Titanium Alloys for Biomedical Applications: Past, Present and Future

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IBTN – Institute of Biomaterials, Tricoborrosion and Nanomedicine

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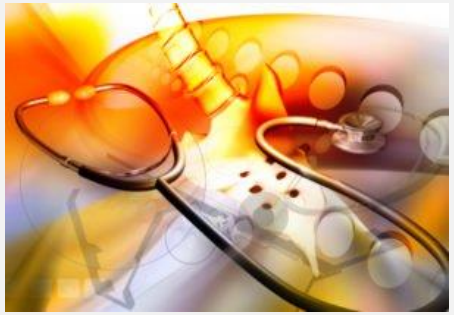
17, 18 y 19 de octubre de 2018

Outline

- New Materials for Healthcare
- Ti Alloys
- Future …
- Summary
- Where are we?



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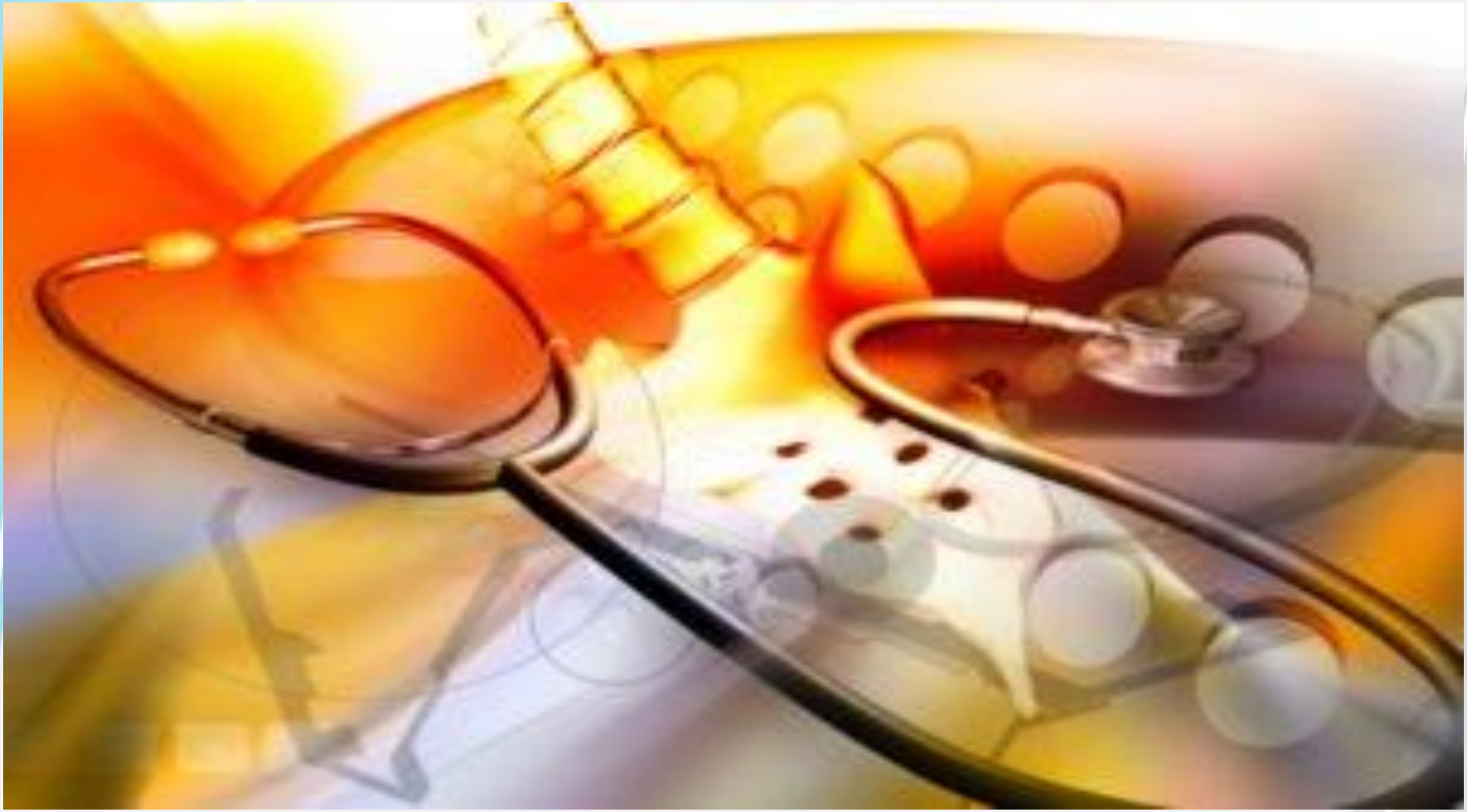

New Materials for Healthcare

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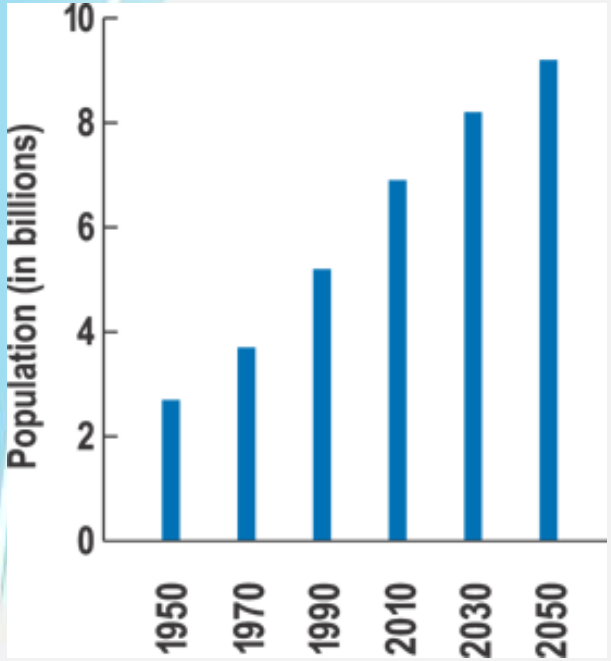
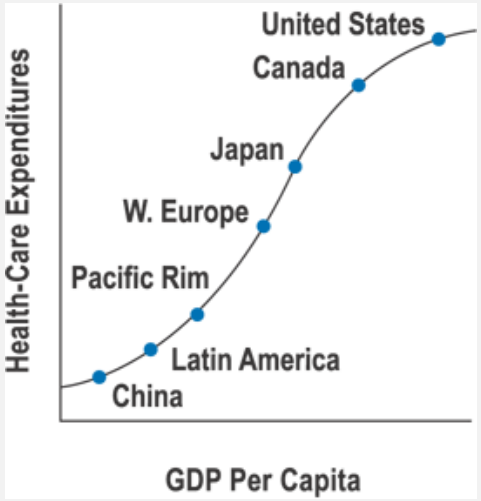
General trends in the use of materials in medicine

World Population 1950-2050



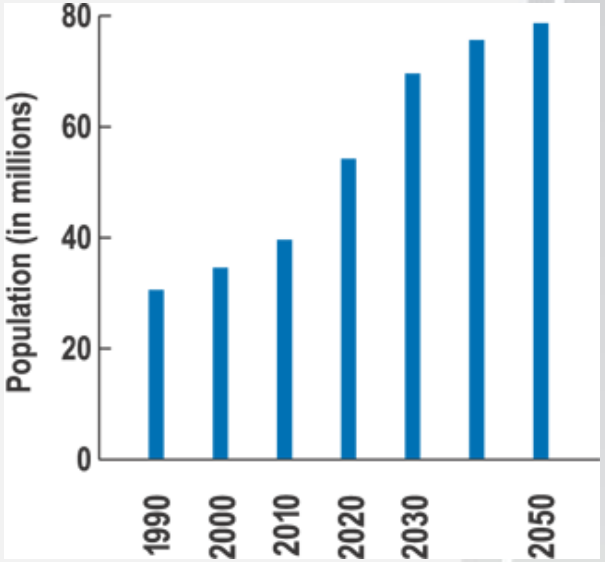
Source: United Nations world population estimates

Health expenses *per capita*

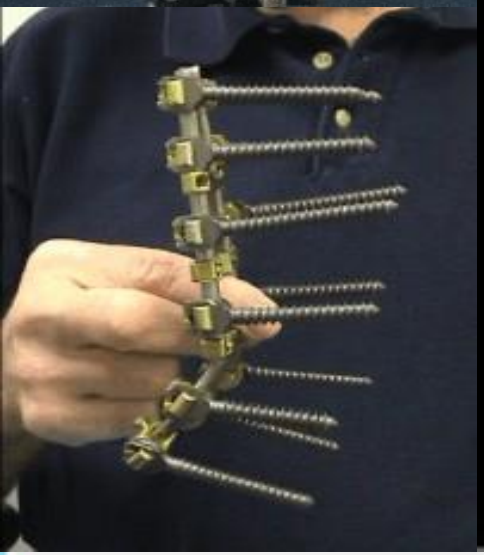


Source: Baxter estimates

Elderly population



Source: U.S. Bureau of the Census



Ti Alloys

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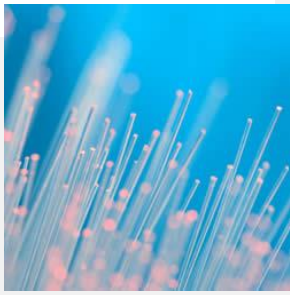
Biomaterials – Second Generation

- Structural materials use;
- Exploit of advanced materials, developed for other applications (automobile and aeronautics industry).



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- **Example:**
  - **Ti alloys in orthopedic and dental applications.**

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Ti Alloys

- Widely used in biomedical applications;
- High corrosion resistance, low elastic modulus, high mechanical strength/density ratio, and good biocompatibility;
- Ti-6Al-4V: most used currently, but studies indicate cytotoxic effects in some tissues caused by V, while Al is associated with neurological disorders;
- The most promising alloys to replace Ti-6Al-4V are those with Nb, Mo, Zr, Mo, Ta and Mn, substituting part of Ti.

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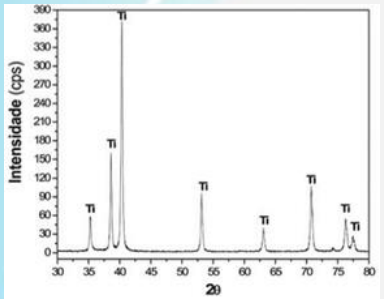
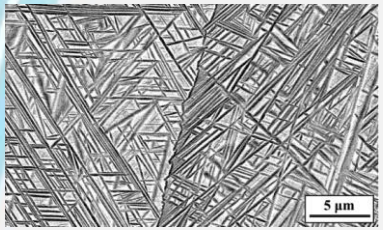
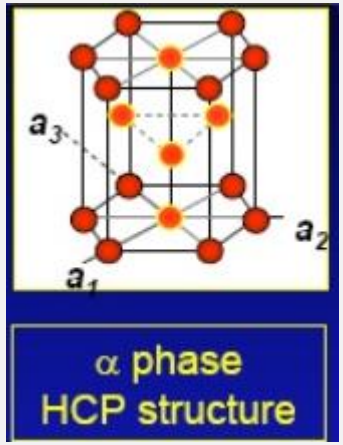
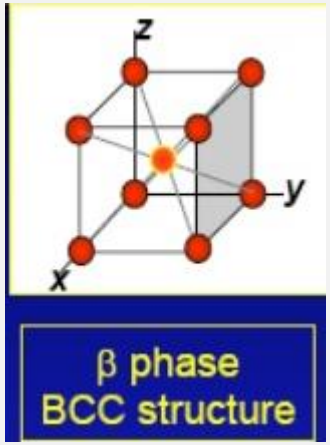
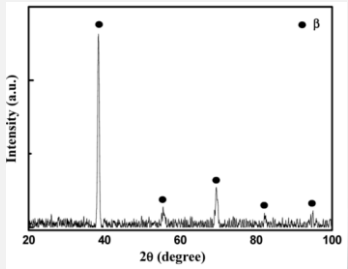
- **Ti exist in two allotropic forms:**

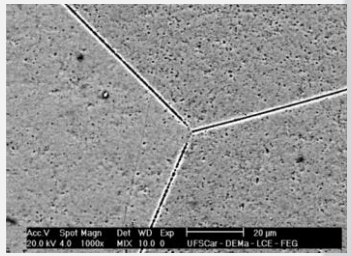




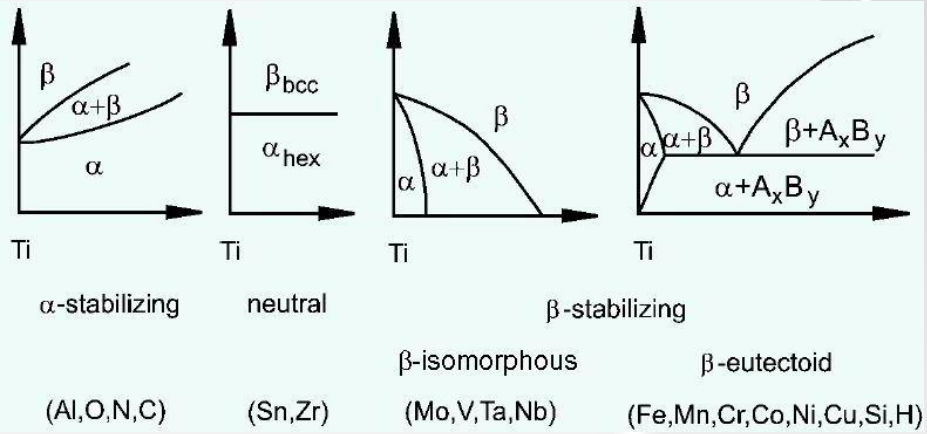








- **Transition temperature depends on substitutional or interstitial element**



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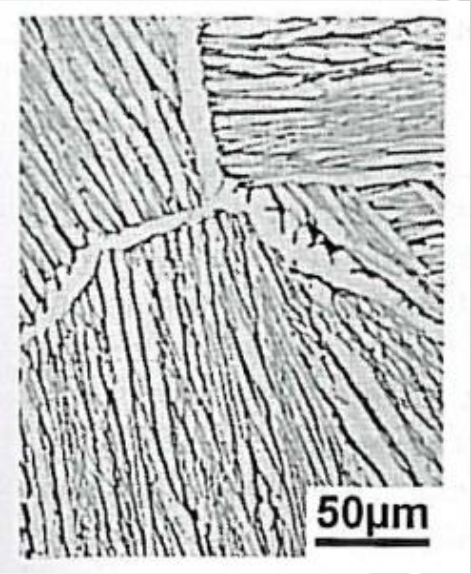
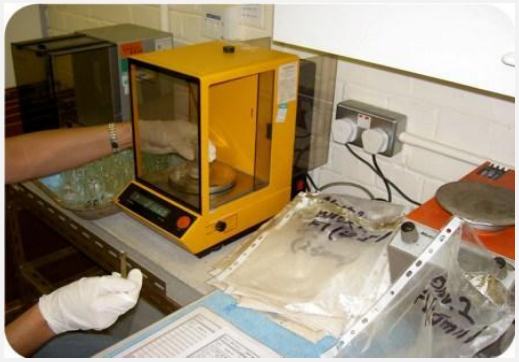
Ti-6Al-4V alloy

- $\alpha + \beta$ alloy;
- The oldest and the most used titanium alloy (denoted Grade 5, just after 4 Grades of Pure Ti);
- 50% of whole titanium and titanium alloys production;
- During recrystalization, both phases are chemically stabilized;
- Typical impurities content: O: 0.2; N: 0.04; H: 0.015; Cu: 0.35; Fe: 0.35 wt%.



Biomaterials – Third Generation

- Improvement;
- Development of materials with specific characteristics according to the application.



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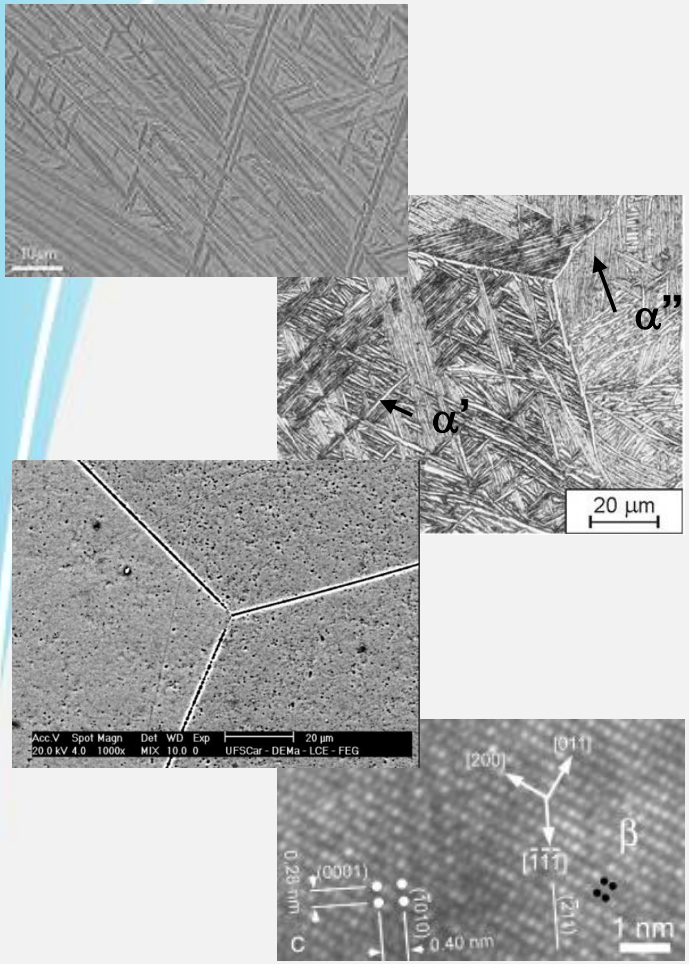
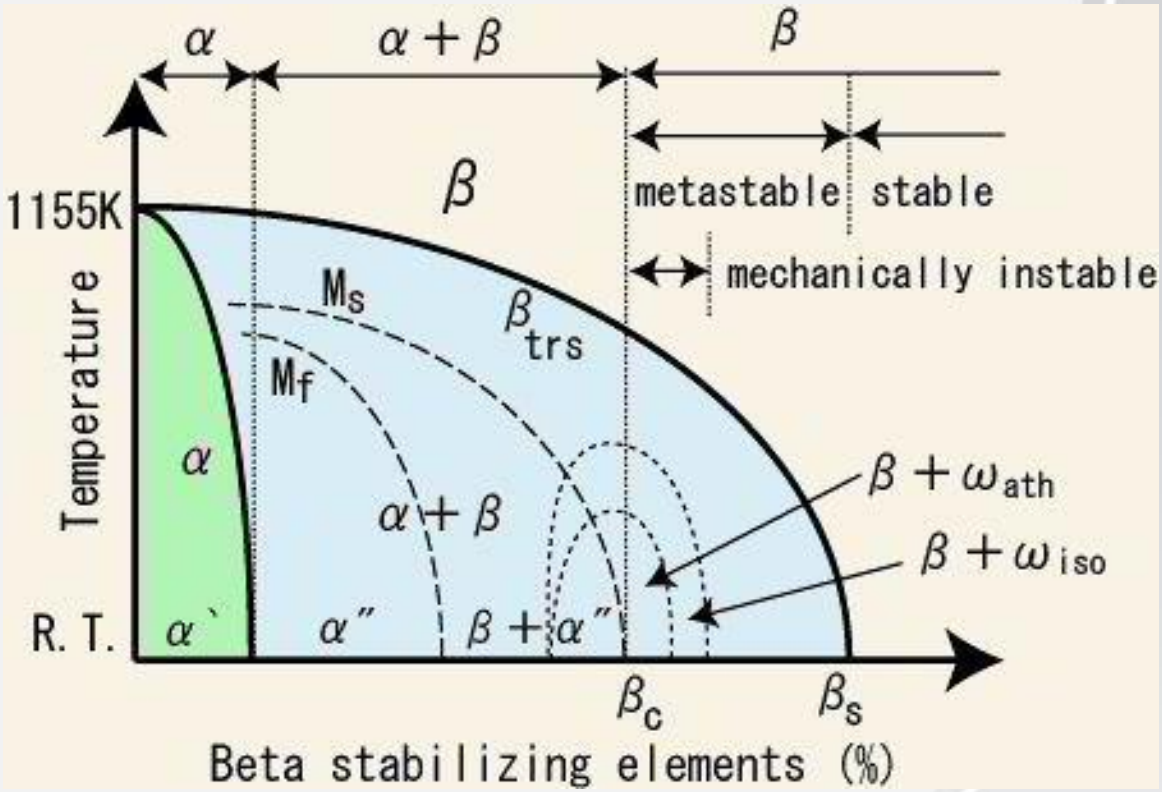
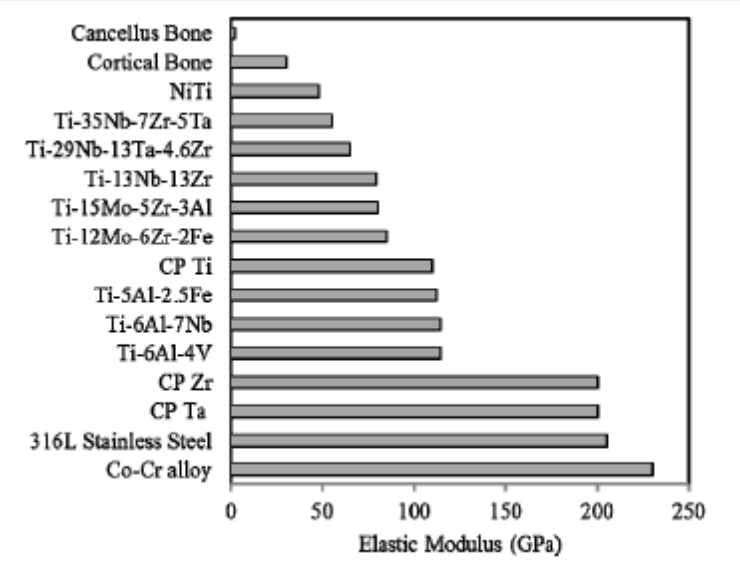
- **After annealing, solution, quenching or aging heat treatments, metastable martensitic α' and α", and ω phases appears;**





- β Ti-based Alloys
  - Light with high strength;
  - Alternatives to Ti-6Al-4V:
    - Ti-13Nb-13Zr;
    - Ti-15Mo;
    - Ti-12Mo-6Zr-2Fe;
    - Ti-35Nb-5Ta-7Zr
    - Ti-29Nb-13Ta-4.6Zr;



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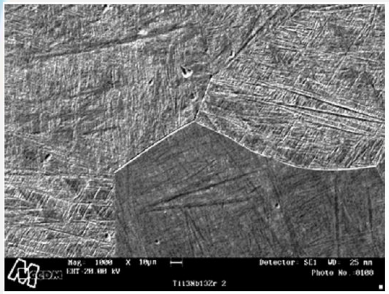

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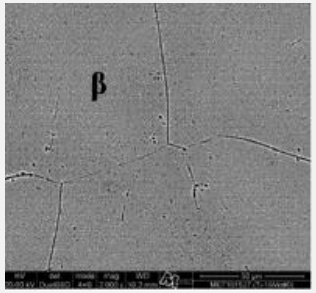

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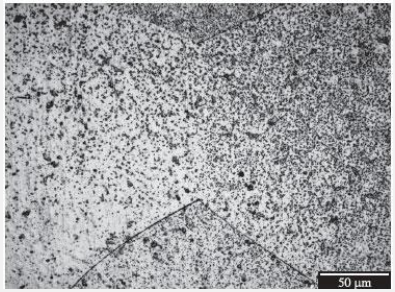

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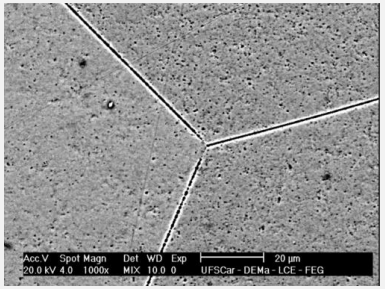

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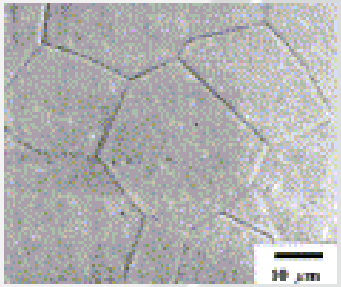
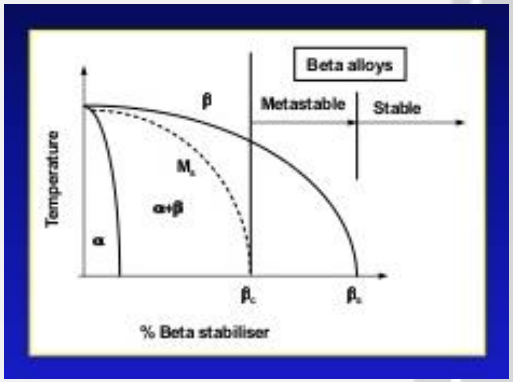
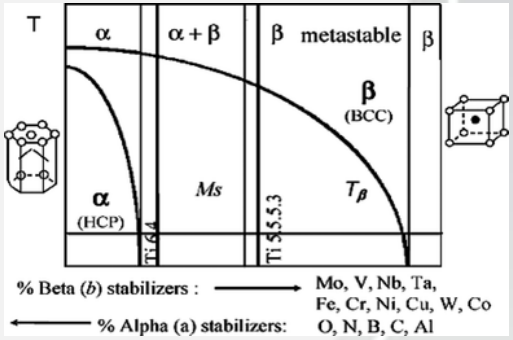


M. Niinomi, Biomaterials 24 2673 (2003).

Metastable β-Ti alloys

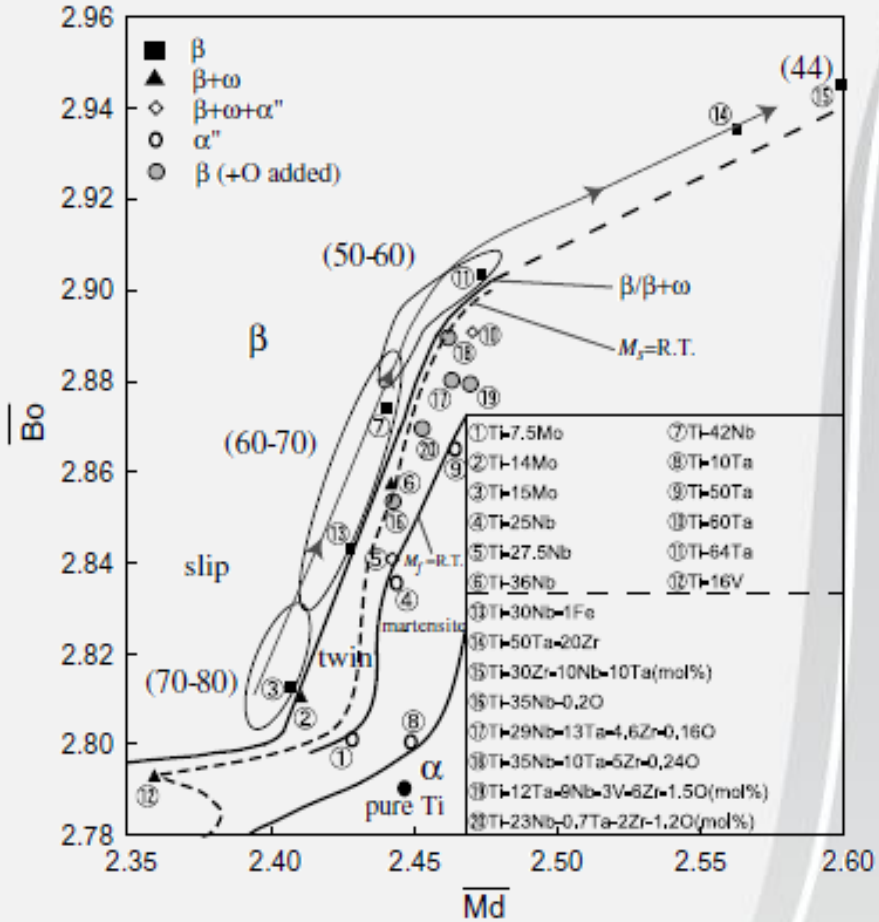
- Metastable β-alloys do not undergo martensitic phase transformation β → α after quenching from β-region;
- Solution treated material consist of pure β-phase, but equilibrium composition is α + β;
- Precipitation hardenable by heat treatment;
- Working can be done after homogenization treatment in β-region (more common) or in α + β field (material is hardened during working, but grain refinement can be achieved);





Alloy Design

- Molecular orbital theory;
- Alloys with beta phase predominance (bcc crystalline structure);
- Elastic modulus bellow 40 GPa.



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Al and Mo equivalent

$$\%Al_{equiv} = Al + \frac{1}{3}Sn + \frac{1}{6}Zr + 10(O + C + 2N)$$

$$Mo_{equiv}\% = 1.0Mo + 0.67V + 0.44W - 0.28Nb + 0.22Ta + 1.6Cr$$

In general:

- $Al_{eq} < 8$ and $Mo_{eq} < 1$: α alloy;
- $6 < Al_{eq} < 10$ and $Mo_{eq} < 2$: near α alloy;
- $5 < Al_{eq} < 10$ and $2 < Mo_{eq} < 8$: α–β alloy;
- $Al_{eq} < 6$ and $Mo_{eq} = 15\text{-}30$: metastable β alloy;
- $Al_{eq} < 6$ and $Mo_{eq} > 30$: stable β alloy.

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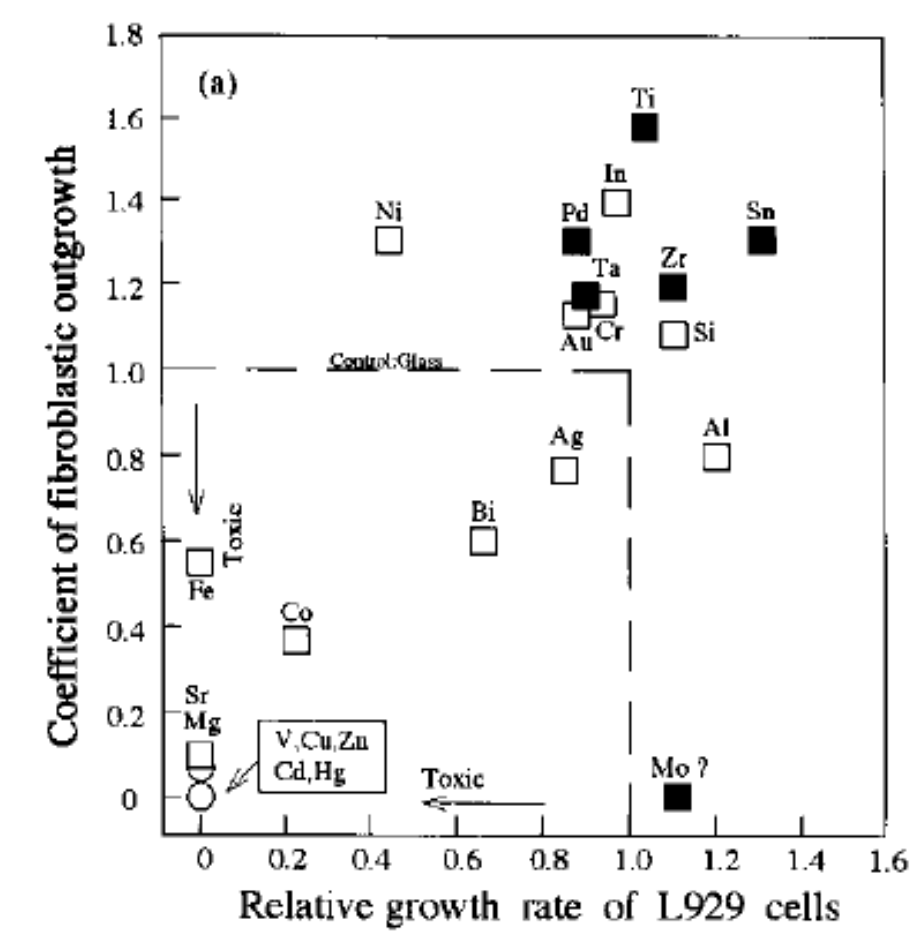
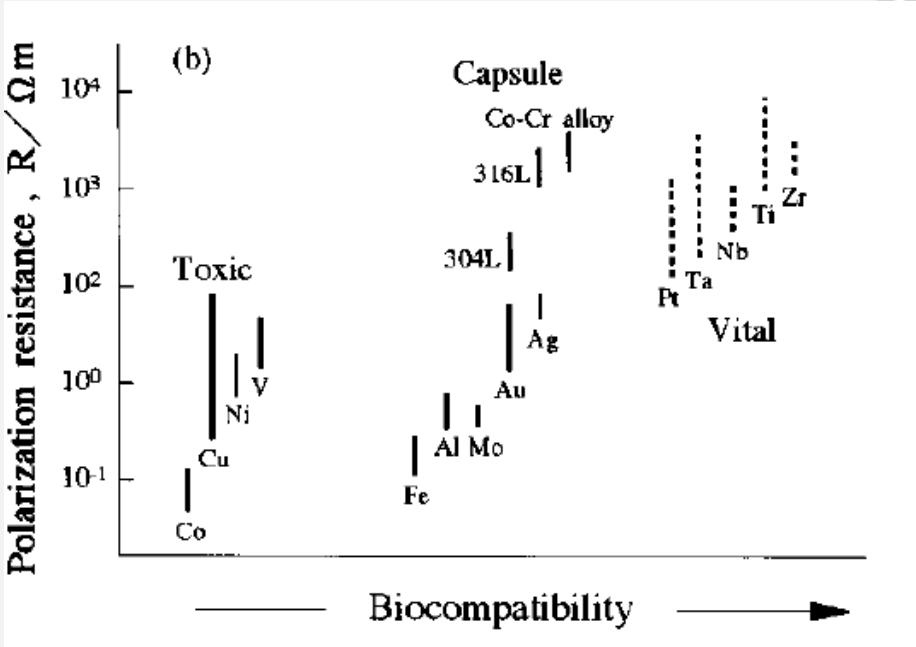
Possible Biocompatibility





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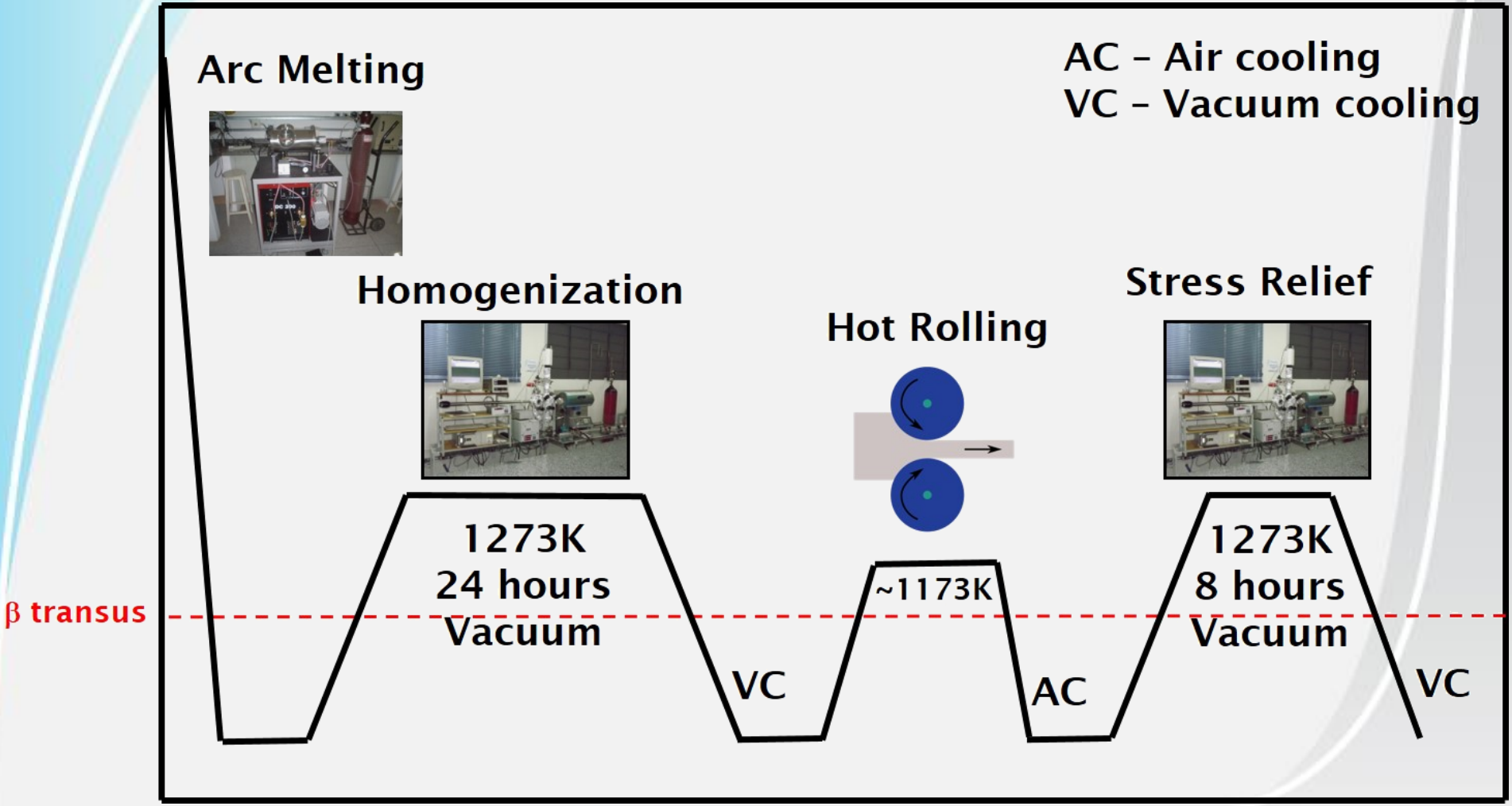
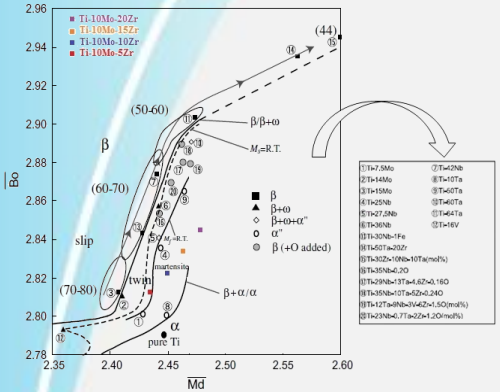
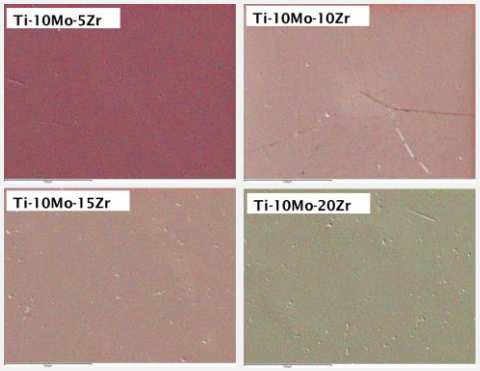
Processing


Arc Melting
AC – Air cooling
VC – Vacuum cooling
Homogenization
Hot Rolling
Stress Relief
1273K
24 hours
Vacuum
~1173K
1273K
8 hours
Vacuum
β transus
VC
AC
VC

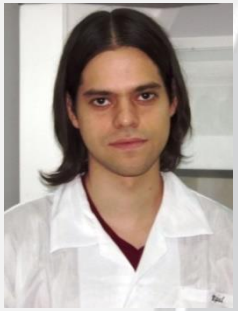
Ti-10Mo-Zr System

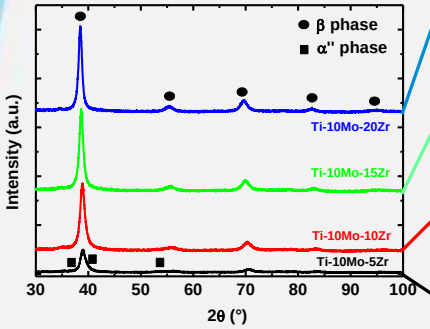


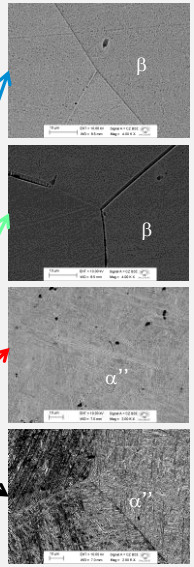
Element (wt%)	Ti-10Mo-5Zr	Ti-10Mo-10Zr	Ti-10Mo-15Zr
Al	0.02	0.05	0.06
Cr	0.004	0.006	0.006
Cu	0.004	0.004	0.004
Ni	0.005	0.006	0.005
Fe	0.04	0.04	0.04
N	0.004	0.003	0.006
O	0.020	0.031	0.048
Zr	5.23	9.82	14.79
Mo	10.01	9.77	10.20
Ti	Balance	Balance	Balance

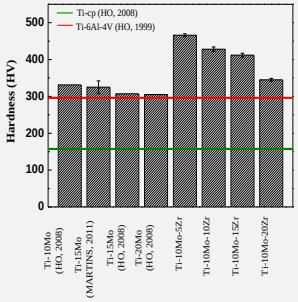


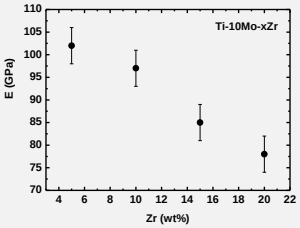
Ti
Mo
Zr

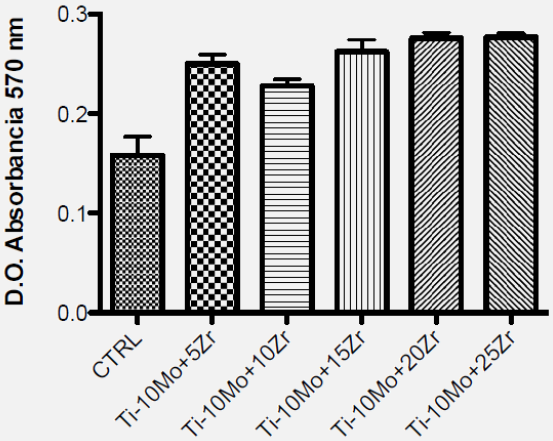












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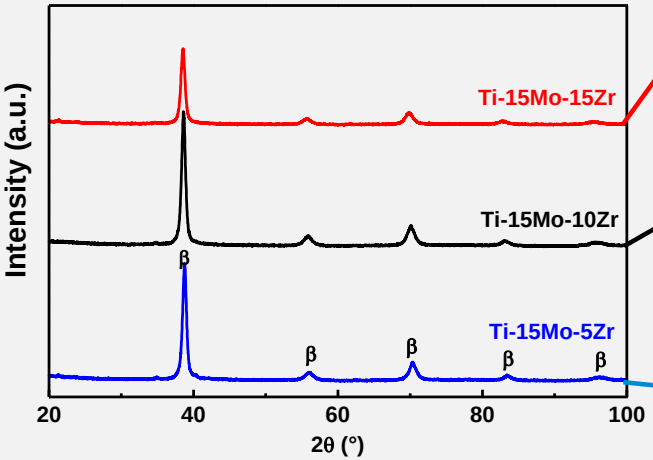
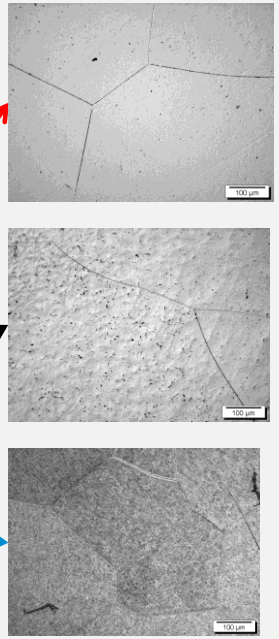
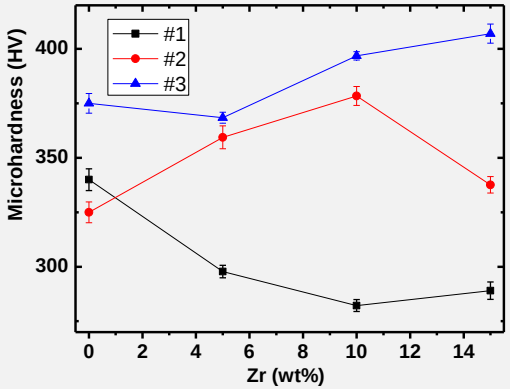
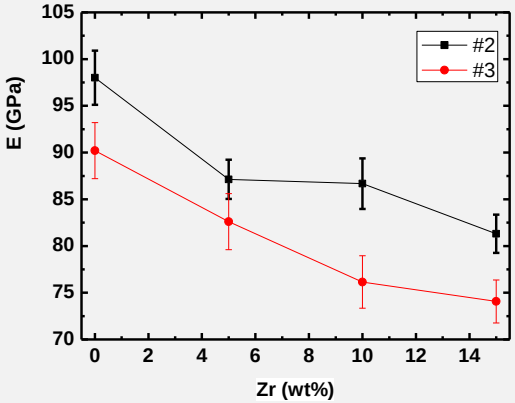
Ti-15Mo-Zr System

Element (wt%)	Ti-15Mo-5Zr	Ti-15Mo-10Zr	Ti-15Mo-15Zr
Al	0.02	0.05	0.06
Cr	0.004	0.006	0.006
Cu	0.004	0.004	0.004
Ni	0.005	0.006	0.005
Fe	0.04	0.04	0.04
N	0.004	0.003	0.006
O	0.020	0.031	0.048
Zr	5.23	9.82	14.79
Mo	15.01	14.77	15.20
Ti	Balance	Balance	Balance









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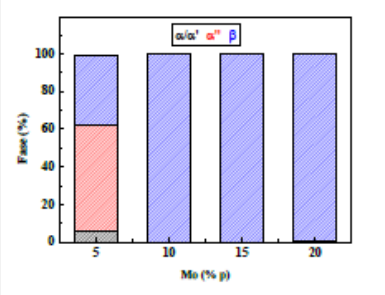
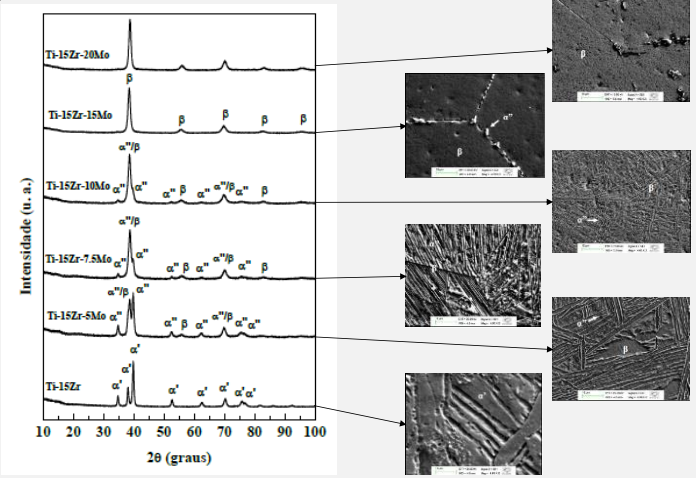
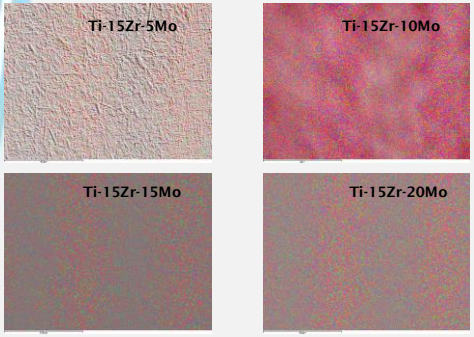
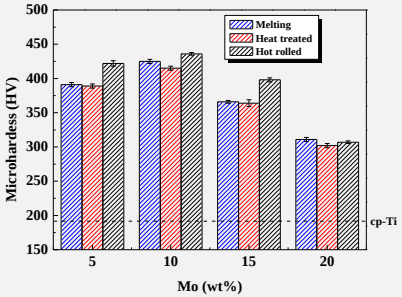
Ti-15Zr-Mo System

Element (wt%)	Ti-15Zr-5Mo	Ti-15Zr-10Mo	Ti-15Zr-15Mo	Ti-15Zr-20Mo
Al	0.02	0.02	0.02	0.02
Cr	0.004	0.003	0.005	0.005
Cu	0.002	0.002	0.006	0.003
Ni	0.004	0.002	0.006	0.006
Fe	0.09	0.01	0.07	0.07
N	0.004	0.004	0.003	0.002
O	0.022	0.023	0.030	0.016
Zr	15.13	15.59	14.80	15.61
Mo	4.82	10.30	14.25	19.91
Ti	Balance	Balance	Balance	Balance





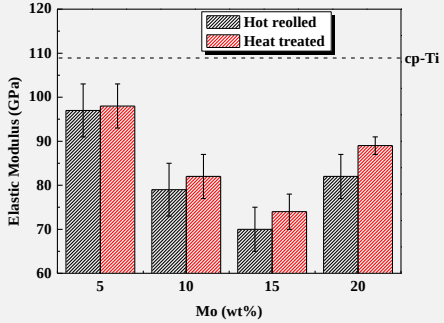


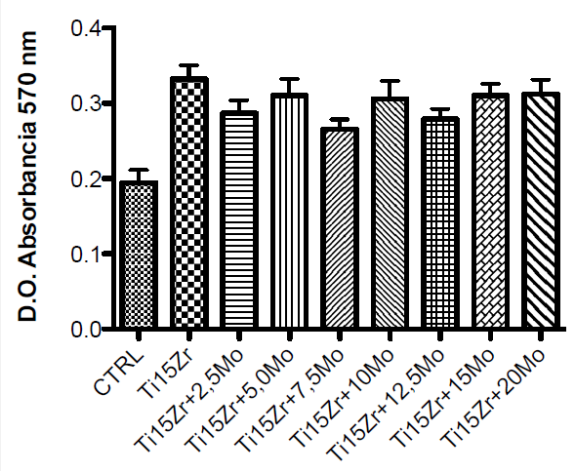


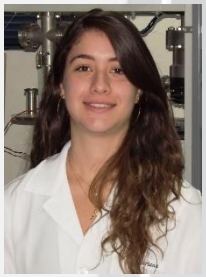
Ti

Zr

Mo







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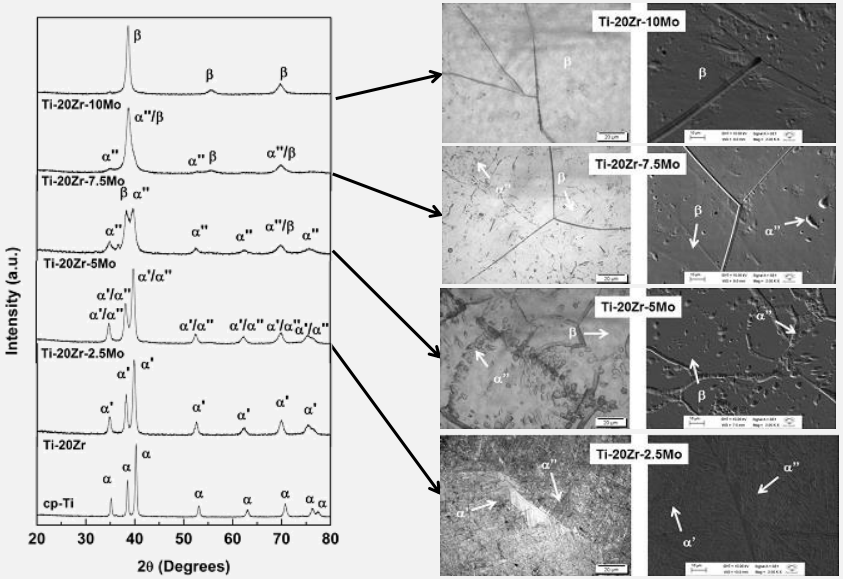
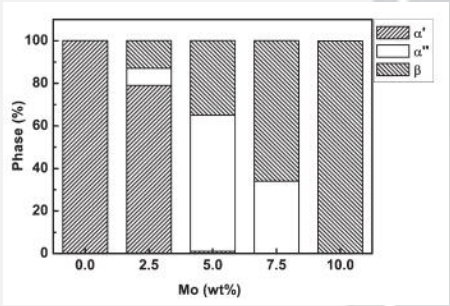
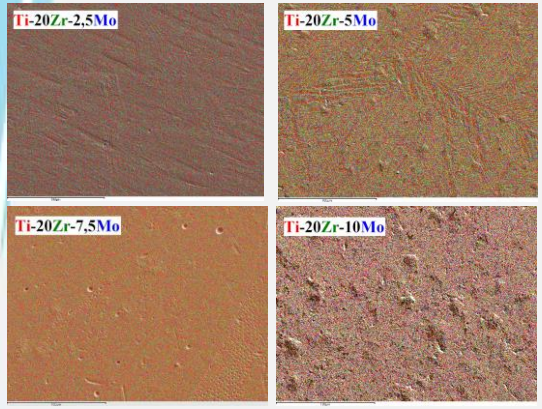
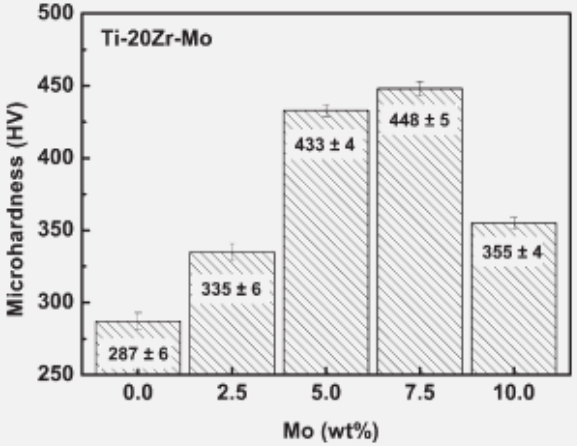
Ti-20Zr-Mo System

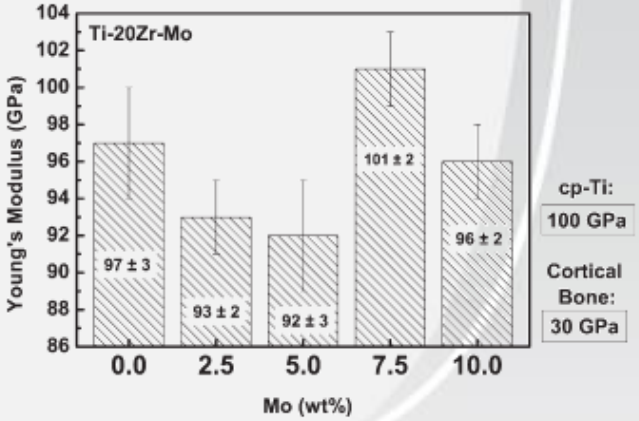
Element (wt%)	Ti-20Zr-2.5Mo	Ti-20Zr-5Mo	Ti-20Zr-7.5Mo	Ti-20Zr-10o
Al	0.02	0.02	0.02	0.02
Cr	0.004	0.003	0.005	0.005
Cu	0.002	0.002	0.006	0.003
Ni	0.004	0.002	0.006	0.006
Fe	0.09	0.01	0.07	0.07
N	0.004	0.004	0.003	0.002
O	0.022	0.023	0.030	0.016
Zr	20.53	20.19	20.60	20.81
Mo	2.52	5.30	7.45	10.91
Ti	Balance	Balance	Balance	Balance











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Chemical Demages

Low resistance to Corrosion and Wear

Metallic ions and debris generation

Toxicity

Mechanical Demages

Low strenght and hardness

Fatigue failure

Fracture

New alloys and surface modifications

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For the development of new metallic materials for implants, consideration should be taken:

- **Removal of toxic elements such as Al and V;**
- **Decreased modulus of elasticity to avoid the effect of stress shielding;**
- **Improvement of compatibility between material and tissue;**

The development must be carried out on the basis of metallurgy and the resulting alloys must have a good balance between mechanical properties and corrosion resistance.

Among the metallic materials, titanium alloys are still considered as the most suitable materials for biomedical applications.

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β-type titanium alloys with Young's modulus variability

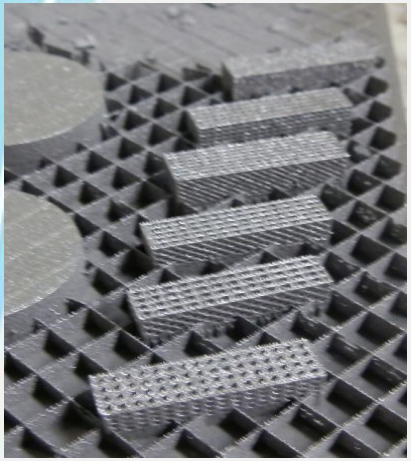
In spinal fixation surgery, along with excellent mechanical properties, the spinal-support materials should possess high Young's modulus for showing small springback during surgery to facilitate manipulation but low Young's modulus close to bone once implanted to avoid stress shielding.

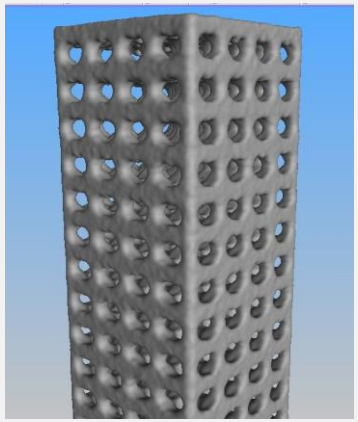
Cellular Metals

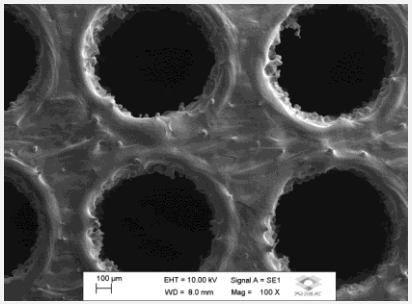
Although low, the Young's modulus of Ti alloys are very high when compared to human bone.

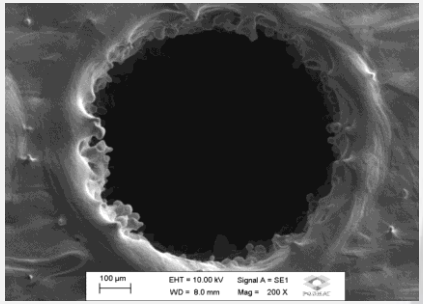
The alternative for this "problem" and better fixation of the implant is the use of biomaterials processed with porous form.

The pores provide a significant reduction of the values of modulus of elasticity and favorable environment for irrigation cell which provides better fixation of the implant.



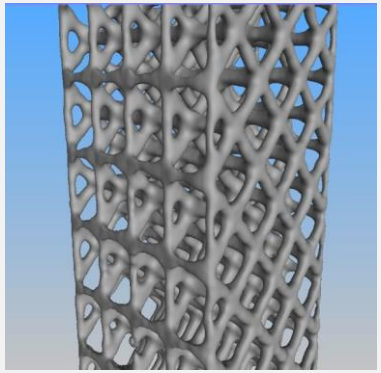


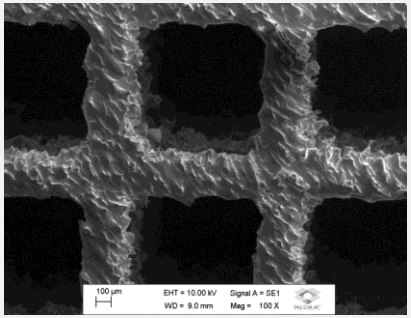


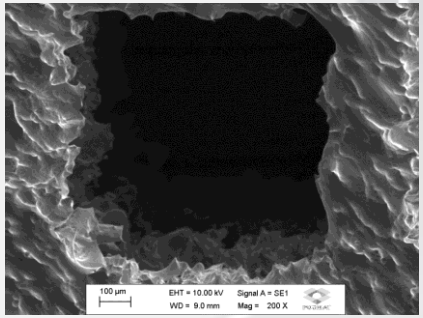


Sample	Microhardness (HV)
Ti-6Al-4V, via RP	350±2
Ti-6Al-4V commercial	289±4
esf_375	334±8
esf_500	356±9
esf_650	379±19
esf_750	387±13
qd_500	393±13
qd_650	396±12
qd_750	401±09

Sample	E (GPa)
esf_375	9,26±2,28
esf_500	12,10±2,56
esf_650	15,63±1,10
esf_750	22, 94±2,14
qd_500	5,66±1,00
qd_650	6,82±1,70
qd_750	9,12±1,69







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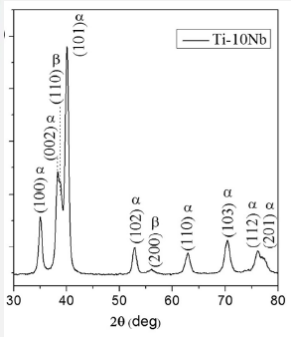
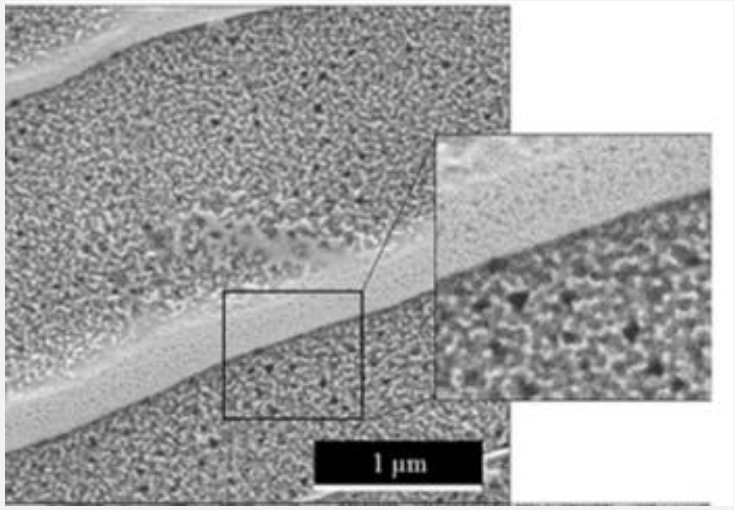
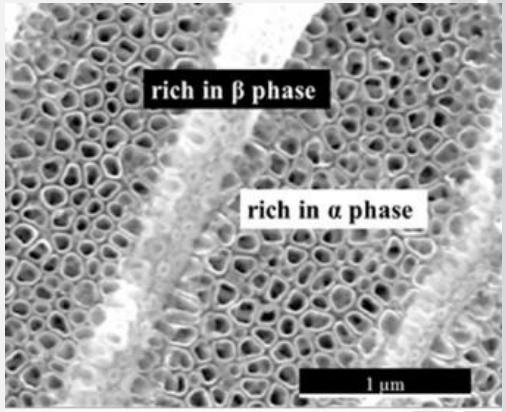
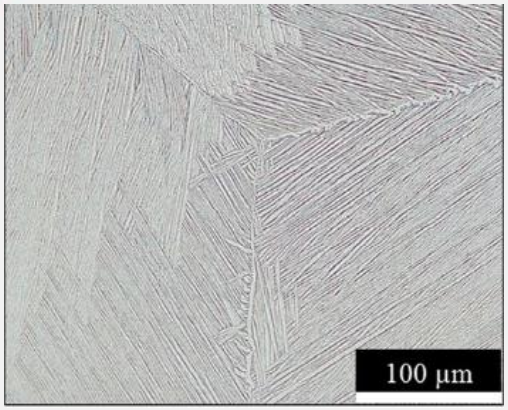
Surface Functionalization

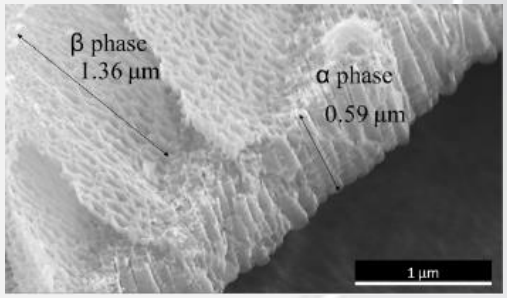
Nanotube arrays on Ti alloys to improve the surface of these materials for biomedical applications











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Summary

- ✓ In the past, Ti-alloys developed to structural applications;
- ✓ Actually, β stable and metastable Ti alloys;
- ✓ Future: new alloys without Cytotoxic elements, cellular metals and surface functionalization.

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Where are we?

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Around 380.000 inhabitants

330 km from São Paulo city

Bauru is known for having large number of Universities and Colleges:

02 Public Universities (USP and UNESP);
03 Private Universities (USC, UNIP and UNINOVE);

02 Public Colleges (FATEC and IFES 2019);
04 Private Colleges (IESB, ITE, FIB and Anhanguera);

More than 30.000 graduate and undergraduate students

http://www.bauru.sp.gov.br

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Universidade Estadual Paulista – UNESP

São Paulo State Presence:
24 Campus

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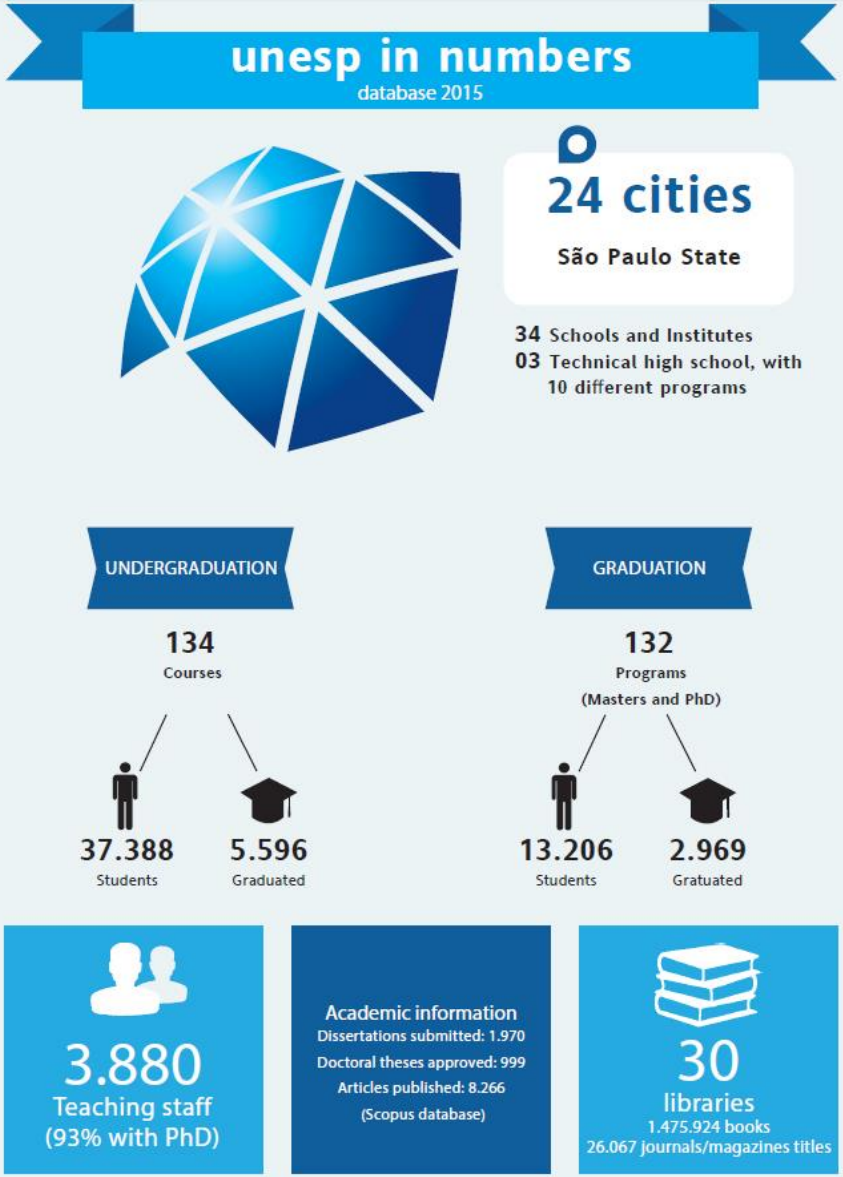

Bauru

- School of Art and Communication
- School of Sciences
- School of Engineering

FACTS & FIGURES

Undergraduate Studies: 19
Graduate Studies: 08
Undergraduate students: 5,073
Graduate students: 732
Faculty: 360
Staff: 274 technical employees

Physics

School of Sciences

Physics Department has 30 PhD full time teachers (3 Professors). Its support staff has 9 technical-administrative servants.

The department is responsible for the undergraduate course of Physics, with emphasis in Materials Science.

Bacharelado em Física
MATERIAIS

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PÓS-GRADUAÇÃO EM CIÊNCIA E TECNOLOGIA DE MATERIAIS

CAPES 6

A Graduation course, multi-campus, focused in a better understanding of materials and its properties … Materials Science and Technology.

Biomaterials is a main topics for research development.

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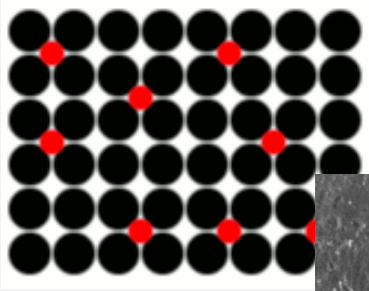
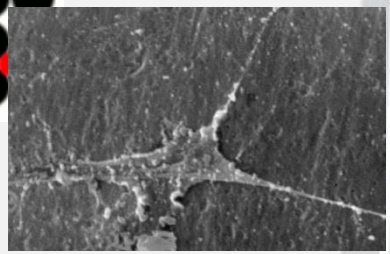
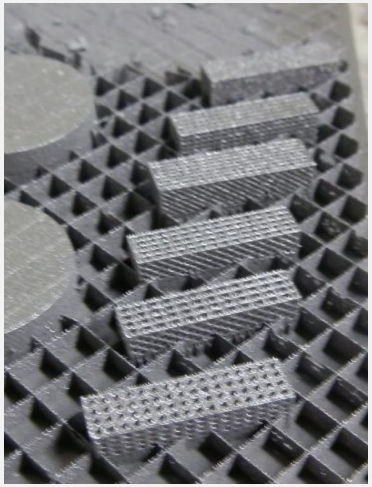
Development of new Ti-based alloys with low Young's modulus

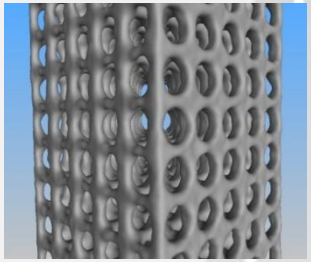
- Development of new Ti Alloys
  - Without cytotoxic elements;
  - Arc-melting;
  - Influence of interstitials.

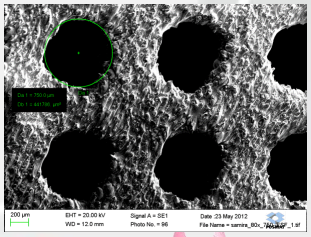




- Cellular metals
  - Controlled porosity;
  - Low density;
  - High mechanical strength.

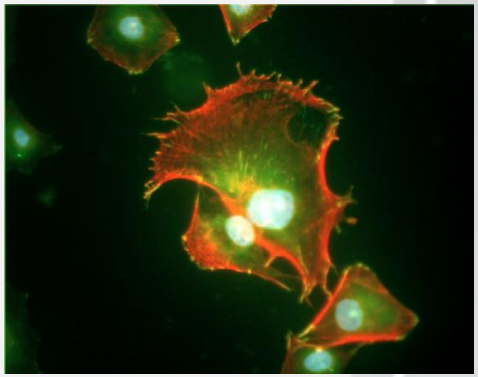




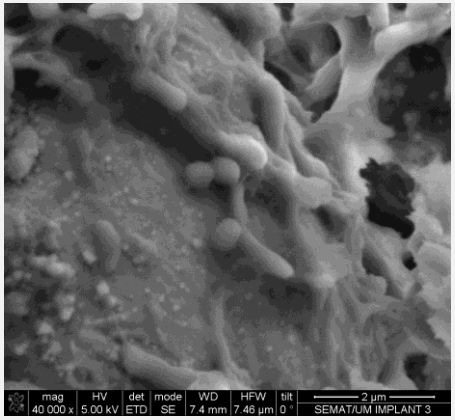


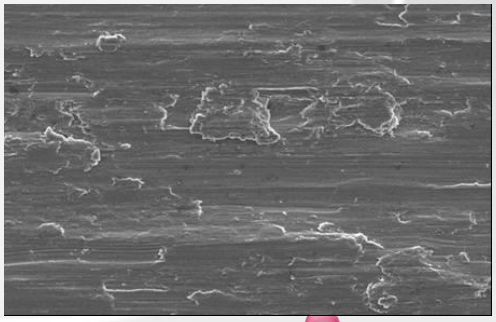
Multifunctional surfaces on Ti-based alloys

- Biofunctionality and bioselectivity
  - Osteoblasts adhesion and proliferation
  - Bone remodeling capability
  - Avoid microbial infection



- Other functions
  - Avoid corrosion
  - Avoid wear
  - Avoid tribocorrosion





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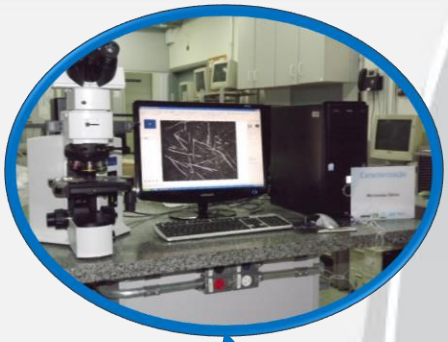
Facilities

Preparation



Characterization

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Staff

Laboratório de Anelasticidade e Biomateriais

Researchers:

- Carlos Roberto Grandini
- Luís Augusto Rocha
- Carlos Alberto Fonzar Pintão

Students

- 04 PosDoc
- 04 PhD
- 02 Master
- 08 Undergraduate

02 Technicians

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Collaborators

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Marília Afonso Rabelo Buzalaf – FOB/USP/Bauru
Rodrigo Oliveira – FOB/USP/Bauru
André Luiz Jardini Munhoz, UNICAMP
Neide Kazuo Kuromoto, UFPr
Roman A. Surmenev, TPU

Aknowledgements

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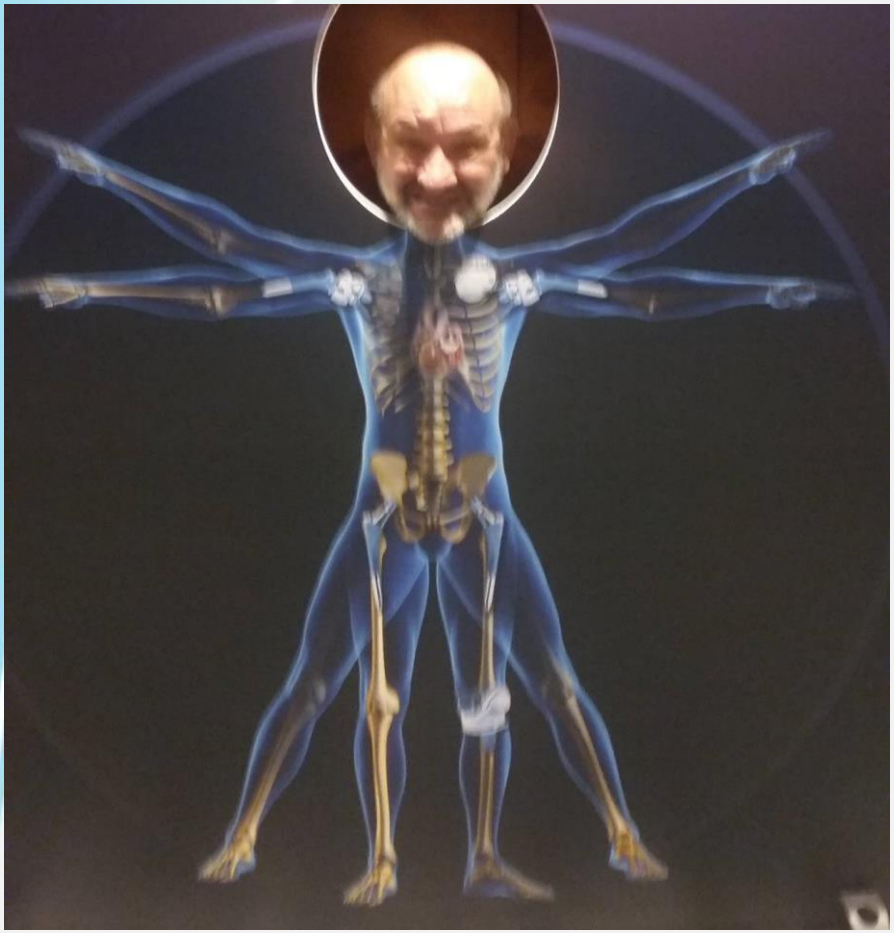

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