

Aspects Regarding Alloying Effect on Electrochemical Stability of the Sintered Titanium

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The titanium alloys Ti6Al4V, Ti5Al2.5Fe and Ti6Al7Nb sintered in high vacuum, about 10^{-3} Pa, at 1300°C, of element powders with 200 μm grain size presents spontaneous passivation in Ringer solution and submicron corrosion rate, higher electrochemical stability properties than sintered pure titanium. Titanium alloying improves the sintering quality, achieving thus a reduction of the material porosity by 10 ÷ 20% and a corresponding increase in mechanical strength. The porosity and the large specific surface area, of about 0.4m²/g, promote cell growth and bone anchoring at the interface. The Ti6Al7Nb sintered titanium alloy was identified as the most valuable candidate for the medical implants manufacturing, based on its best passivation and hFOB cells citocompatibility properties.

Keywords: titanium alloys, powder metallurgy, cyclic voltametry, passivity, Ringer solution, scanning electron microscopy, cytotoxicity

Although the titanium and titanium alloys are widely used in medicine since 1960, due to the high strength to weight ratio and remarkable stability in human body, getting new titanium implants and new biocompatibility formulæ of these surface, presents even today a great scientific and practical interest [1- 4].

A way of achieving these materials is powder metallurgy, an economically attractive and flexible technique [5- 7]. The sintered materials porosity award ability to conduct through capillarity the biological fluids, to lodge a cellular growth and to secure good conditions of setting and clamping adjacent tissue to the implant. These materials must be carefully rated concerning the stability, because the electrochemical instability in the oral medium of dental devices and in time metal ions release, like: Ti⁴⁺, Fe³⁺, V⁵⁺ which are responsible for cytological genotoxic and allergic effects that can occur.

The study presents processing technique of the powder metallurgy, microstructure, micro composition and analyses the stability performances of the sintered titanium alloys: Ti6Al4V, Ti6Al7Nb and Ti5Al2.5Fe, in a synthetic biological solution, compared with pure sintered titanium. Conclusions of the electrochemical examination made on experimental materials are reported, in two cases, to those the cellular biology regarding this biocompatibility.

Experimental part

Titanium and experimental titanium alloys, table 1, were made of elemental powders with 200 μm grain size: 99.7% titanium powder, manufactured in Romania; 99.5% aluminum powder, manufactured in Romania; 99.5% vanadium powder and 99.5% niobium powder, manufactured in Switzerland; 98% iron powder manufactured in Sweden. After sieve classification and dosing titanium and mechanic alloying powders were homogenized but subsequent were die pressed with

600MPa. The sintering was made in high vacuum, about 10^{-3} Pa and temperature 1300°C. Total porosity and total specific surface area of the sintered samples were estimated with a mercury porosimeter- Pascal 140/240, density was estimated using analytical balance Partner WAS 220/C/2 and micrometer cl.2, and Vickers micro hardness (HV 0.5) with micro hardness meter MX8 – Foundrax. The samples were used for micro structural and micro composition analysis on electronic microscope SEM-FEI Quanta Inspect F with EDS.

Electrochemical investigations were performed with VOLTALAB 40 RADIOMETER electrochemical equipment. Electrochemical cell was a cell 200mL capacity, with three electrodes, platinum accessory electrode with 1cm² surface and saturated calomel electrode was the reference electrode which was a (e.s.c.), connected to cell through salt bridge and a Luggin capillary. The electrolyte used, was a Ringer solution prepared with distilled water and quality salts p.a. Investigated surface was in all case 0.28cm², limited on the samples through joint elastic gasket. The electrochemical tests were performed at 26°C lab temperature. There were applied tree investigation technics : following evolution in time of E_{inc} potential specific corrosion for 30min, Tafel line polarization (Tafel diagram) for evaluation of chemical corrosion rate (i_{corr} , v), a polarization resistance (R_p) and cyclic voltametry. The cyclic voltametry was performed in two serial polarization cycles, without ohmic loss compensation and it was applied 1000 ÷ 4000mV.e.s.c range, with 100mV/s. speed polarization The techniques applied have allowed experimental characterization of the samples, regarding the passivation capacity and their stability in work solution. Biocompatibility of the sintered samples was evaluated in vitro, through (3-(4, 5-dimethylthiazol -2-il)-2, 5-diphenyl-tetrazolium bromide) MTT cytotoxicity assay, on human fetal osteoblast progenitor cells lines (hFOB).

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No.	Sample	Sintered material	Average density [g/cm ³]	Total porosity [%]	Total specific surface area [m ² /g]	Average hardness [HV]
1	Ti - Sin	Ti	3.53	36	0.402	323
2	Ti6Al4V- Sin	Ti6Al4V	3.48	33	0.625	310
3	Ti6Al7Nb - Sin	Ti6Al7Nb	3.59	30	0.393	344
4	Ti5Al2.5Fe - Sin	Ti5Al2.5Fe	3.61	16	0.448	363

Table 1
PHYSICO-MECHANICAL
CHARACTERISTICS OF THE
EXPERIMENTAL SAMPLES

Results and discussions

In table 1 are presented the physico-mechanical characteristics of the experimental samples. There were obtained mostly high values of the total porosity that are correlated with relatively brutish size of the processed metal powders. For porous sintered materials hardness is a function of density, by binding force between powder particles, as well as strength degree of powder particles in the attempt position and these characteristics are determined by sintered materials composition.

Microstructural examination of the samples relieved the porous and heterogenic aspect of all these materials, figure 1, this sintered titanium alloys aspect the is mostly similar, due to the used of only one grain size of powder, inclusive identical conditions of applied processes. The titanium alloy sample with iron has the best compactness, after sintering was obtained a porosity about twice lesser in regard of the other experimental materials, due to a more increased local melting; at the sintering the aluminum particles situated close to the pores, where there is air, causes aluminothermy reactions, exothermic reactions, this having as effect getting a local high temperature (about 3000°C), which favours the heavy fusible melting particle for niobium, titanium, vanadium and iron.

Qualitative microanalysis has pointed out a good distribution of the alloy elements: niobium, vanadium, iron and aluminum in the titanium matrix. Figure 2 presents an

EDAX qualitative X-ray microanalysis, a SEI image and elements distribution for the sintered titanium alloy sample - Ti6Al7Nb.

In the figure 3 is shown the electro evolution mixed potential of the samples, maintained on Ringer's solution for 30 min., at 26°C temperature. The sintered titanium is passivating in Ringer's solution, his mixed of corrosion potential, continually ennobling and due to the advanced oxidation in the air, during the sintered operation, this sample has a maximum porosity. The samples Ti6Al4V-Sin and Ti6Al7Nb-Sin are easily activated with 20mV and respectively 60mV, during the whole time of exposure, though with a trend of limit at the end.

Ti6Al7Nb-Sin sample is recording mixed potential corrosion with a 50mV than Ti6Al4V-Sin sample, at the end of imersion. The iron damages to the electrochemical behavior of sintered titanium, even if it enabled a better sintering, the iron samples had lower porosity. Iron is responsible for the mixed corrosion potential of each sample at values 200 mV more negative, than the samples which do not contain this element and for those which loose this content during the immersion. Niobium alloying ensure a better evolution of the mixed corrosion potential.

The resulted electrochemical characteristics of the samples from the data from Tafel linear polarization are synthetically shown in table 2. In the table 2 are noted

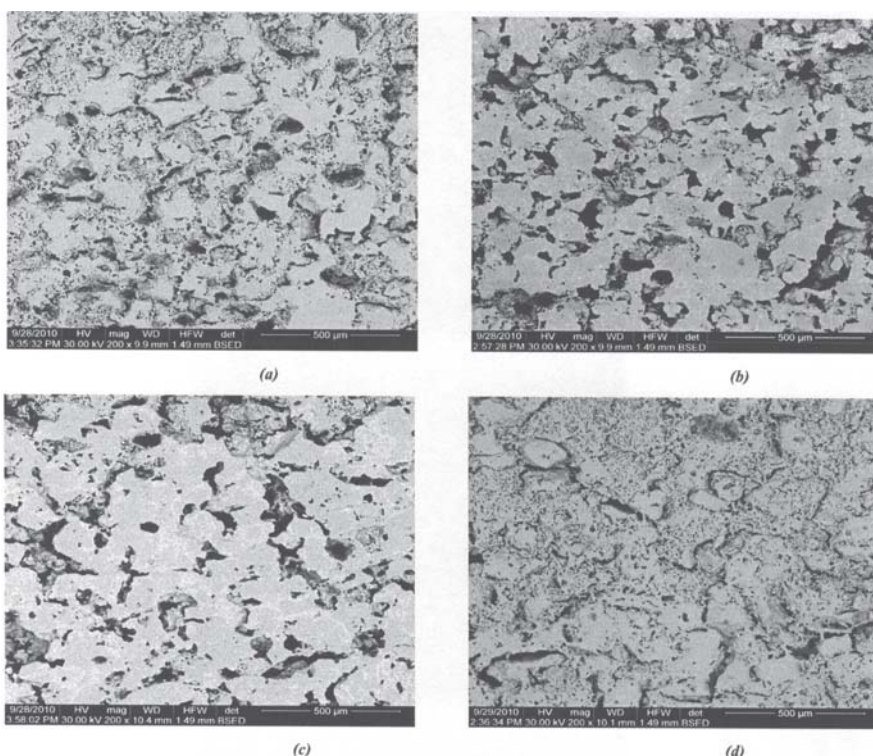


Fig.1 SEM micrographs – Sintered materials from titanium and titanium alloys (X200)
(a)Ti6Al4V-Sin, (b) Ti6Al7Nb-Sin,
(c) Ti5Al2.5Fe-Sin; (d) Ti-Sin

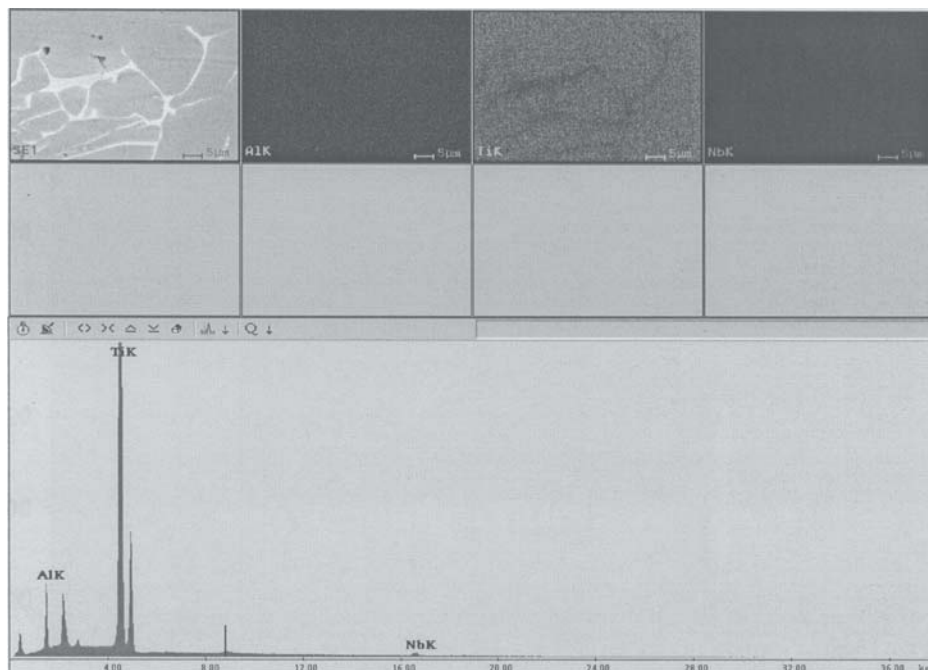


Fig. 2 SEI elements distribution (Al, Ti, Nb) and qualitative microanalysis EDAX for experimental sample Ti 6Al7Nb-Sin

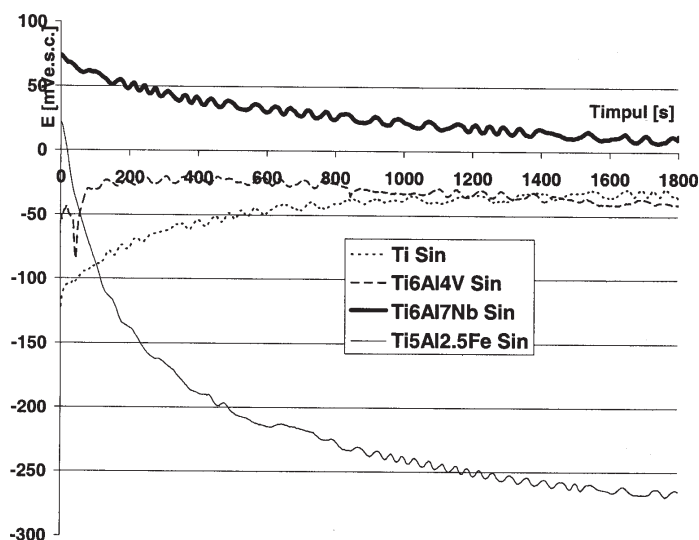


Fig.3 Mixed potential evolutions of corrosion – time, in Ringer solution at 26°C

Tafel gradient, anodic and cathodic (Ba and respectively Bc). One of these curves of polarization and its processed graphic are shown in figure 4. The samples record very different currents and rate of corrosions because of the different chemical composition and high specific area. For the sintered samples are measured the corrosion between ten to hundred of microns per year, 156 $\mu\text{m}/\text{year}$ is the a value registered for sintered titanium, these sample present also the biggest porosity; therefore the electrolyte penetrates, more the structure of this sample, having available a big specific surface 0.402 m^2/g , with three orders of range (tabel 1). Generally, the rates are calculated reporting the current at a plane surface of 0.28 cm^2 , limited on the samples by using gasket, however real exposed surface being howerer as it was shown much bigger.

Therefore, the reported values for the sintered porouse materials, as those examined, have comparative value, and the rates of 10÷20 $\mu\text{m}/\text{year}$ are in reality submicronics (less with two, three orders of dimensions) and thus completely satisfactory.

According to these evaluations, the sample with content of iron have showed the lowest anticorrosive performance; it must be taken in account the fact that in this case, the iron which oxidizes and which is responsible for these high values, it is not toxic for human body. The samples Ti6Al4V-Sin and Ti6Al7Nb-Sin present comparable rates of corrosion in Ringer solution. The polarization applied at cyclic voltametry generally increases the passivity state of the sintered material. This passivation is emphasized by different route of the cycle two of polarization situated under first cycle, figure 5. Mostly it can be observed the presence of passivity ranges until 1000m Ve.s.c., then oxidative processes begin depending on the content of water from the solution.

All samples show spontaneous pasivization in Ringer's solution at 500mVe.s.c., Ti6Al7Nb-Sin sample has recorded

Table 2
ELECTROCHEMICAL CHARACTERISTICS MEASURE BY A TAFEL LINEAR POLARIZATION

Ti-Sin	-111.9	0.83	109.5	-62.5	16.418	156
Ti6Al4V-Sin	-83.3	12.05	85.1	-83.4	1.162	11.08
Ti6Al7Nb-Sin	-39.7	6.75	96	-81	2.135	20.36
Ti5Al2,5Fe-Sin	-363.5	0.93	85.4	-87.5	14.841	141.6

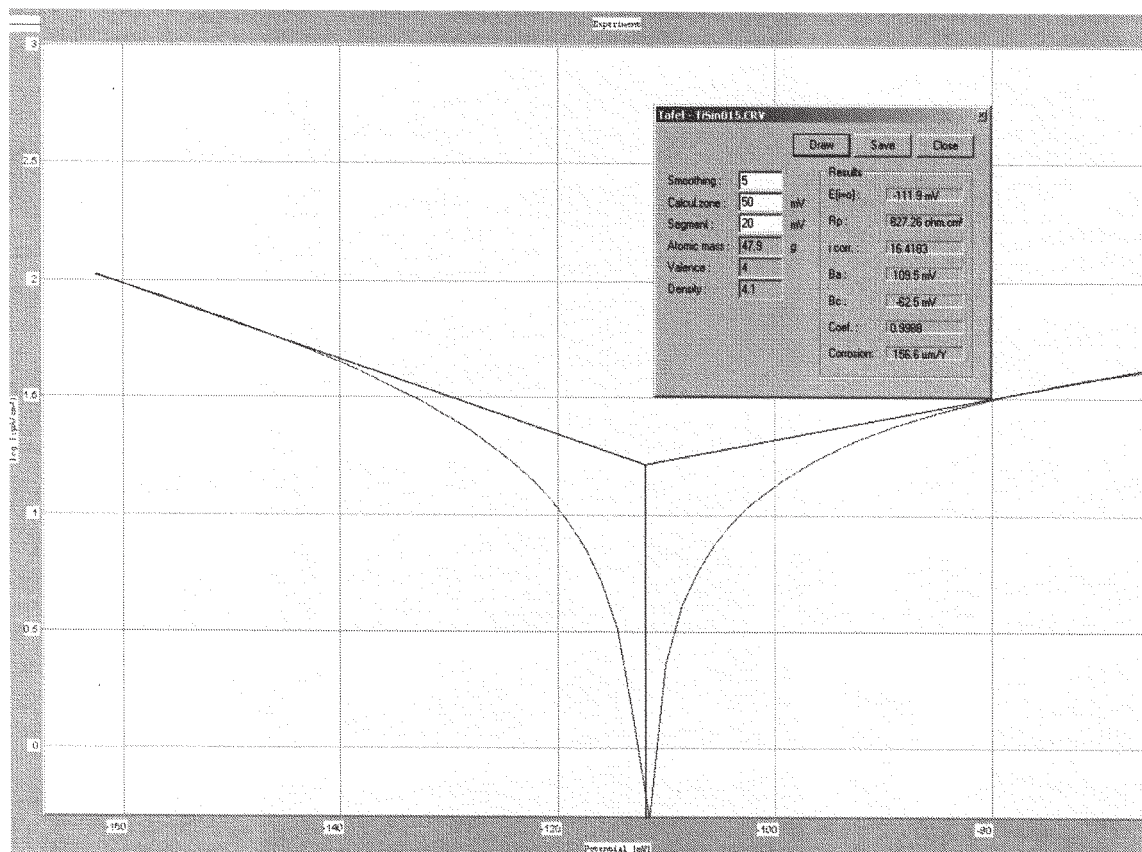


Fig.4. Tafel linear polarization, sample Ti-Sin

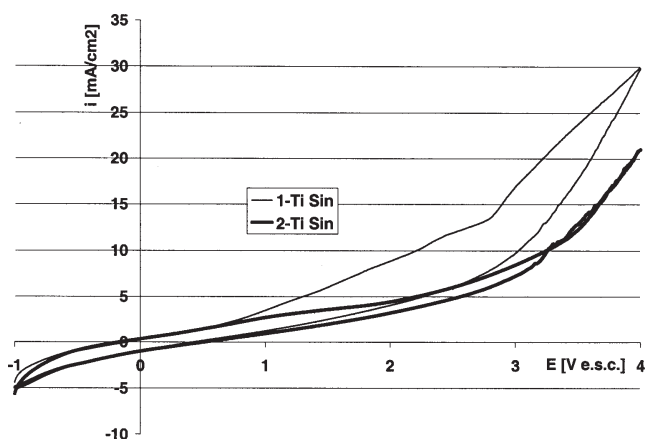


Fig.5. Curves of cyclic polarization, cycles 1 and 2, Ringer solution at 26°C assigned with a speed of 100mV/s for the sample Ti-Sin

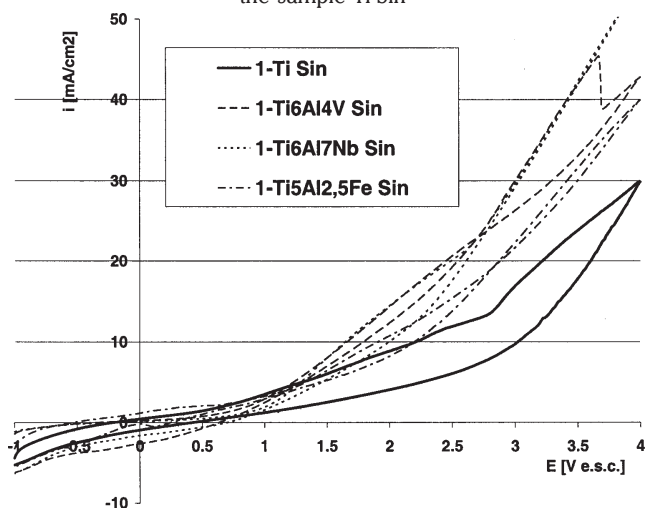


Fig.6. Curves of cyclic polarization, cycle 1, Ringer solution, at 26°C, with 100mV/s speed

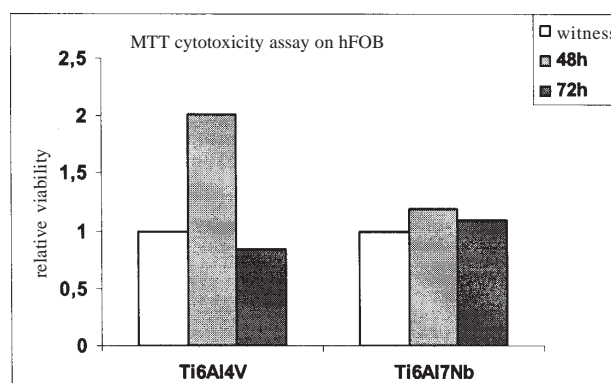


Fig.7. MTT cytotoxicity assay on human fetal osteoblast progenitor cells lines (hFOB) in presence of Ti6Al4V-Sin și Ti6Al7Nb-Sin samples

the smallest value of 0.46mA/cm² pasivization current; the same sample shows the smallest overtonsen of oxigen discharge. On the other hand the samples Ti6Al4V-Sin and Ti6Al2.5Fe-Sin (and the sample Ti-Sin, in the second cycle of polarization, fig. 5) have return routes from the high limit of the range potential investigated, situated over the direct branch, 2800 mV.e.s.c., this one indicated a trend of surface activation. Moreover, in the case of vanadium alloy sample it was an abrupt significant increment of current to 3690mV.e.s.c. on return, followed by surface repassivation. This manifestation is specific to the initiation of the local corrosive process, pitting or crevasse, (fig. 6), phenomen favoured examined materials porosity. The sample Ti6Al7Nb-Sin has demonstrated the best electro-chemical performances to cyclic voltametry.

MTT cytotoxicity assay on human fetal osteoblast progenitor cells lines (hFOB), figure 7 emphasizes the fact that both after 48 and 72 h of incubation is observed, a

decrease light, insignificant, of cellular viability in the presence of Ti6Al4V-Sin sample, whereas in case of sample from Ti6Al7Nb-Sin alloy, the cellular viability is a little higher than the control cells a coherent remark with electrochemical examination conclusions.

Conclusions

The sintered titanium alloyed with aluminum, vanadium and niobium are spontaneous passivated in Ringer's solution and presents higher electrochemical performance (velocity of corrosion, passivity current) relative to the sintered pure titanium. Alloying titanium improves sintering quality, thus obtaining a reduction of material porosity to 10÷20% and an adequate increase of strength illustrated here by hardness. The presented results allow the estimation that sintered titanium alloys especially that with Ti6Al7Nb-Sin formula presents both electrochemical stability in Ringer's solution and citocompatibility properties with hFOB cells. Also specific porous microstructure is suitable to anchoring and cell increasing at the interface.

These characteristics make of these materials a serious candidate for medical implants manufacturing. It is expected that the application on their surface of adhesive bioceramic layers to increase this convenient characteristics.

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