

Mechanical, physical, and chemical characterization of Ti–35Nb–5Zr and Ti–35Nb–10Zr casting alloys

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Abstract Titanium is used due its excellent properties in medical and dentistry areas. With the objective of exploiting better mechanical properties, not altering its biocompatibility, it was intended to add niobium and zirconium to the titanium, being formulated two alloys Ti–35%Nb–5%Zr (alloy 1) and Ti–35%Nb–10%Zr (alloy 2) wt% produced by an arc melting method. The chemical analysis of the samples was accomplished by X-ray fluorescence, and the microstructural evaluation by scanning electron microscopy and X-ray diffraction. The mechanical tests were: Vickers hardness, tensile strength, mechanical cycling, and fracture analysis. The results allowed characterizing the alloy 1 as $\alpha + \beta$ type and the alloy 2 as β type. It is found that the alloy 1 presented larger hardness and smaller tensile strength than the alloy 2. The fractures, after the tensile test, were of the ductile type and, after the mechanical cycling, they were of the mixed type for both alloys.

1 Introduction

Titanium and its alloys attract attention for application as biomaterial in medical and dentistry areas due to a favorable combination of mechanical, chemical, and physical properties such as low density, high mechanical resistance, excellent corrosion resistance, and good biocompatibility [1–5].

Another important factor of implants developed to substitute or interact with bone is the modulus of elasticity. This modulus should be low and closest to that of the bone for promoting bone healing and remodeling [6, 7]. The cortical bone has modulus of elasticity between 10 and 30 GPa [6, 8] and the commercially pure titanium, around 104 GPa [8].

Since 1985 [9], implants biocompatible materials have been developed to substitute the main titanium alloy, Ti–6Al–4 V, due to the probable toxicity of vanadium and aluminum [10, 11] and the advantage of using a material with low elastic modulus [12, 13]. The Ti–6Al–4 V has modulus of elasticity around 105 GPa [14].

A presented solution was to add niobium (Nb) and zirconium (Zr) to titanium (Ti), since the first one acts as β -stabilizer, which improve the material mechanical properties, and the second one is used as solid-solution hardener and it has similar chemical properties to titanium.

Titanium alloys associated with Nb and/or Zr have potential for dental alloys since its mechanical properties [2, 4, 13, 15–18], corrosion resistance [3, 19, 20], and biocompatibility [4, 17, 21–24]. For example, Wang [13] found that the alloy Ti–13Nb–13Zr has lower elastic modulus and better tensile strength when comparing to Ti–6Al–4 V. Godley et al. [19] analyzed that Ti–45Nb has better corrosion resistance than Ti–6Al–4 V. Okasaki et al. [24] and Okasaki and Gotoh [23] found that Ti–Zr–Nb–Ta

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alloy has less metals release than alloy with vanadium in its structure showing better biocompatibility, in vivo and in vitro studies, respectively.

Although there is in the literature works showing Ti alloys combined with Nb and/or Zr, it is necessary to find a good mass proportion of those elements, and a melting method associated to an appropriate sequence of heat treatments for better characterize the material mechanical, physics and chemical properties.

In the present work the alloys Ti–35%Nb–5%Zr and Ti–35%Nb–10%Zr (wt%) were analyzed to validate their application as a biomaterial for osseointegrated fixture manufacturing in dentistry. The mechanical, physics, and chemical characteristics of those alloys were evaluated through chemical analysis, X-ray diffraction, Vickers hardness, scanning electron microscopy, tensile strength and mechanical cycling, and fracture analysis.

2 Materials and methods

Two alloys were evaluated in this work. The nominal composition were Ti–35Nb–5Zr, called alloy 1 and Ti–35Nb–10Zr, called alloy 2. All compositions in this study are given in wt%. The starting materials Ti, Nb, and Zr presented purity degrees equal or superior 99.00%. The ingots of 30–70 g were arc melted utilizing a water-cooled copper hearth under an argon atmosphere, and in order to ensure chemical homogeneity, they were flipped and remelted 3–5 times. The ingots were then heat treated at 1000°C for 8 h, under argon atmosphere, and furnace cooled. Then, the ingots were machined as discs (diameter: 6 mm and height: 5 mm) and in samples (according to ASTM E606 [25] and ASTM E8 M [26]). Afterwards, the samples were encapsulated in quartz, under argon atmosphere, and then, they were submitted to another heat treatment at 1000°C for 1 h and air cooled to improve the alloys mechanical behavior and to relieve tensions generated during the machining.

The chemical composition was checked by X-ray fluorescence (Shimadzu EDX-800) and microstructural analysis of the alloys were performed using scanning electron microscopy (SEM, Carl Zeiss, 440) and X-ray diffraction (XRD, Siemens, D-5000), in discs samples. Samples were prepared by standard metallographic

techniques used for Ti and Ti alloys and etched with Kroll's reagent containing distilled water, nitric acid, and hydrofluoric acid (5:2:1 in volume).

Mechanical characterization of these alloys was based on hardness test, tensile strength and mechanical cycling, and fracture analysis. Vickers hardness was measured through a Buehler equipment with a load of 500 gf applied for 15 s in eight regions of eight discs of each alloy. Tensile tests were carried out in a servo-hydraulic machine (MTS-810), equipped with Test Star II with a 10 kN load cell at a constant speed of 1 mm/min, to determine the tensile strength in five samples of each alloy. Mechanical cycling tests were carried out in the same MTS machine set to a frequency of 15 Hz with 10^4 cycles and load with a value of 60% of the ultimate tensile strength mean, in five samples of each alloy. The fracture surfaces were examined using SEM and fractography analysis was performed according to literature [27]. The results of hardness and tensile tests were analyzed with *t*-student test ($P \leq 0.05$) to compare the two alloys.

3 Results and discussion

The chemical compositions of the alloys are presented in Table 1 and show that the final compositions are close to the planned.

Figure 1 presents X-ray diffractogram of Ti–35Nb–5Zr (alloy 1) where α and β phases were formed and Fig. 2 presents X-ray diffractogram of Ti–35Nb–10Zr (alloy 2) where only β phase was formed.

The α phase in alloy 1 precipitated, probably, during the air cooling after the 1 h heat treatment at 1000°C. This result confirms that can have α precipitation during the cooling of a heat treatment accomplished in β field, above β -transus.

As the alloy 2 diffractogram shows no α precipitation and this alloy has more Zr concentration, it can be suggested that Zr inhibits α precipitation, according to Tang et al. [28].

In this study no metastable phases were formed as martensites or ω , which is desirable as those phases can increase the values of hardness and elastic modulus. Since those phases can make alloys more fragile, they should be avoided [28].

Table 1 Nominal and measured compositions of the alloys Ti–35Nb–5Zr and Ti–35Nb–10Zr

Alloys	Nominal composition (wt%)			Measured composition (wt%)		
	Balance Ti	Nb	Zr	Balance Ti	Nb	Zr
Ti–35Nb–5Zr	60	35	5	54.19	38.27	6.20
Ti–35Nb–10Zr	55	35	10	52.31	36.61	9.74

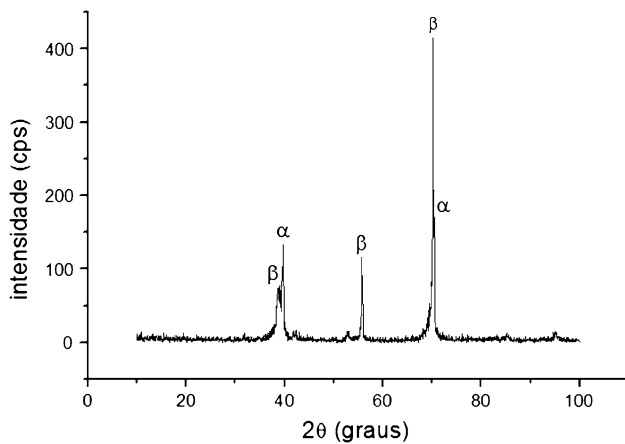


Fig. 1 X-ray diffractogram of Ti-35Nb-5Zr

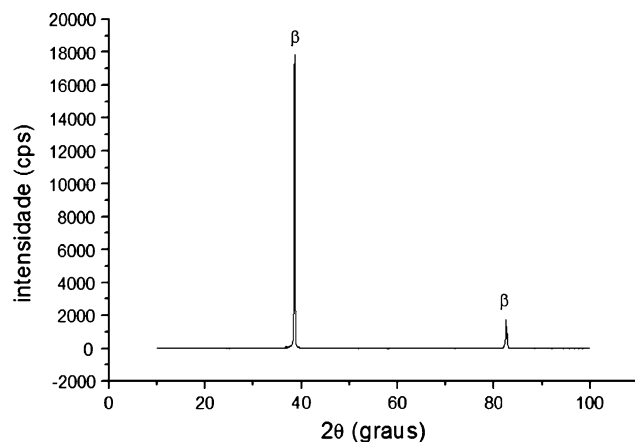


Fig. 2 X-ray diffractogram of Ti-35Nb-10Zr

Usually, metastable phases are formed during heat treatment cooling when the alloy has limited amounts of β -stabilizers elements [8, 28, 29].

Besides the high concentration of β -stabilizer Nb presents in alloys 1 and 2, the no ω phase precipitation it is due to the Zr addition in their compositions [28, 30, 31], although it is considered as a neutral element [29].

In addition, those phases can be identified by SEM micrographs. The samples of alloy 1 (Fig. 3) exhibit β grains with coarse boundaries that can indicate, probably, the presence of α phase at those boundaries once α phase preferentially occurs at grain boundaries rather than in grains [32]. Niinomi in 2003 [4] had difficulty to find α phase precipitated on micrographs too. Figure 4 shows the presence of β phases on alloy 2.

The mean values of Vickers hardness were 240 ± 28 HV for alloy 1 and 185 ± 14 HV for alloy 2. These results are statistically different ($P < 0.0001$). These findings confirm the Kobayashi et al. [2] conclusions that $\alpha + \beta$ alloys had

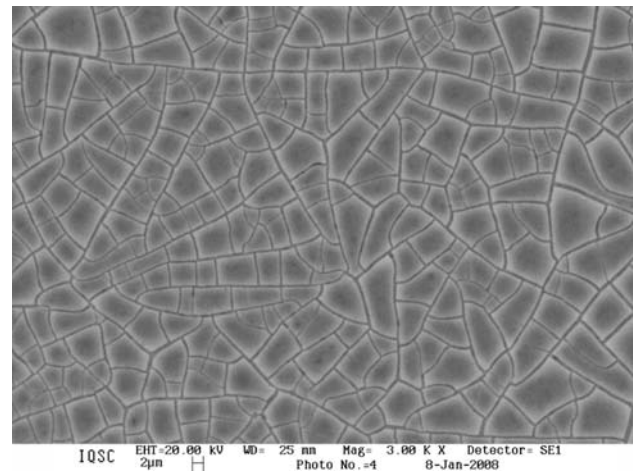


Fig. 3 Microstructure of Ti-35Nb-5Zr

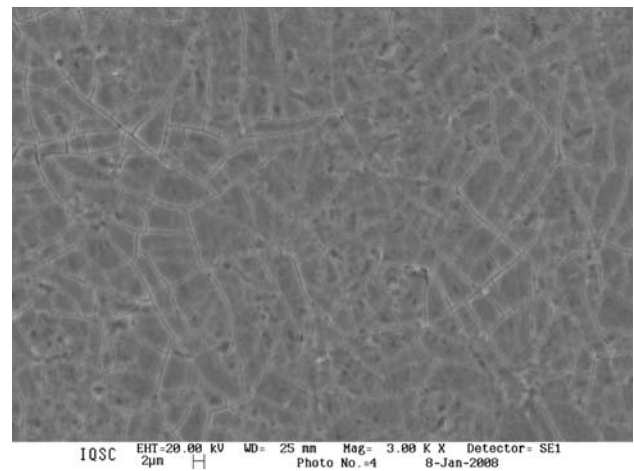


Fig. 4 Microstructure of Ti-35Nb-10Zr

higher value of hardness than β ones, when comparing the Ti-Nb-Zr alloys, with different Nb concentrations.

The larger hardness values of alloy 1 can be related with the α phase on its structure exercising the function of hardening phase. Niinomi, in 2003 [4], had observed increase of the hardness value of Ti-29Nb-13Ta-4.6Zr alloy that, when heat treated, had α phase precipitation.

Another important fact found by Ferrandini et al. [16] is the presence of Zr in the Ti alloys acting as an element that hinders hardness improvement, when those alloys are heat treated. Probably, the zirconium in larger amount in alloy 2 had eliminated α phase, making this alloy more susceptible to indentation and, consequently, with lower mean hardness value.

By alloy 2 results, what in its structure has only the presence of β phase, it is verified lower mean hardness value in relation to alloy 1. That outcome indicates that alloy 2, possibly, it is more ductile and, then, should have better forming when compared to alloy 1.

Although the hardness values presented are different, they are low and in accordance with the established variation of 150–330 HV for titanium hardness values, depending on the titanium degree, its purity and on the other chemical elements present in titanium alloys [33]. The found results are in agreement with the expected, because the hardness can be defined as resistance to permanent deformation, and the biomaterial should not present that value high when requested for dental implants.

Accordingly to X-ray diffraction and microstructures characteristics and obtained hardness values, it can be established that α and β phases are present in alloy 1 and just β phase in alloy 2.

The mean values of maximum tensile strength, obtained from tensile strength, were 486 ± 20 MPa for alloy 1 and 546 ± 54 MPa for alloy 2 ($P = 0.0497$), and they are in agreement with the parameters considered satisfactory for titanium alloys biomaterials [8]. Those results are similar to the found by Schenider et al. [18], in 2005, for the Ti–1.1Nb–7.1Zr alloy, that it was of 499 MPa, and also for Elias et al. [15], in 2006, for the Ti–41.1Nb–7.1Zr and Ti–35.3Nb–7.1Zr–5.1Ta, with values of 490 ± 27 MPa and 550 ± 10 MPa, respectively.

As a result of statistical analysis, the alloy 2 presented higher maximum tensile strength mean value compared to alloy 1 ($P < 0.0497$). That result is, possibly, correlated with the largest amount of Zr present in alloy 2. That fact demonstrates that Zr increases the mechanical resistance of titanium alloy verifying its function as solid solution hardening.

In agreement with those resistance and with the stress-strain curves (Figs. 5, 6), it is verified that the alloys 1 and 2 are characterized by an elastic perfectly plastic behavior, because the same ones do not have hardening ability [15, 18]. That property is interesting for biomaterials that need to be easily conformed that are the case of

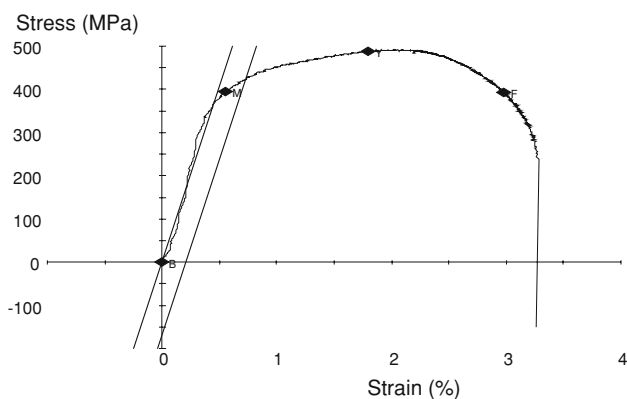


Fig. 5 Stress–strain curve of Ti–35Nb–5Zr

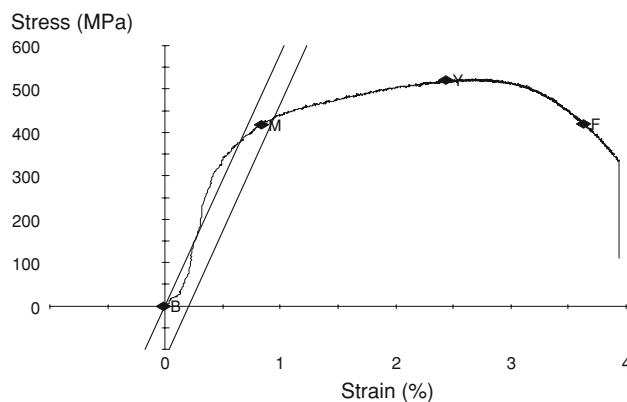


Fig. 6 Stress–strain curve of Ti–35Nb–10Zr

the Ti dental implants that, as they possess a complex geometry, they demand such conformity process during its production.

Another important data, obtained in the tensile test, it refers to the maximum load (N), once 60% of the resistance mean were used for the accomplishment of the mechanical cycling test, according to display the Table 2.

After the dynamic test, three samples of each alloy supported the 10^4 cycles established in that study at a frequency of 15 Hz. Lin et al. [34], in 2005, verified that Ti–Nb–Zr alloys, when submitted to high repetitive loads, they supported 10^5 cycles, at a frequency of 10 Hz.

The titanium alloys capacity to support high repetitive loads it is associated to the crystalline structure and the processes of solid state reactions.

The crystalline structures of the alloys 1 and 2 are compose by $\alpha + \beta$ and β phases, respectively, reminding that α phase is characterized by a hexagonal compact structure, and β phase as a cubic centered body structure.

Table 2 Mean values of maximum tensile strength and fixed load to mechanical cycling test (N)

Alloys	Maximum tensile strength mean values (N)	Fixed load to mechanical cycling test (N)
Ti–35Nb–5Zr	3440 ± 144	2064
Ti–35Nb–10Zr	3863 ± 382	2318



Fig. 7 Fractured sample after tensile test with cup–cone fracture

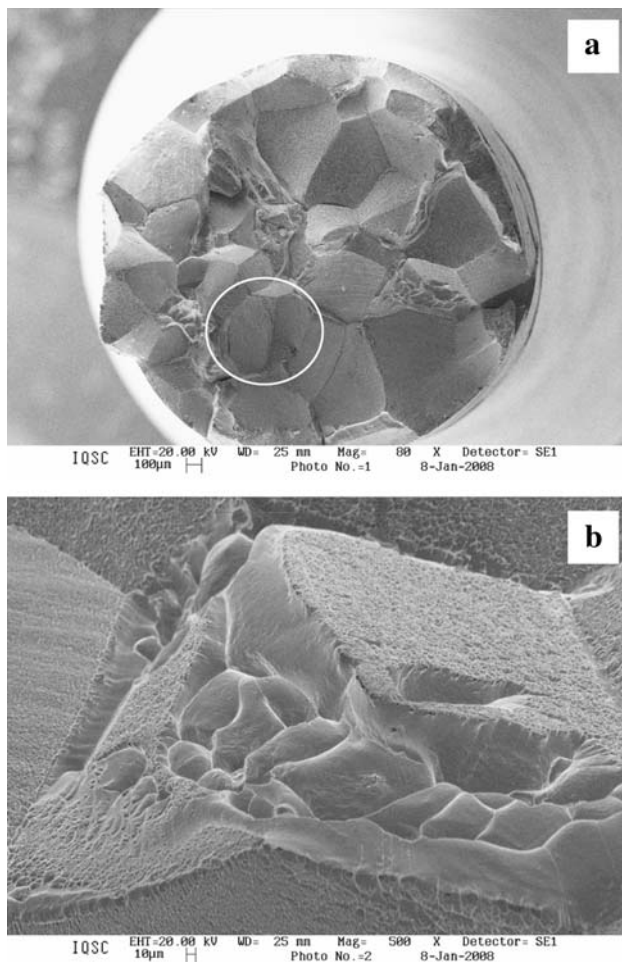


Fig. 8 SEM images of Ti35Nb–5Zr alloy sample 80× (a) and 500× (b) regarding the circle, showing the *dimples* presence, after tensile test

Those structures are very ordinate and they form a very defined crystalline grating.

The solid solution is characterized by the mixture of two or more chemical elements forming a single phase, taking to the homogeneity when that reaction is complete [33], fact that happened with the alloys 1 and 2, that presented high ductility, and they propitiated mechanical cycling resistance in the studied conditions.

However, the other two samples of each alloy did not support the 10^4 cycles, probably, due to limitations in the casting process, since the presence of porosity induced by casting is a critical paper in the materials performance front to the fatigue [3].

That fact is supported by Lin et al. [34], who consider that three factors affect their studied materials behavior significantly front to fatigue, as the Ti–13Nb–13Zr alloy. Those factors were: presence of surface pores induced by casting, pores location, and inherent material mechanical property. Besides, when the stress on a certain point, as in

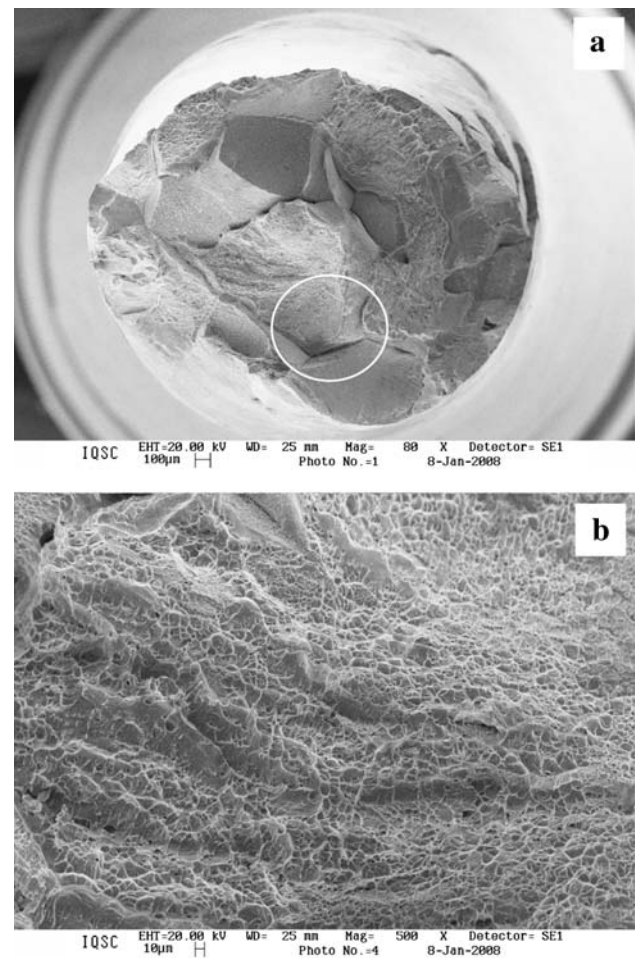


Fig. 9 SEM images of Ti35Nb–10Zr alloy sample 80× (a) and 500× (b) regarding the circle, showing the *dimples* presence, after tensile test

the pore, becomes larger than the conventional elastic limit of the material, a plastic deformation can happen at each cycle, taking to a potential of initial fracture by fatigue [35].

The presence of pores is practically inevitable during the melting process [34], and it can justify the beginning of the fractures in the alloys, that failed during the mechanical cycling in this study.

Macroscopically, it was observed a reduction of section of the halters samples during the tensile test, and after the rupture, a cup–cone fracture (Fig. 7), that are characteristic of ductile materials, that is, they have plastic deformation.

The plastic deformation is characterized by low stress variation by high deformation, taking to the decrease of the tested material cross-sectional area. That characteristic is important in the metallic materials shaping, as, for instance, in the manufacturing process of dental implants.

Microscopically, it was verified by SEM the predominance of ductile fracture with *dimples* after the tensile test

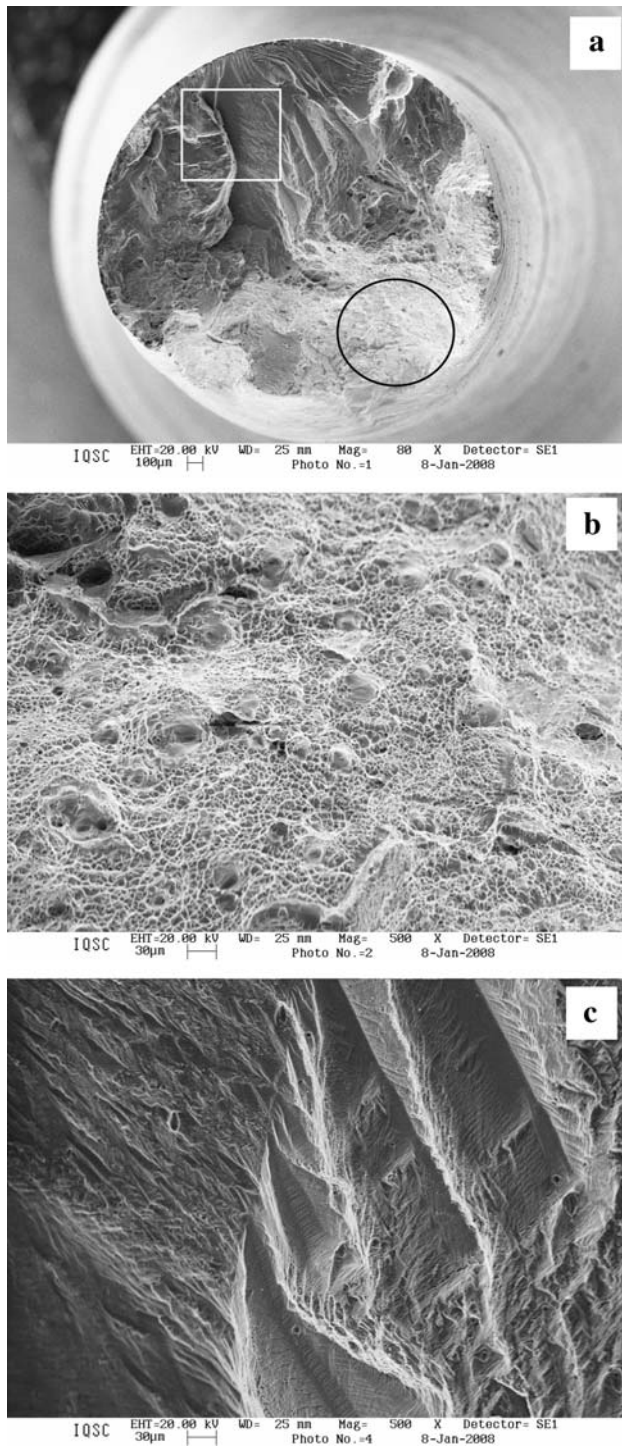


Fig. 10 SEM images of Ti35Nb–5Zr alloy sample 80× (a), 500× (b) regarding the circle, showing the *dimples* presence and 500× (c), regarding the square, showing the cleavage presence, after mechanical cycling

(Figs. 8, 9), and mixed fracture with the presence of *dimples* and cleavage after the mechanical cycling on the halters that were fractured (Figs. 10, 11), for alloys 1 and 2.

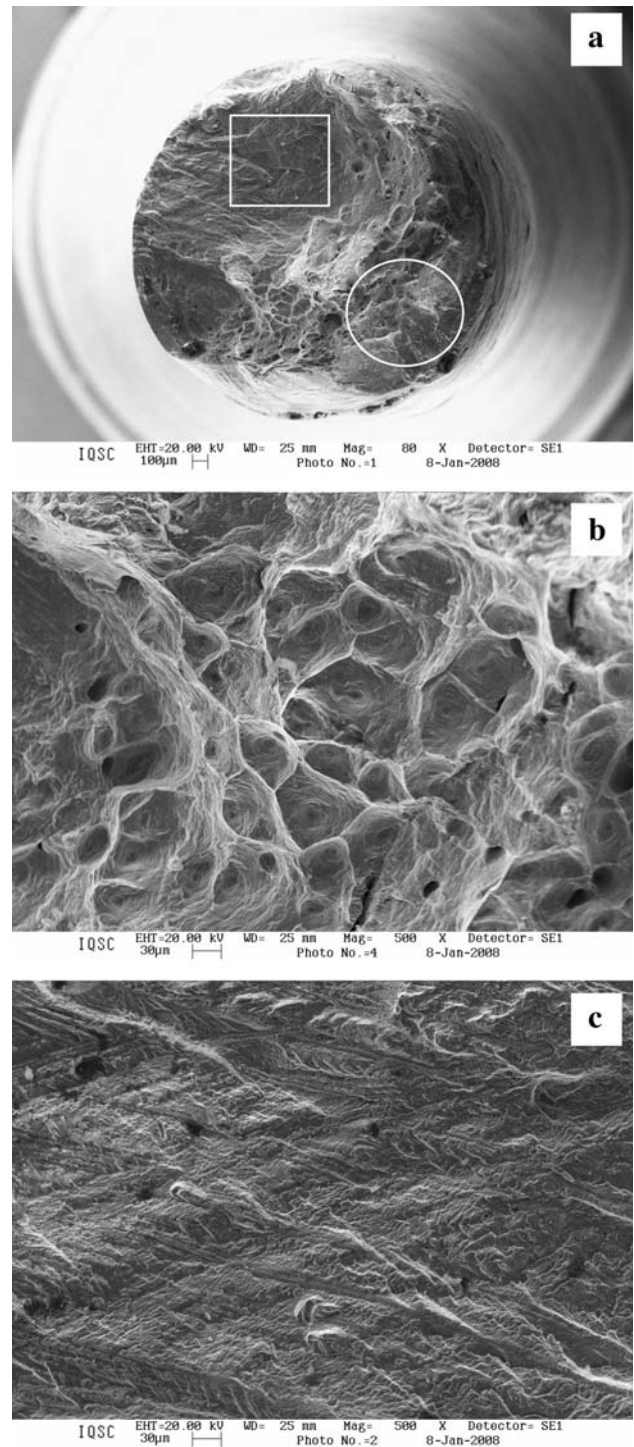


Fig. 11 SEM images of Ti35Nb–10Zr alloy sample 80× (a), 500× (b) regarding the circle, showing the *dimples* presence and 500× (c) regarding the square, showing the cleavage presence, after mechanical cycling

As final consideration, it was verified that the two alloys, front to the studied processes, are able to be used in dental implant manufacturing. However, new tests are necessary as corrosion resistance and biocompatibility.

4 Conclusions

The present study characterized the alloys Ti–35Nb–5Zr (alloy 1) and Ti–35Nb–10Zr (alloys 2) by different methods and after the analysis of the results, it was possible to conclude that:

1. The alloy is of $\alpha + \beta$ type, and alloy 2 is of β type;
2. The alloy 1 has higher hardness mean value than the alloy 2;
3. The alloy 2 has higher maximum tensile strength mean value than alloy 1;
4. The fractures, after the tensile test, are of the ductile type for both alloys;
5. The fractures, after the mechanical cycling, are of the mixed type for the two alloys.

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