

Implanturi mici din sticle metalice masive?

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AARD, iunie 2022

Metal vs. aliaj

Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

metale

Fe + Cr + Ni =
aliaj (oțel inoxidabil)

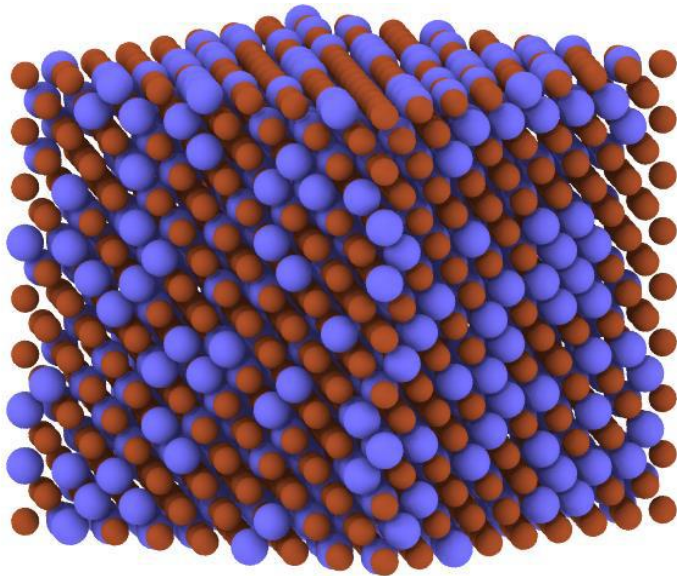
Ce este sticla metalică?

Majoritatea aliajelor sunt cristaline

Sticla metalică sau aliaj amorf (fără cristalinitate)

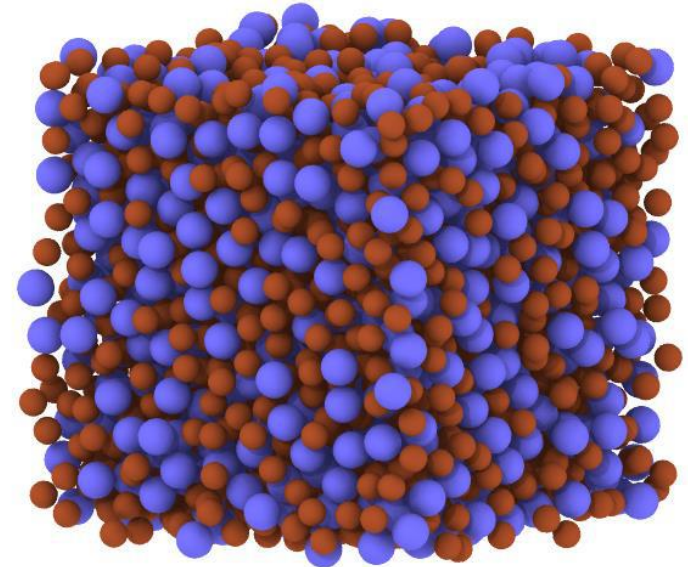
Aranjament atomi, comportament termic și mecanic similar sticlei clasice

aliaj cristalin



Atomii sunt aranjați
ordonat

aliaj amorf (sau sticla metalică)



Atomii sunt aranjați
DEZordonat

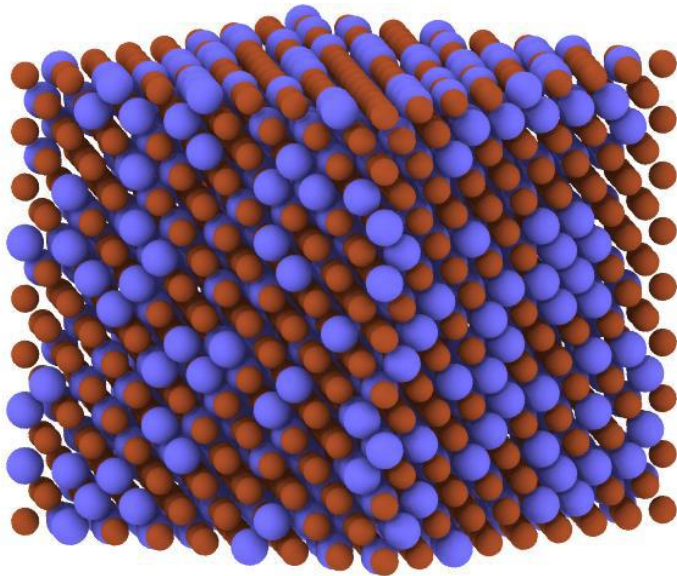
Sticlă metalică: rezistență mecanică mare

Aliaje cristaline: Aranjament ordonat, planuri atomice

Alunecare planuri atomice -> deformare la stres mic, dar plasticitate

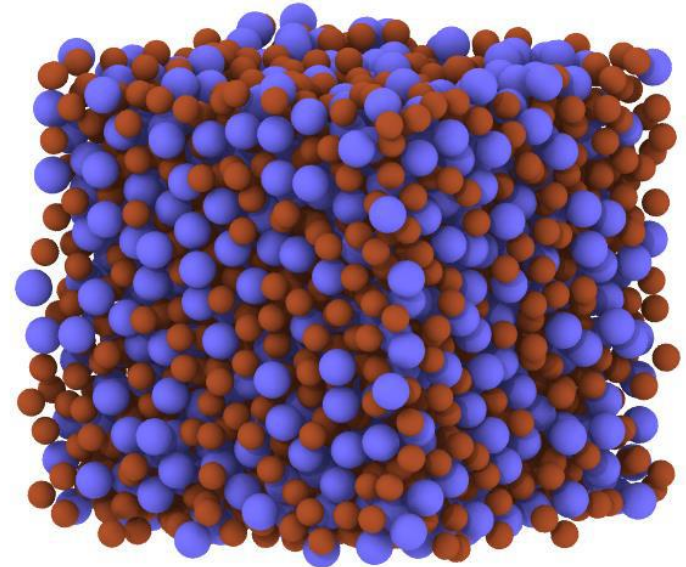
Sticlă metalică, lipsă planuri atomice -> lipsă alunecare -> rezistență la stres

aliaj cristalin



Atomii sunt aranjati
ordonat

aliaj amorf (sau sticla metalica)



Atomii sunt aranjati
DEZordonat

Cum obținem sticla metalică?

Toate topiturile metalice tind să cristalizeze când sunt răcite sub temperatura lor de solidificare

Principiul: previne cristalizarea

Structura amorfă este structura lichidului (topitura) înghețată

Răcirea mai rapidă decât procesul de aranjare al atomilor într-o structură ordonată

Compoziția aliajului, rol decisiv în viteza critică de răcire



<https://nusteelfab.com/nu-steel-fabricators-is-working-on-revolutionary-flex-mill/>

Sticla metalică *masivă*

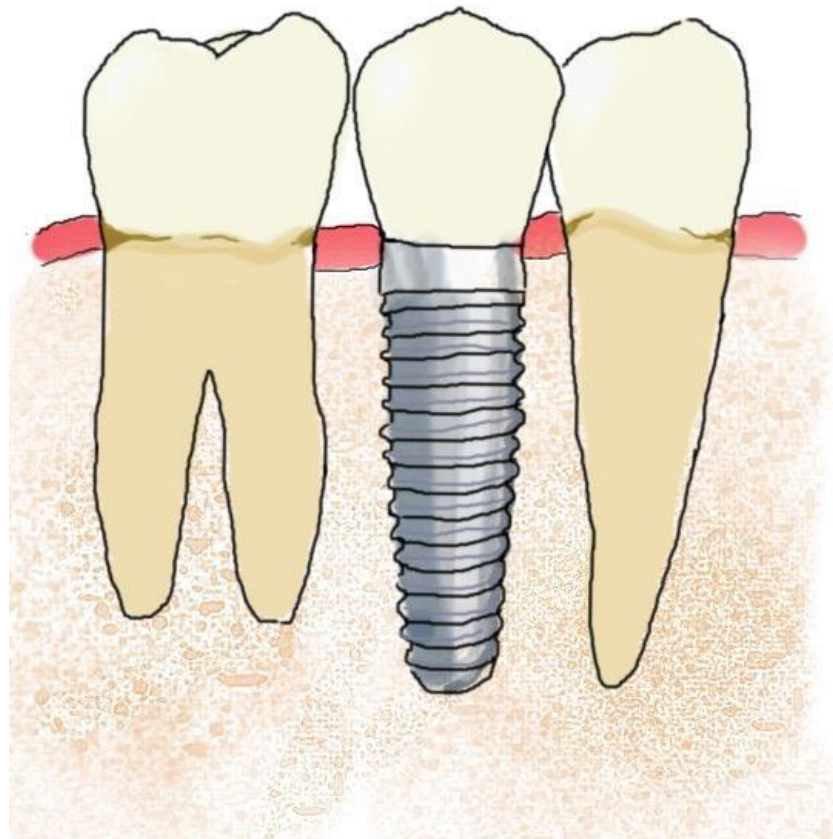
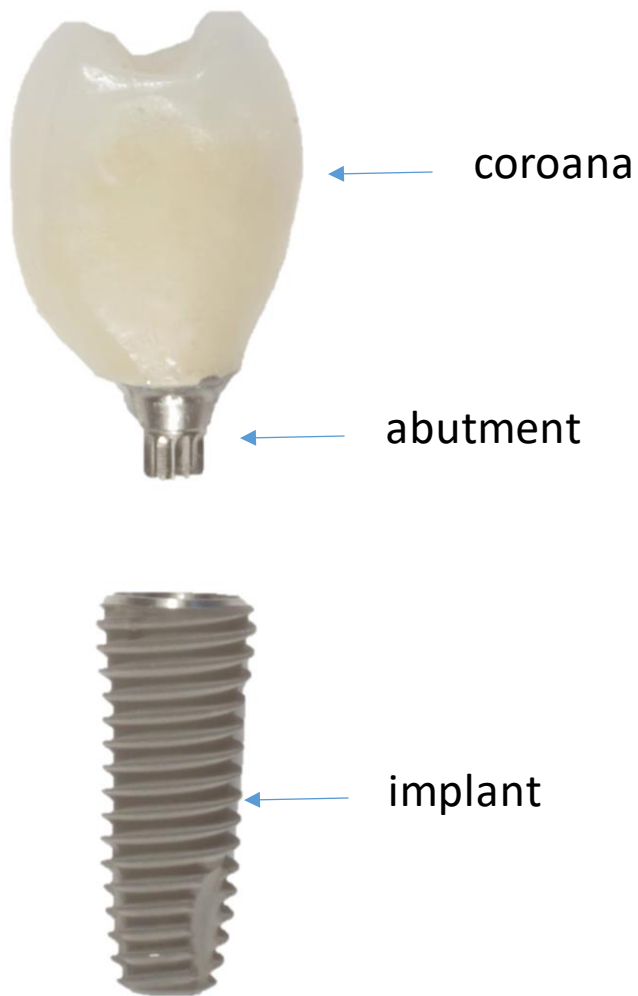
Bulk metallic glass

Grosime mare -> racire încetă

Grosime critică

Sticla metalică masivă: $D > 1 \text{ mm}$

Ce este un implant dentar?



Fabricate din metalul Titan sau aliaj de Titan cu Aluminiu si Vanadiu

- > 35 milioane cetateni americani au toti dintii sau toti dintii de sus sau de jos lipsa
- 3 milioane au implanturi dentare
- in fiecare an numarul creste cu 0.5 milioane
- piata US + EU estimata la 4.2 miliarde US\$ pana in 2022

American Academy of Implant Dentistry

http://www.aaid.com/about/Press_Room/Dental_Implants_FAQ.html

'Narrow diameter implants'

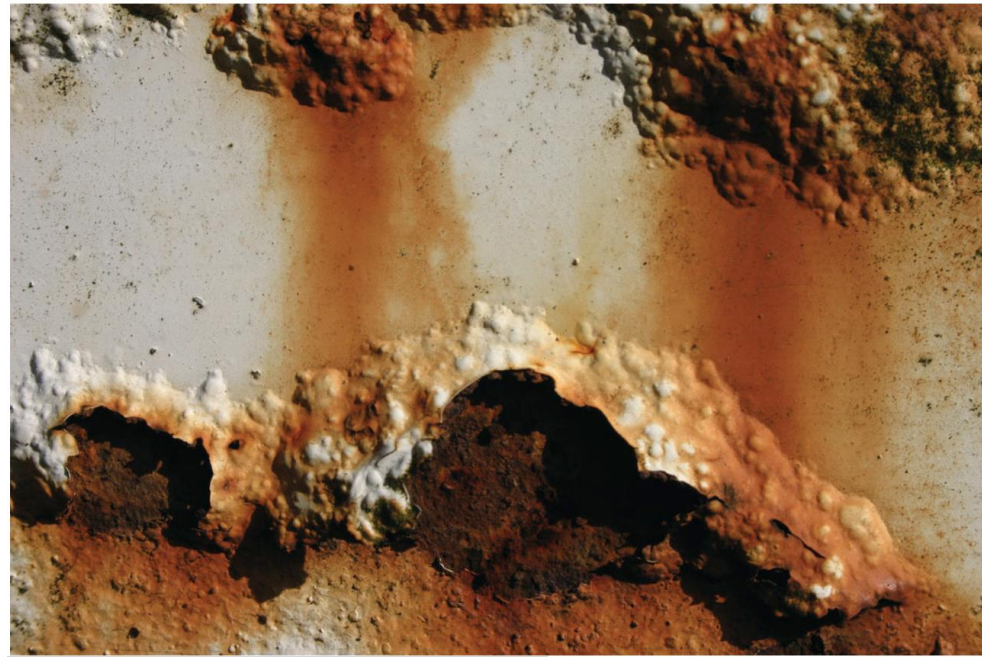
Implanturi mici

- Implanturi cu diametrul < 3 mm
- necesare cand creasta alveolara este subtire
- implant de dimensiuni mici \rightarrow solicitare mecanica ridicata:
~~metalul Titan si aliajul Ti-6Al-4V~~
- avem nevoie de materiale cu rezistenta mecanica mai mare!

Obiectiv proiect

- Evaluare “suitability” sticle metalice massive de Ti pentru implanturi mici
- Anthogyr se ocupa de toate proprietatile urmand cerintele standard
- Noi introducem o metodologie noua de evaluare a biocompatibilitatii
- Standard: evalueaza daca aliajul se corodeaza
- Noi: presupunem ca se corodeaza, studiem care sunt produsii de coroziune, studiem care este efectul acestora asupra unor tesuturi specifice

De ce produse de coroziune?



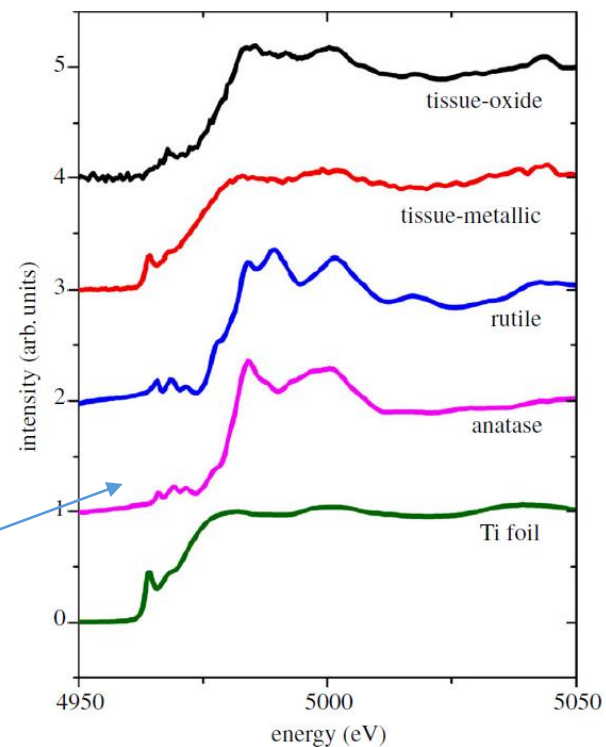
http://all-free-download.com/free-photos/download/bridge-railway-rusted_235457.html

<http://www.european-coatings.com/>

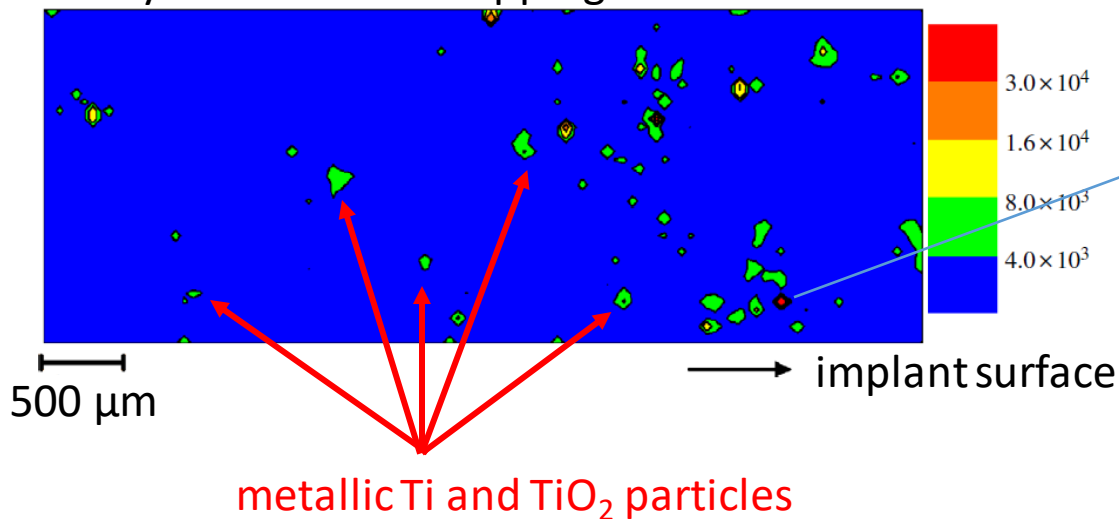
Coroziunea implanturilor in vivo

Tesut prelevat din vecinatatea unui implant cochlear care cauza inflamatie

XANES

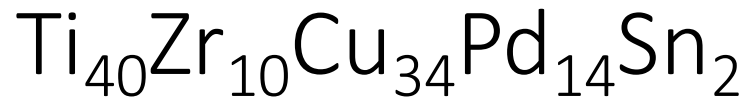


X-ray fluorescence mapping



Addison et al, 2012

The metallic glass under investigation:



- Very good glass forming ability for a Ti-based composition (d= 12 mm)
- Yield strength 2000 MPa

NIKKEI TECHNOLOGY
Tech & Industry Analysis from Japan/Asia *online*

Japanese Universities Develop Ti-based Metallic Glass for Artificial Finger Joint

Masaaki Maruyama, Nikkei BP Producer

Jun 11, 2009



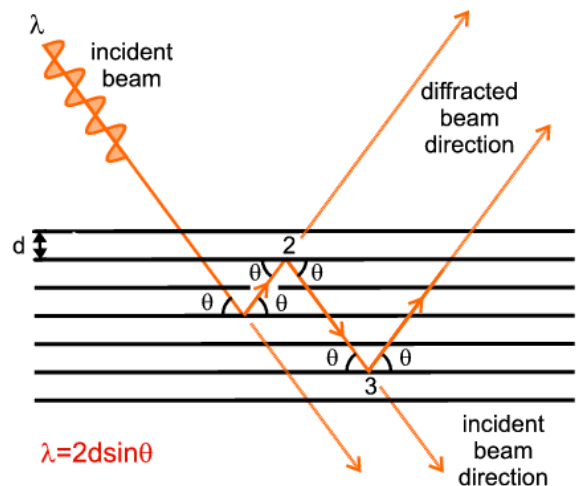
The artificial finger joint prototype made of Ti-based metallic glass. The saddle-shaped structure on the upper side is a

(Zhu et al 2008 Intermetallics)

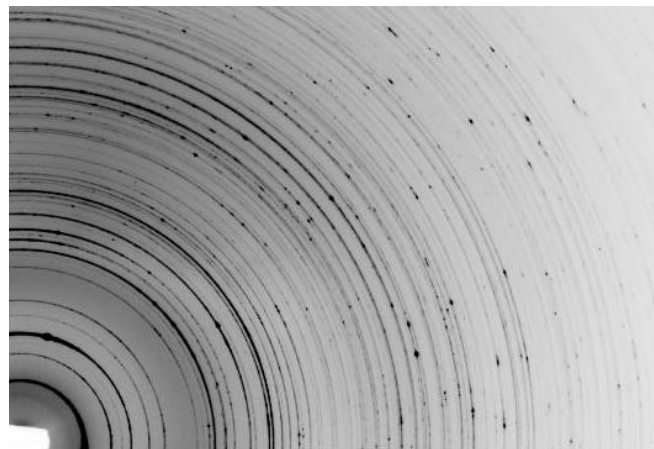
Cum putem investiga produsii de coroziune ai sticlei metalice?

Experimente de difracție

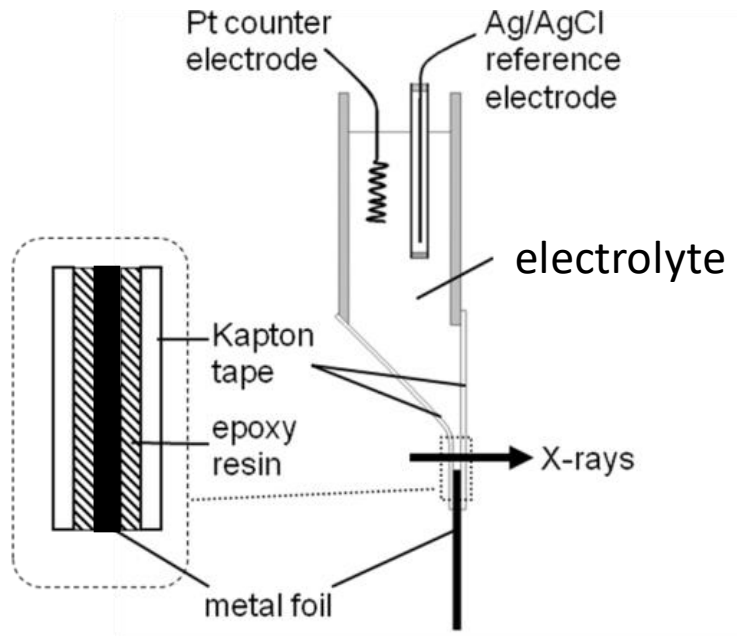
- Fiecare metal/compus chimic are o structură ordonată a atomilor componenți
- Datorită acesteia, radiația X suferă difracție dând naștere unei difractograme cu ajutorul căreia se poate identifica metalul/compusul respectiv



Difractograma $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$



Celula de coroziune speciala pentru investigarea produsilor de coroziune



- Foil: $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{34}\text{Pd}_{14}\text{Sn}_2$ metallic glass 50-100 μm
- Solution: physiological saline (0.9 % NaCl)
- Pits grown at: 1.3 V and 0.7/0.5/0 V vs Ag/AgCl

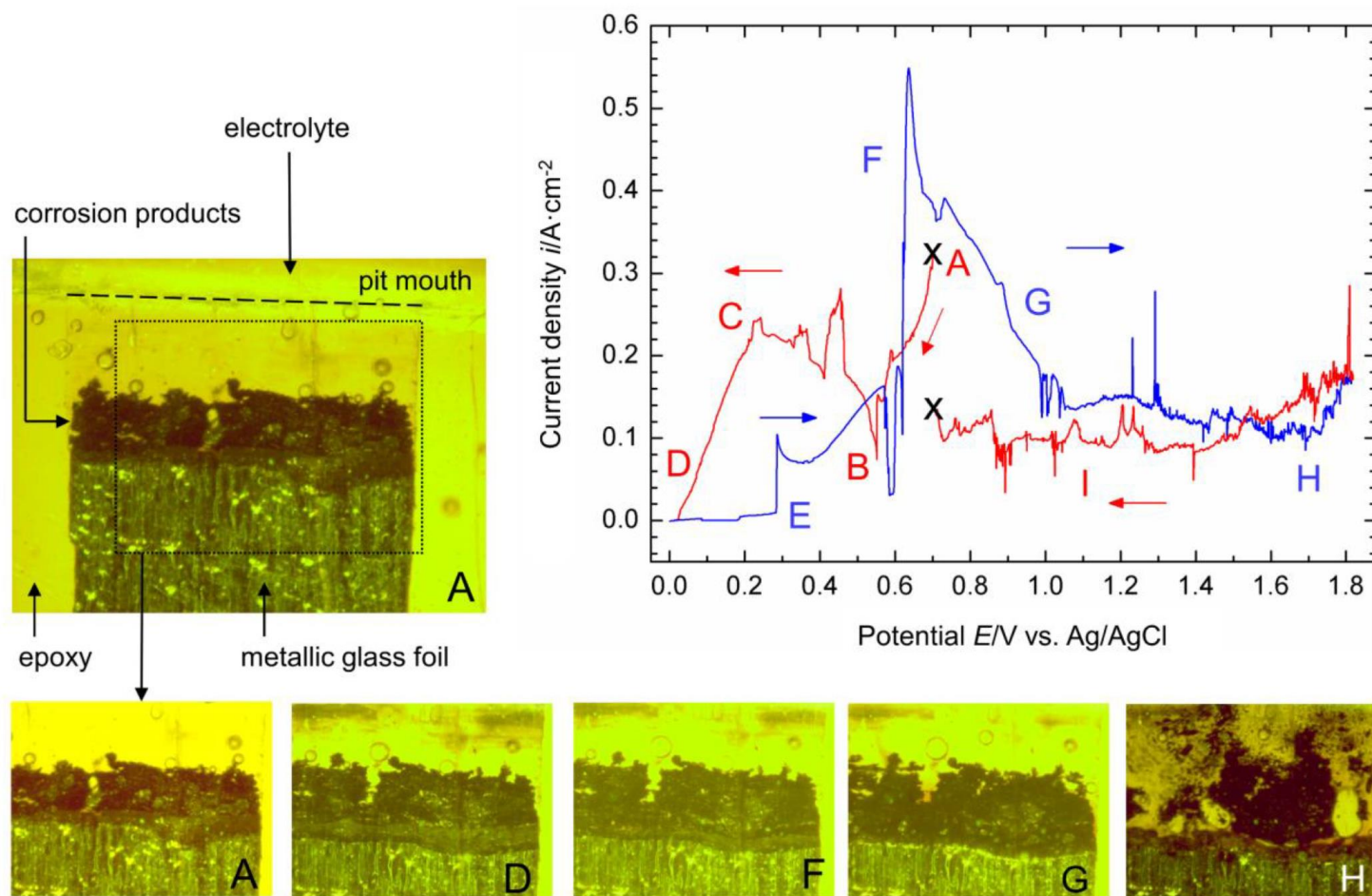


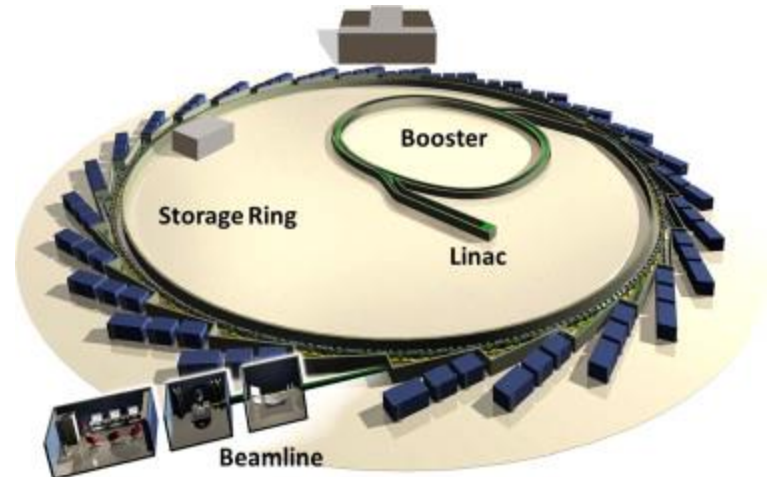
Figure S5. Cyclic polarisation curve for an artificial pit on $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{34}\text{Pd}_{14}\text{Sn}_2$ metallic glass in 0.9% NaCl. The pit was initially grown at constant potential 0.7 V for ≈ 40 min (depth ≈ 0.4 mm). Also shown, optical microscope images of the artificial pit at points indicated on the polarisation curve.

Investigatii la scara micrometrica folosind radiatie X de sincrotron

Fascicul foarte subtire de ordinul micrometrilor



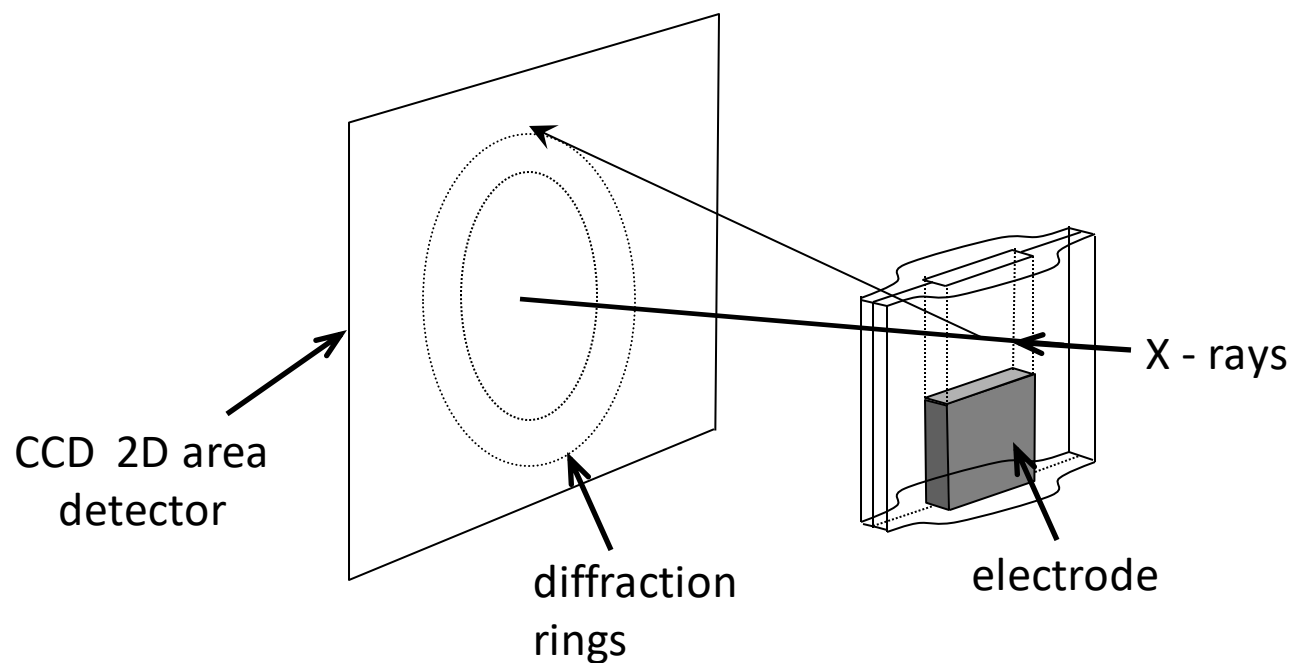
Sursa de radiatie X de 100 de miliarde de ori mai intensa decat radiatia folosita in spitale



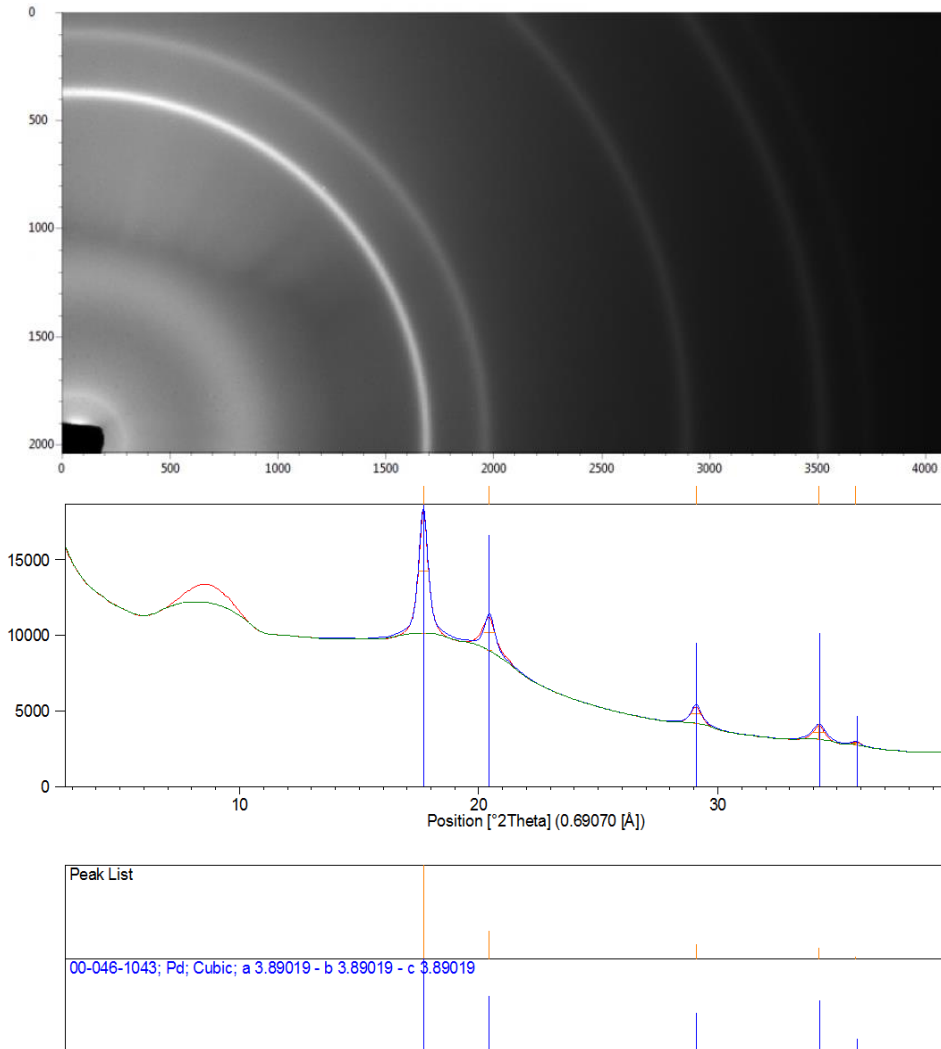
Experimente de:
difractie, spectroscopie etc.

In situ X-ray diffraction experiment

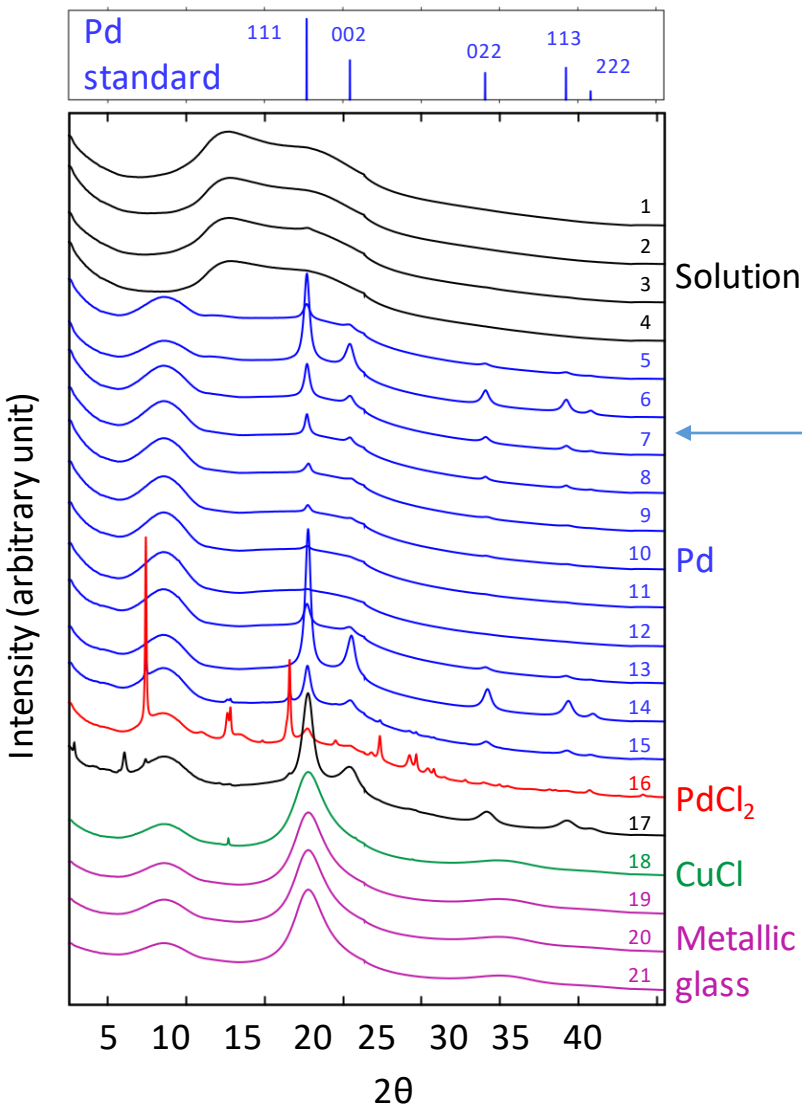
- Focus the beam ($3 \times 10 \mu\text{m}^2$) on the solution above the corrosion products then
- move the sample up, so that the beam passes through the interface in $3 \div 100 \mu\text{m}$ steps (20 s per frame)
- The dissolution rate is ca $3 \mu\text{m}/\text{min}$



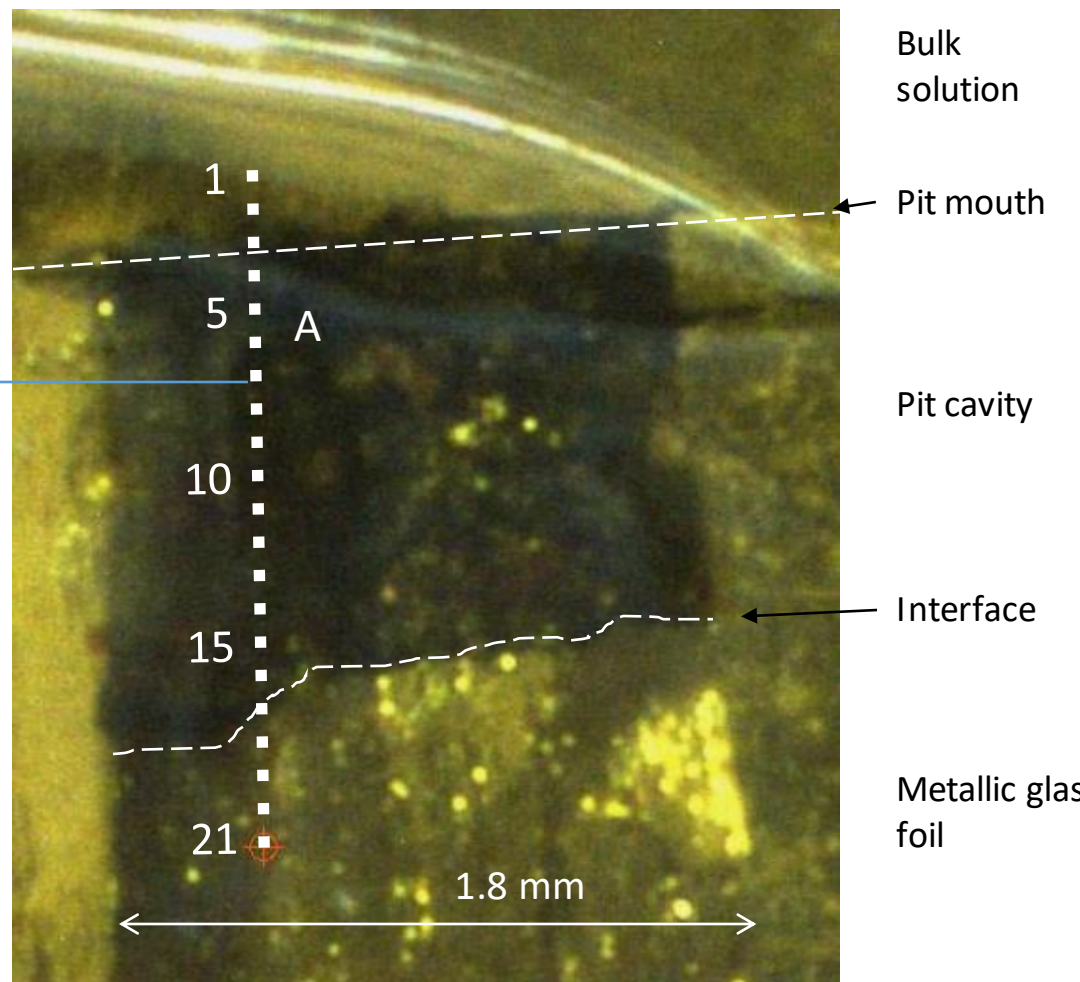
Diffractogramă 2D -> diffractogramă 1D



Ti₄₀Zr₁₀Cu₃₄Pd₁₄Sn₂ metallic glass foil
 0.9 % NaCl, 1.3 V vs Ag/AgCl

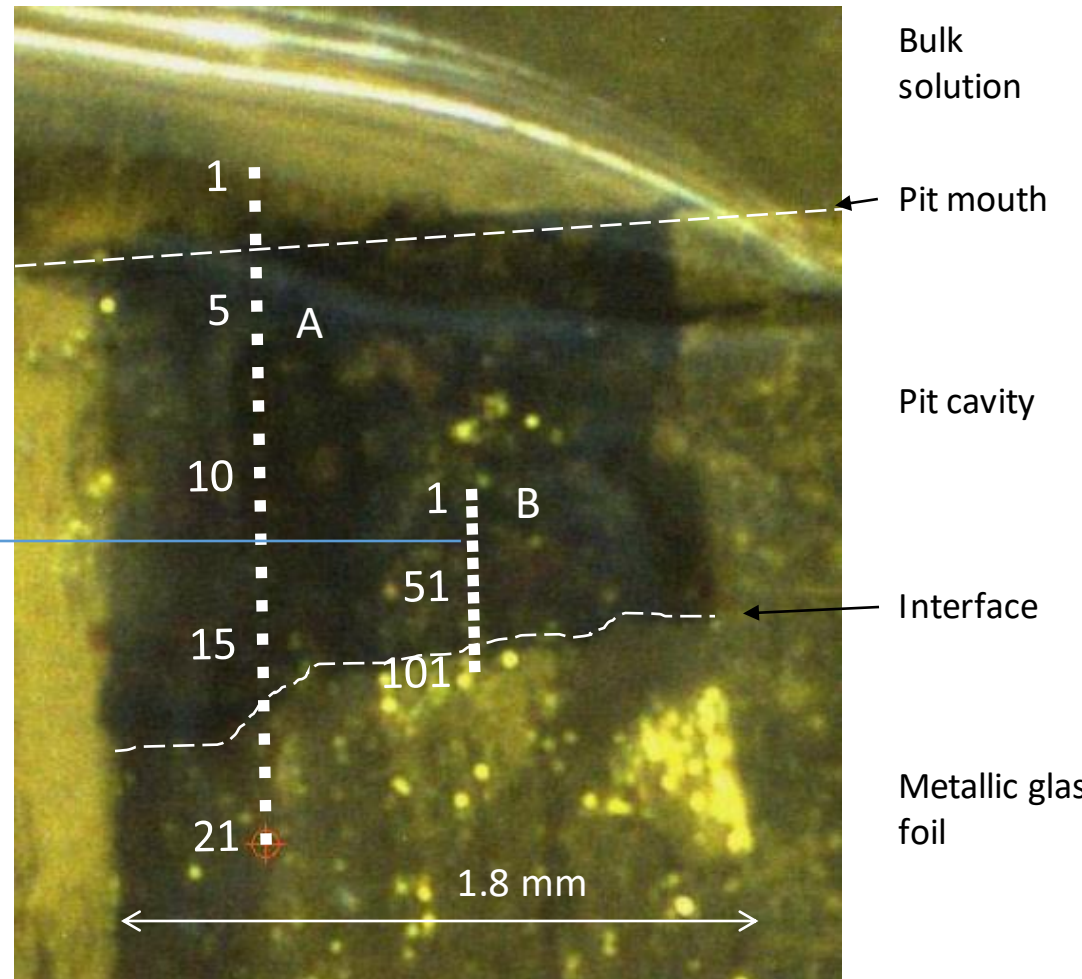
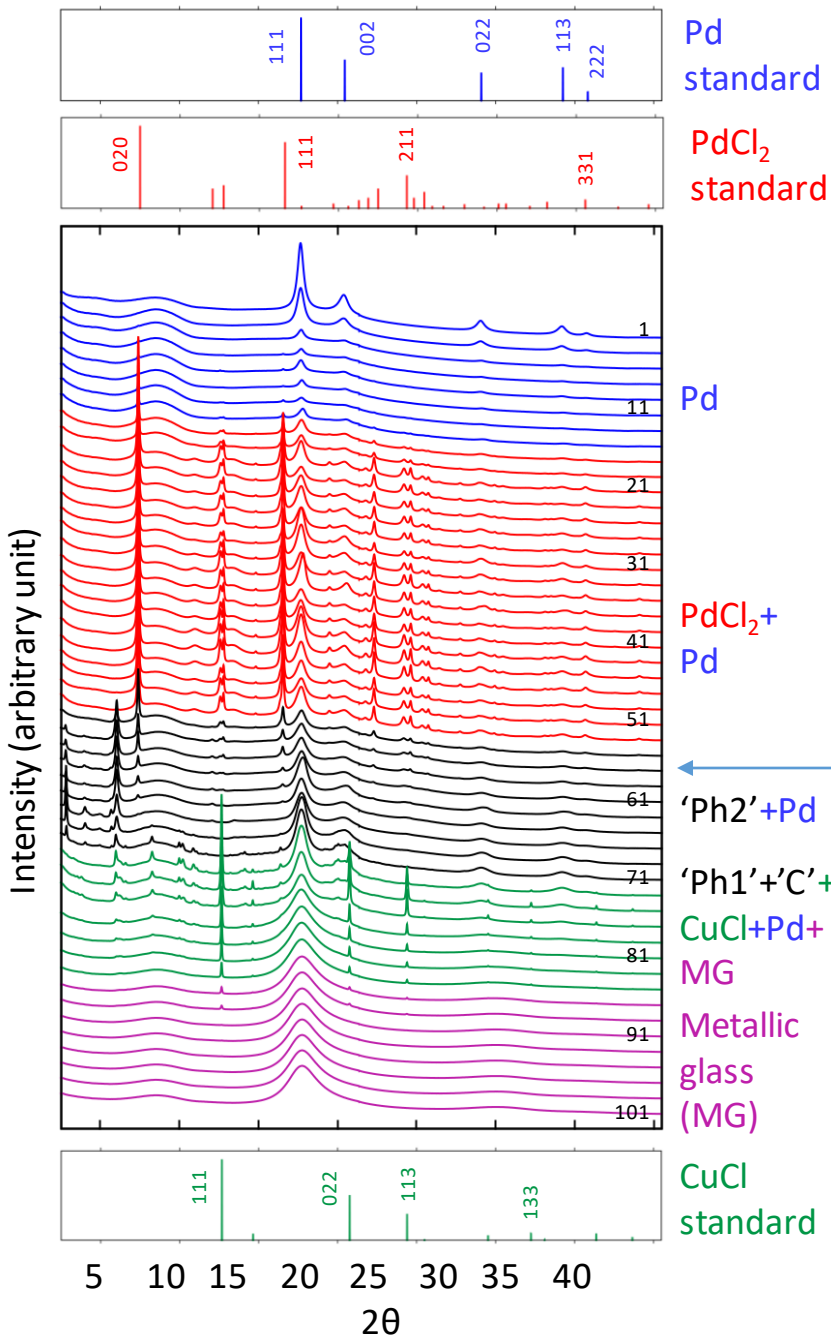


In situ, after 4 h of corroding ...

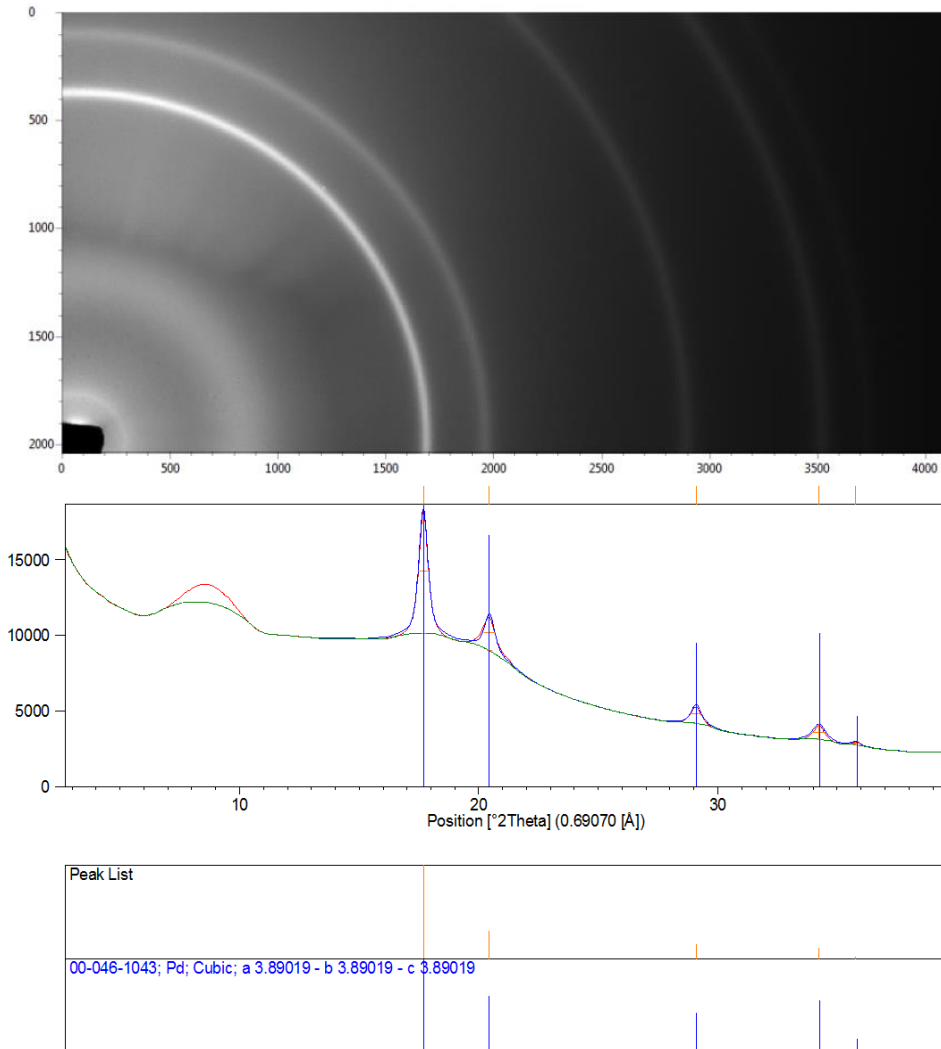


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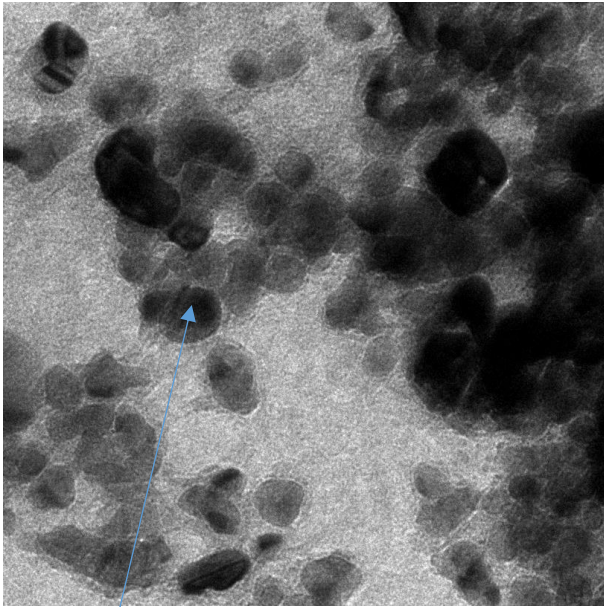


Corrosion products consist mostly of Pd nanoparticles



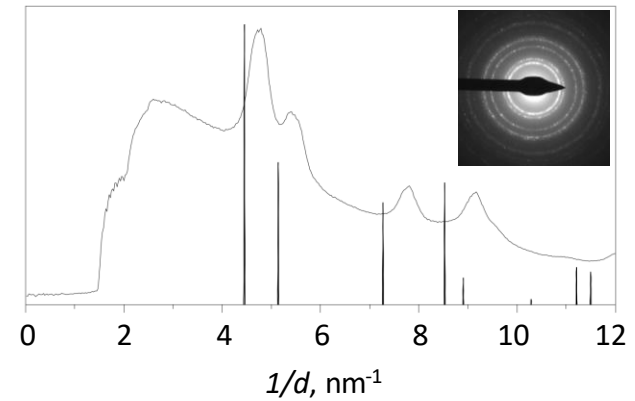
Scherrer
formula:
 ≈ 5 nm
particle size

Microscopie electronică de transmisie



50 nm

Particule de Paladiu cu dimensiunea 5-40 nm



EDX

	Ti	Zr	Cu	Pd	Sn
Mean value (at. %)	5	5	3	85	2
Standard deviation	2.7	2.5	0.8	5.9	0.8

Rezumat

- Implanturile dentare mici necesită aliaje cu rezistență mecanică mare
- Precum: sticle metalice masive
- Precum: $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{34}\text{Pd}_{14}\text{Sn}_2$
- Anthogyr: load to failure 1.5-times higher than that of Ti-6Al-4V, similar fatigue limit
- Produși de coroziune: nano-particule de Pd, PdCl₂, CuCl, etc

Următoarea etapă

Studierea impactului nano-particulelor de Pd etc asupra celulelor structurale și imune (osteoblasts, neutrophils etc)

Implanturi mici din sticle metalice masive? : încă nu