voltage is 100-500 V;
- current density is 0.1-2.0 A/mm^2;

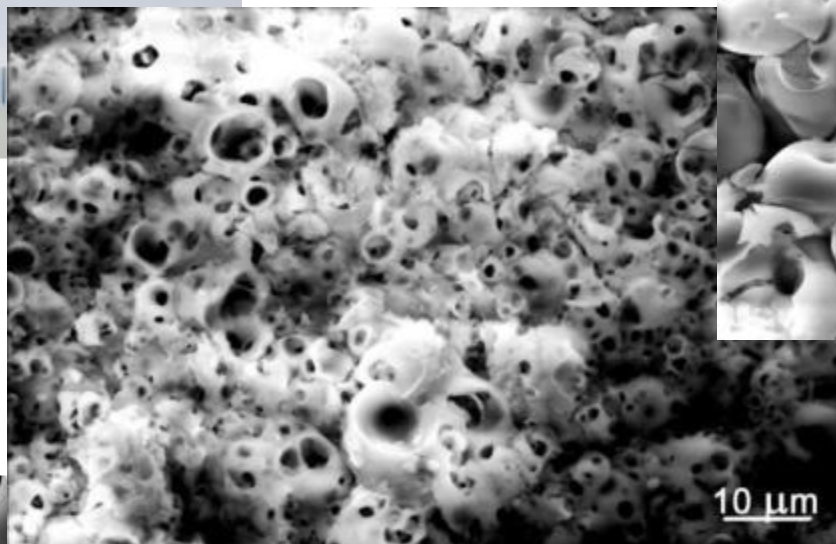
Microarc oxidation coatings



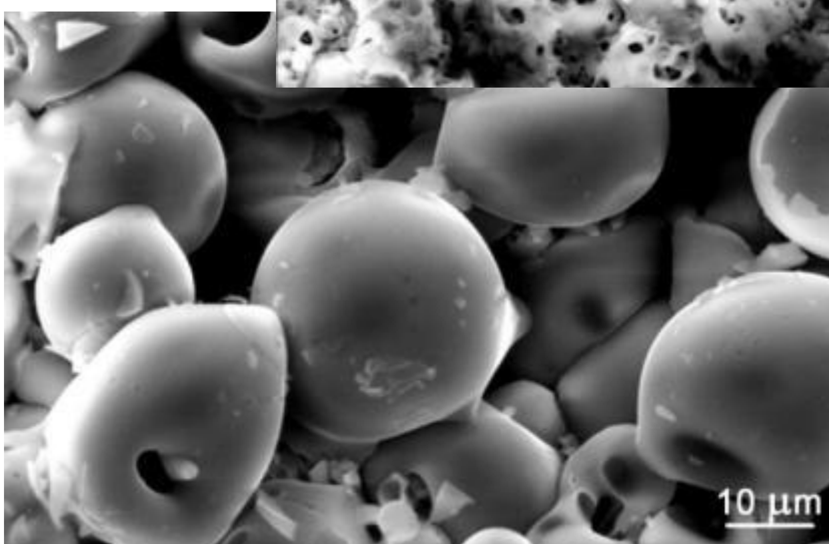
200 V



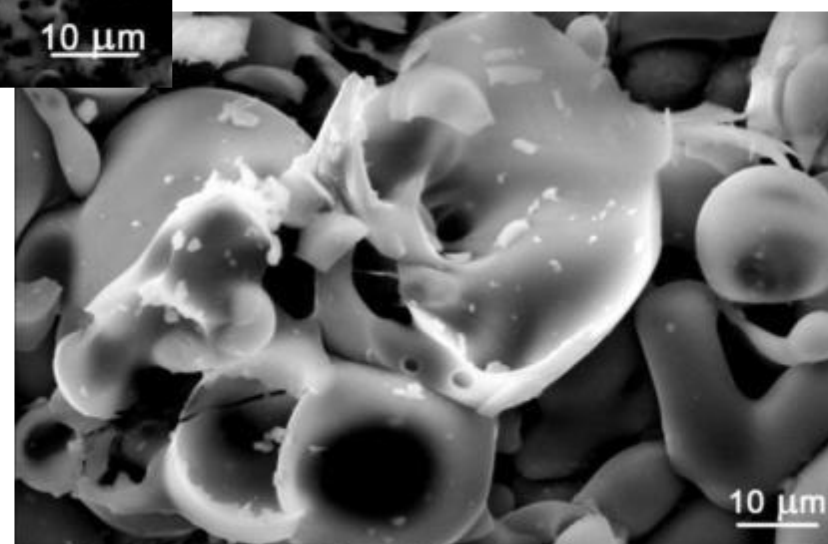
150 V



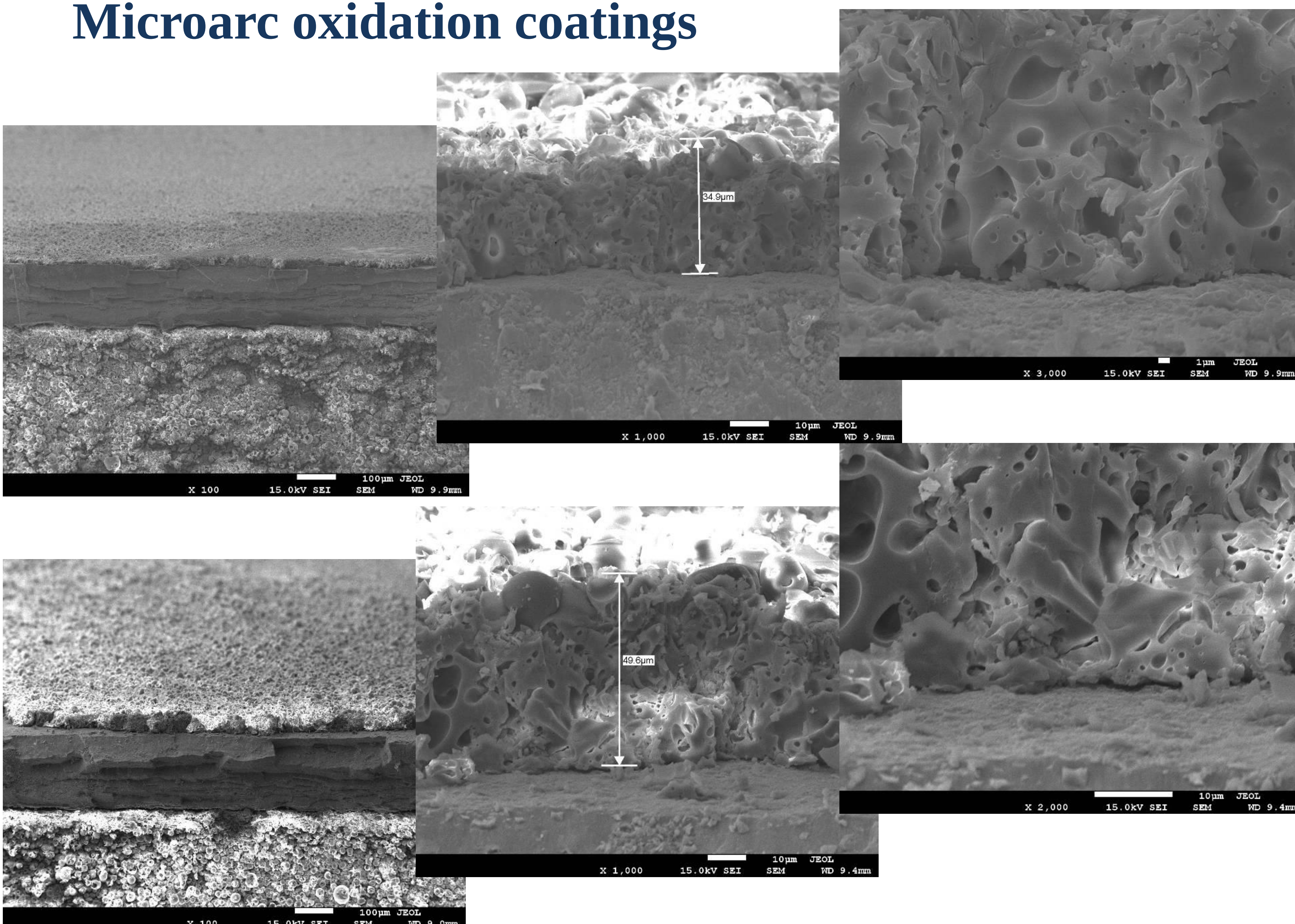
300 V



400 V



Microarc oxidation coatings

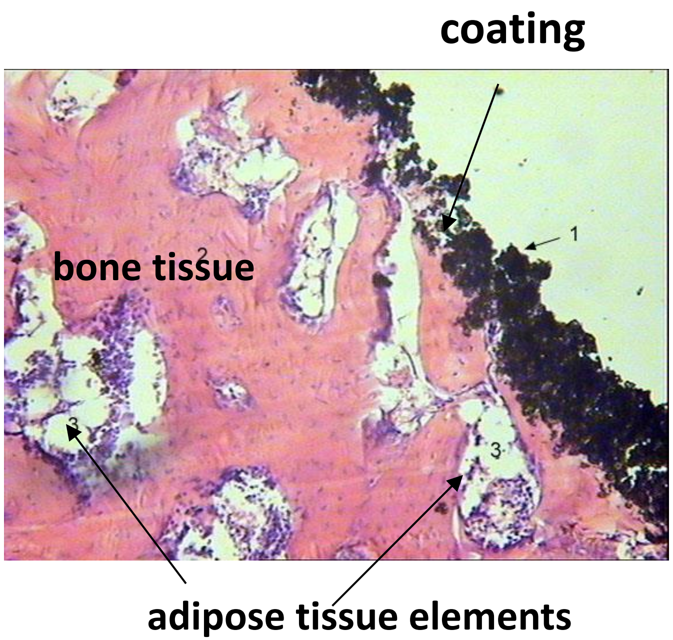


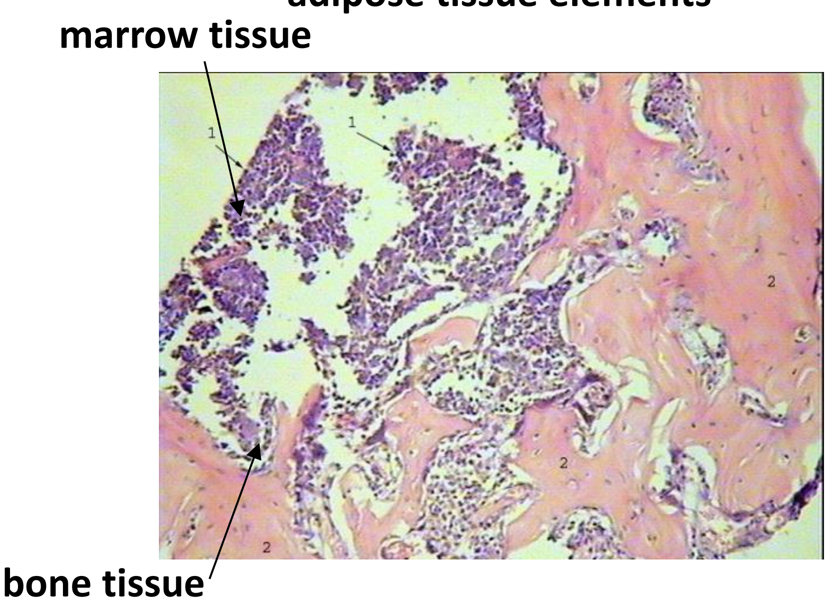
The optimal characteristics of CaP coating

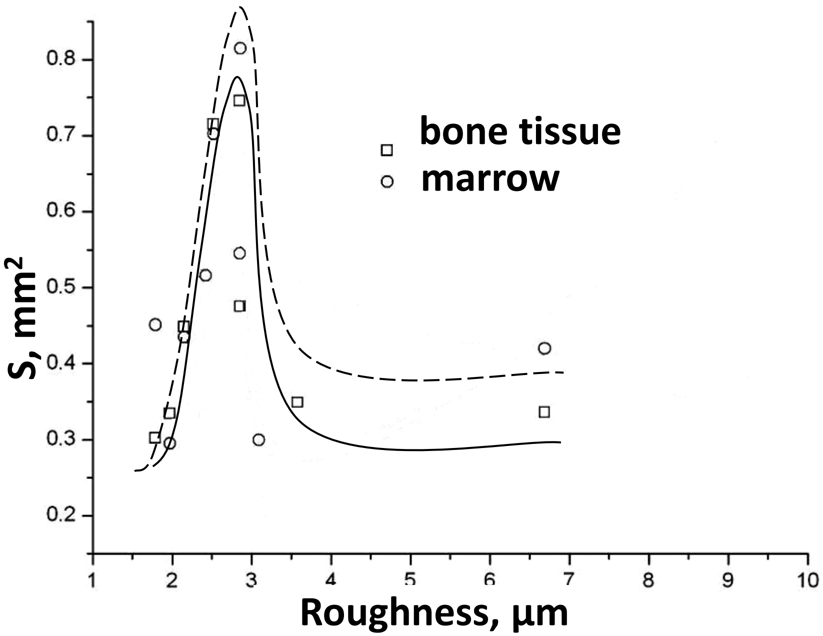
Properties	Value
Thickness, μm	40-50
Roughness, μm	2.5-3.0
Porosity, %	25-35
Adhesion strength, MPa	25-35
Ca/P ratio	0.7-1.0
Phase composition	quasiamorphous states

To produce the coatings with optimal characteristics the electro-physical parameters of micro-arc oxidation were experimentally found. The optimal characteristics of CaP coatings are presented on this slide.

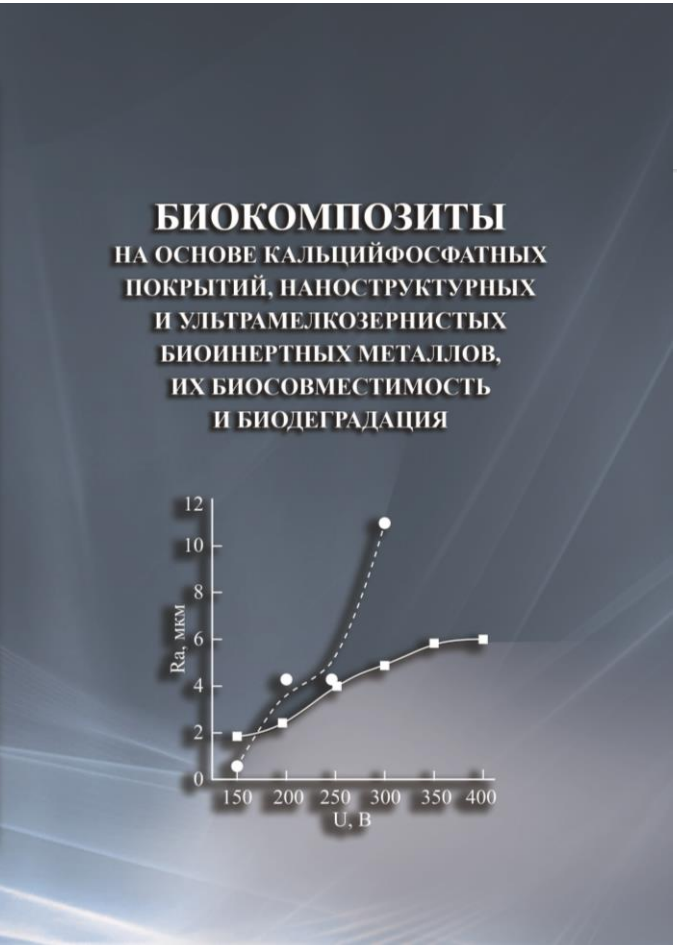
Biological test in vivo







Probability of bone tissue growth on CaP coating was 83%. In the other case marrow sites, adipose tissue and connective tissue were revealed. Thus biological tests have proved that formation of CaP coating on implant surface gives it bioactive and osteogenic properties.



ISPMS SB RAS, IC FEB RAS, SSMU, NSI PM, IIC SB RAS,
JSC SCC, TPU, AltSTU, CRID and Maxillofacial Surgery,
FSBI SibFSCC FMBA of Russia,
SEC «BMB» at TPU, SSMU and ISPMS SB RAS

BIOCOMPOSITES ON BASE OF CALCIUM-PHOSPHATE COATINGS, NANOSTRUCTURAL AND ULTRA-FINED GRAINED BIOINERT METALS, THEIR BIOCOMPATIBILITY AND BIODEGRADATION

Editor-in-chief
Nikolai Lyakhov, Academician of RAS

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2014

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B63

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B63 **Biocomposites on base of calcium-phosphate coatings, nanostructural and ultra-fined grained bioinert metals, their biocompatibility and biodegradation** / editor-in-chief academician of RAS Nikolai Lyakhov. – Tomsk : Publishing House of Tomsk State University, 2014. – 596 p.

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The results of experimental and theoretical research and development of biocomposites based on calcium-phosphate coatings, nanostructured and ultrafine-grained bioinert alloys – commercially pure VT1-0 titanium and niobium alloyed with zirconium, are presented. The regularities of the formation of calcium-phosphate coatings by the methods of micro-arc and plasma electrolytic oxidation, and detonation-gas spraying are studied. Electrochemical, tribological and biological degradation of biocomposites is analyzed.

The monograph is dedicated to experts in bioengineering, biocompatible materials and coatings fields, including scientists, post-graduates, under-graduates and students dealing with the obtaining of biocoatings on bioinert metal and alloy surfaces, analyzing their properties, structure and practical use.

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Biocomposites on a Base of Calcium-Phosphate Coatings, Nanostructural and Ultra-fined Grained Bioinert Metals, their Biocompatibility and Biodegradation

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Editor-in-chief
Academician of RAS Lyakhov Nikolai

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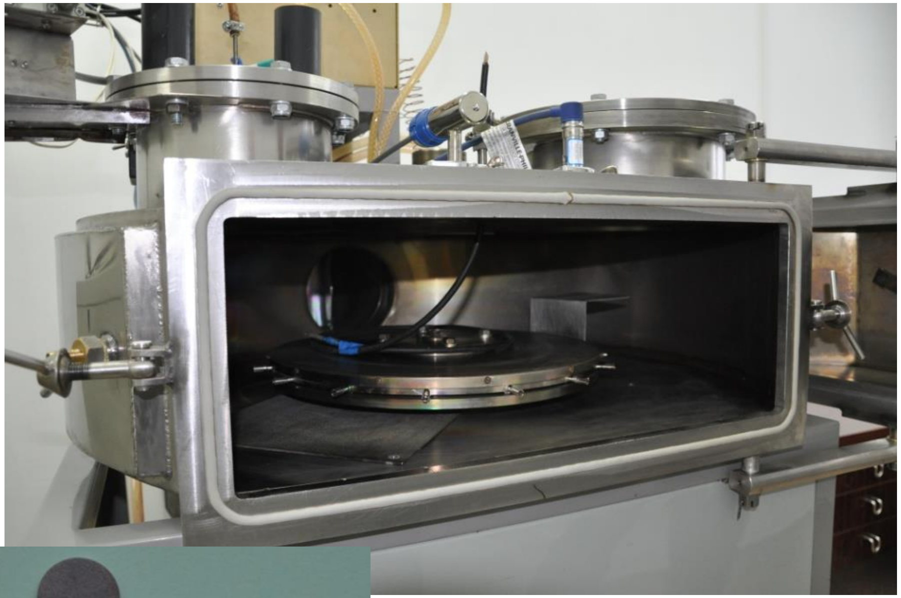
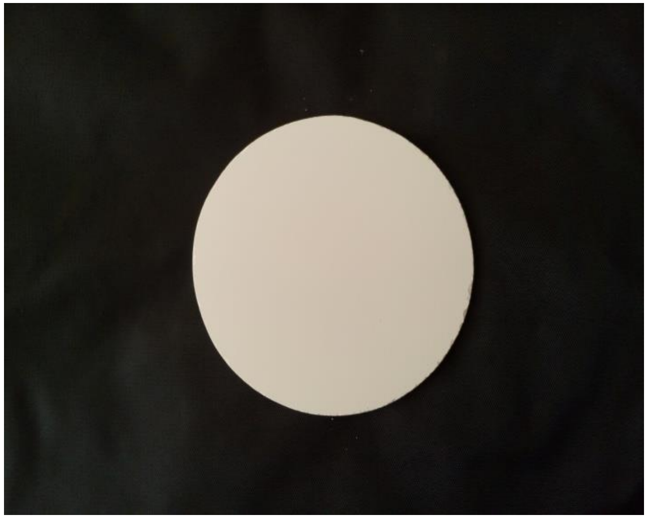
Volume is 560 pages

Rf –MAGNETRON VACUUM SETUP for FORMING CALCIUM-PHOSPHATE BIOCOATINGS

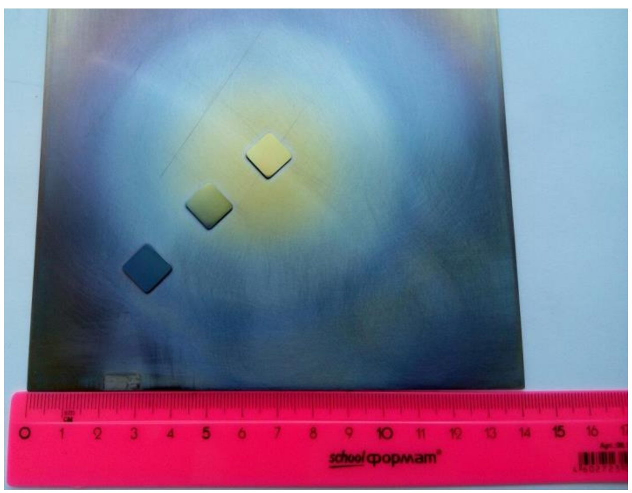


Magnetron Sputtering Process



Sintered target of HA that will be placed on the magnetron

Sputtering process

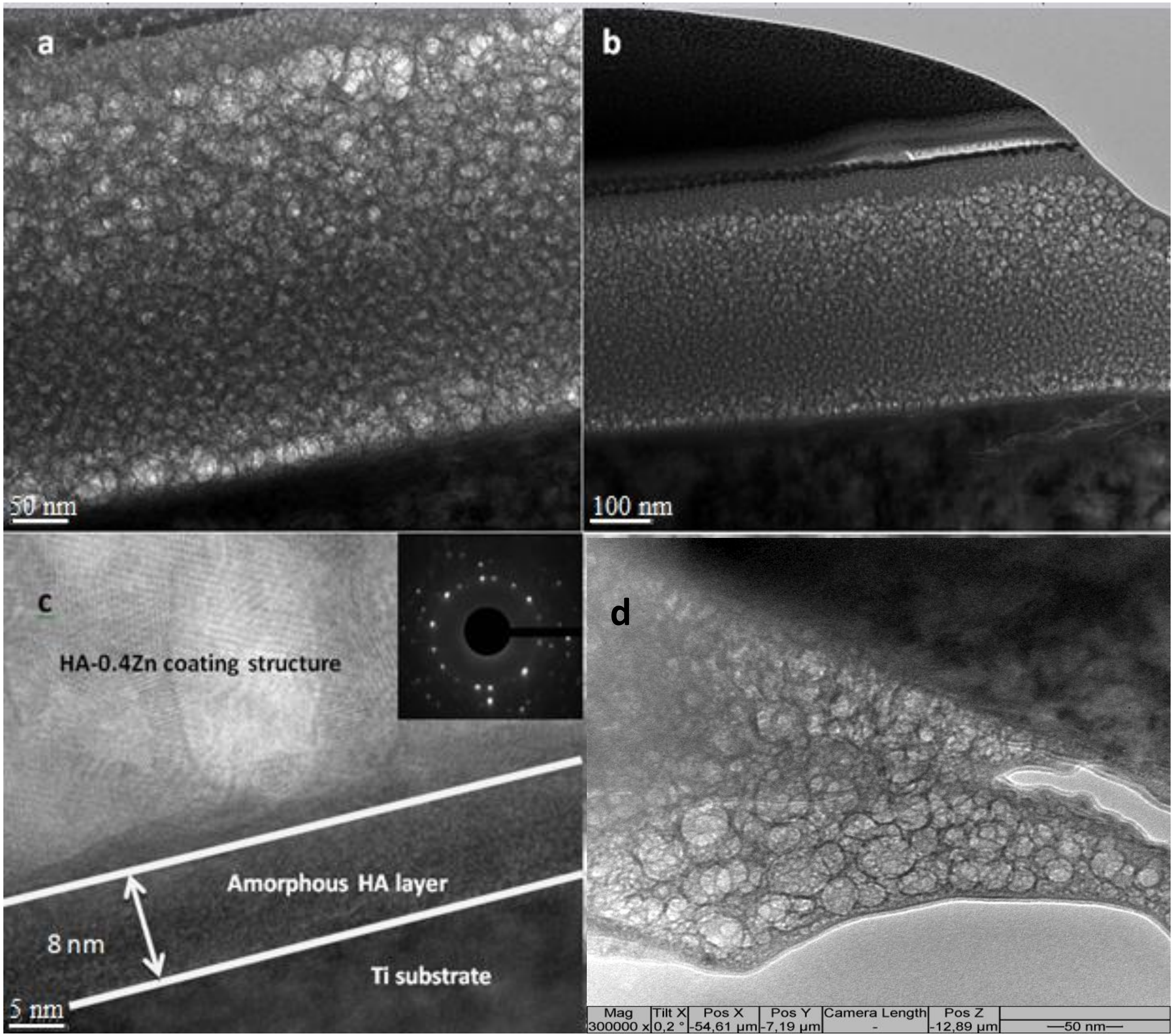


Calcium-phosphate coating

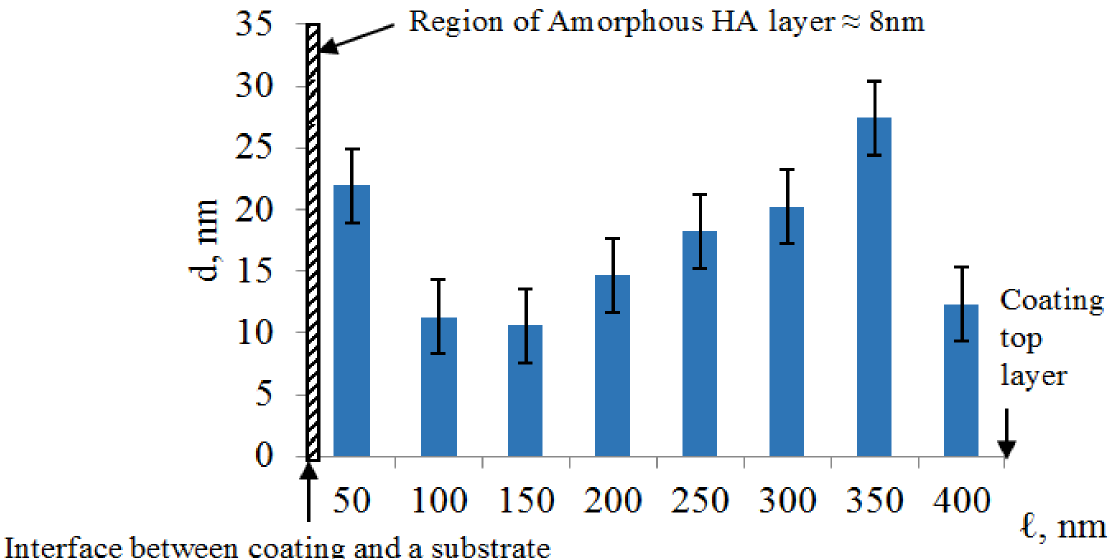
Erosion on the target surface

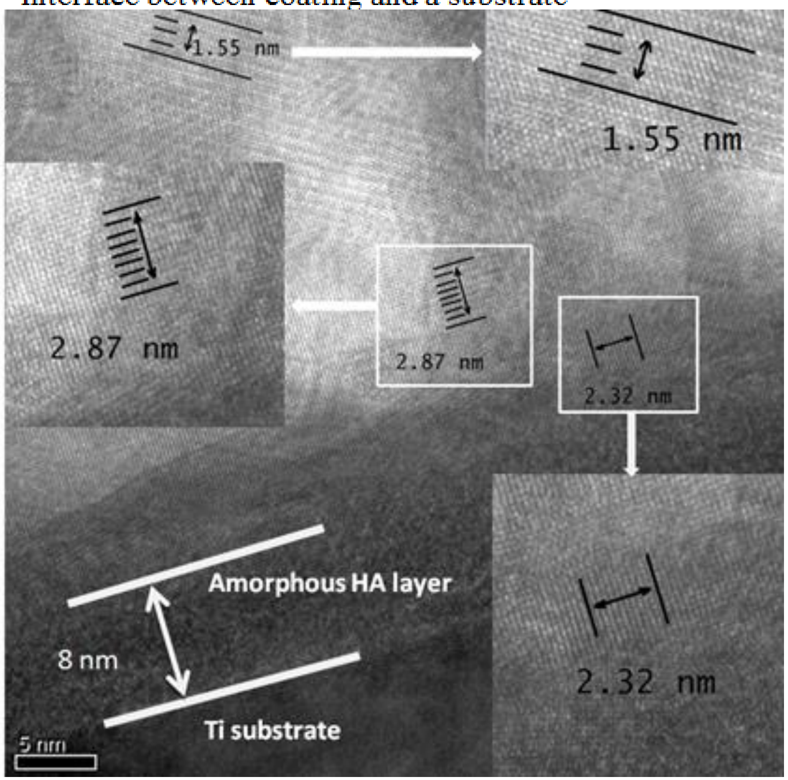
39

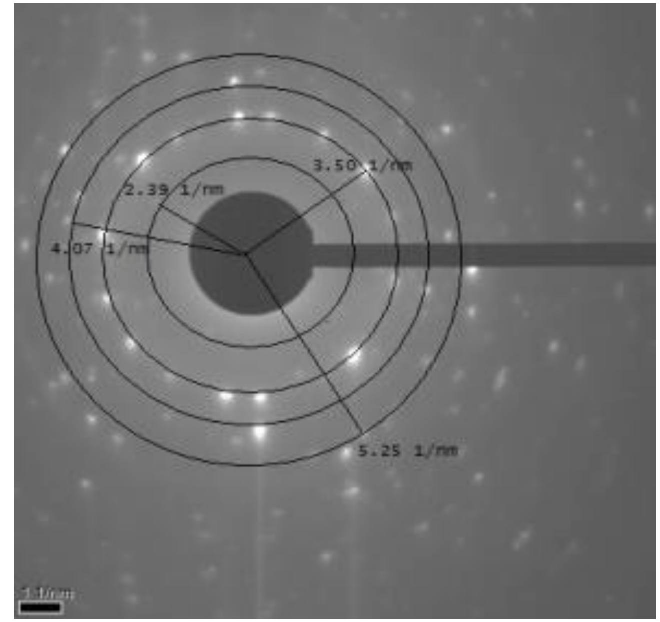
High resolution TEM images



XTEM images of HA-0.4Zn. Coating. Overview of the coating structure (a, b). Coating to substrate interface with a presence of amorphous layer(c). Image form the JEOL JEM microscope (d)







Selected area diffraction (SAD) shows the polycrystalline state of the coating. Interplanar d-spacing were calculated (2.39, 3.50, 4.07, 5.25 Å) and compared with standard numbers that are in good agreement with each other. Those interplanar spacings corresponds to the (122), (200), (201) and (101) lattice planes for hexagonal HA.*

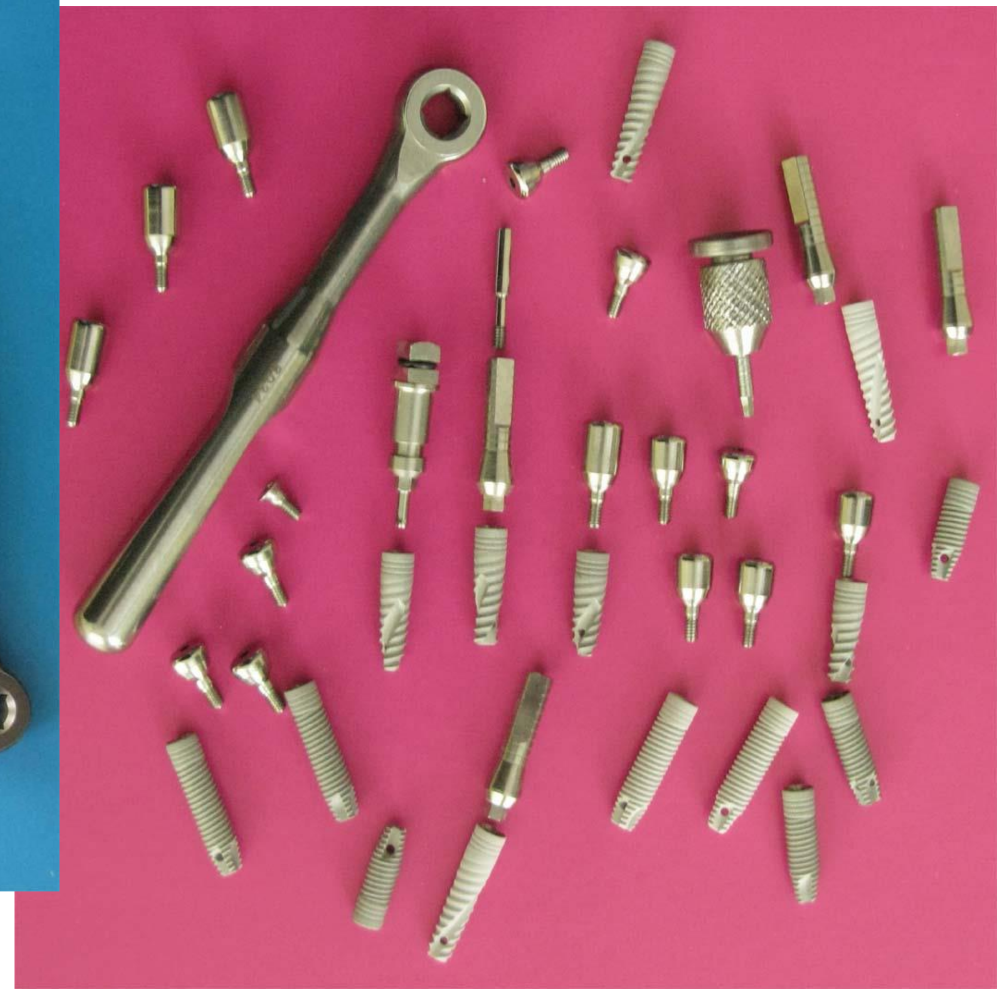
*Free database RRUFF was used as reference data RRUFF ID: R060180

Dental intraosteal screw implants from

the nanosructured titanium with microarc oxidation CaP coatings

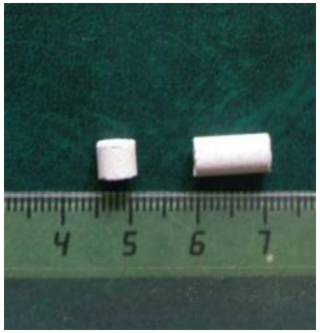
Titanium billets in nanostructared and ultrafine grained state with high mechanical properties can be successfully applied for design and production of medical implants of wide range including dental implants.
The images of dental implants from nanostructured titanium are represented.
The dental implants have been designed in ISPSM of RAS in cooperation with stomatologists from Novokuznetsk (Professor Vladimir Polenichkin).

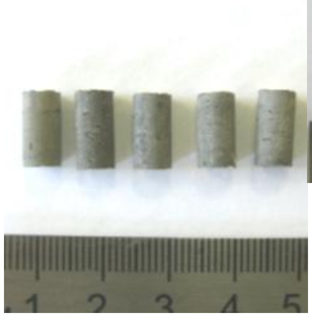
Set of dental intraosteal screw implants from nanosructured titanium with tools and accessories

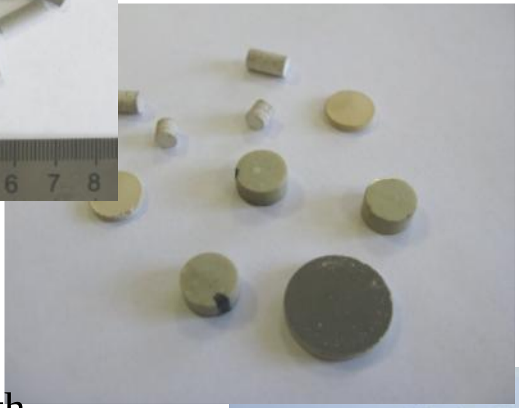


The dental implants from nanosructured titanium have been tested in clinics of Moscow, Novosibirsk, Novokuznetsk and Tomsk. The results are positive.

Ceramic Samples with RF-Magnetron CaP Coatings

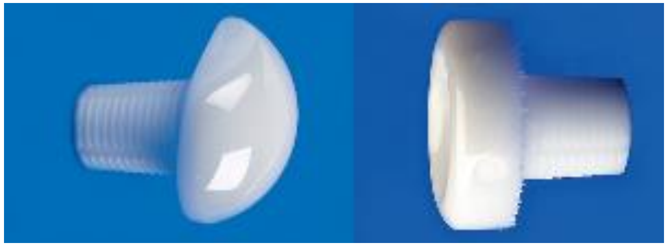






Ceramic samples without CaP coating

Ceramic samples with CaP coating

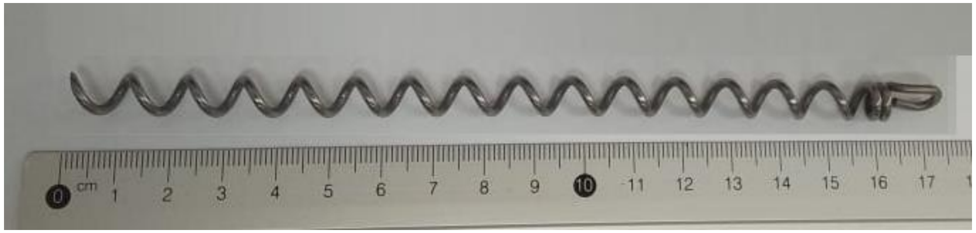


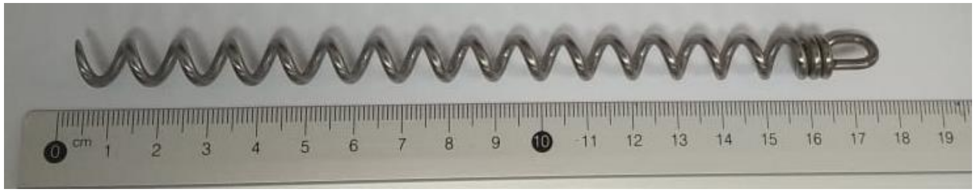
SINTEL

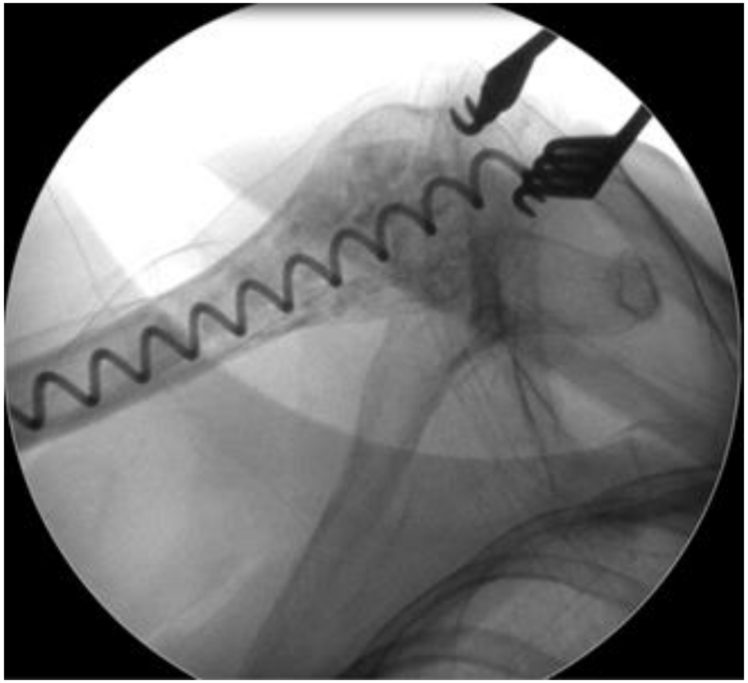
Intramedullary implants

ISPMS SB RAS

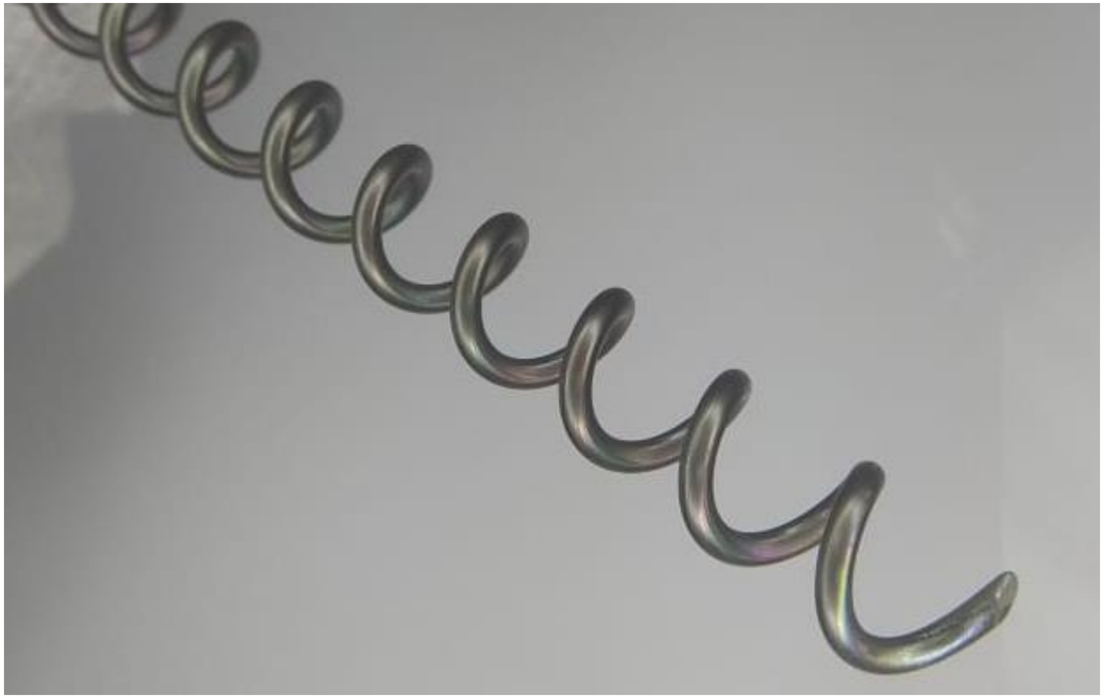
Intramedullary implants made of Ti6Al4V and Ti6Al7Nb with varied size







Visual Appearance of the Cu-HA Coating on Implants



Homogeneous coating distribution!


Struers
TegraPol-15

Thank you very much!

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