Microstructural characterization of Ni-Cr-Mo-Ti and Ti-6Al-4V alloys used in prosthetic abutments

Caracterização microestrutural das ligas Ni-Cr-Mo-Ti e Ti-6Al-4V utilizadas para pilares de próteses

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Abstract

Purpose: Titanium alloys are commonly used for prosthetic abutments fabrication, but these alloys present high cost and difficult handling. Alternative Ni-Cr alloys with Mo and Ti combination have been proposed. This study compared the alloys Ti-6Al-4V and Ni-Cr-Ti-Mo by analyzing their surface properties such as hardness, morphology and microstructural characterization.

Methods: Five discs (5x2 mm) of commercially Ti-6Al-4V and Ni-Cr-Ti-Mo alloys were used to evaluate Vickers hardness by hardness micro indentation test. The same specimens were analyzed by scanning electron microscopy (SEM) regarding surface morphology and subjected to a metallographic analysis of the microstructure by optical microscopy. Data on surface hardness were analyzed using one-way ANOVA followed by Tukey test ($\alpha = 0.05$).

Results: The Ni-Cr-Mo-Ti alloy showed significantly higher Vickers hardness (kg/mm^2) values (452.2 ± 3.9) than the Ti-6Al-4V alloy (375.7 ± 15.2). The surface morphology evaluated by SEM revealed differences between the alloys. Metallographic analyses, for both alloys, showed a two-phase equilibrium microstructure, with the presence of e $\alpha + \beta$ phase for Ti-6Al-4V; and gamma (γ) primary phase and gamma-prime (γ') as a second phase for Ni-Cr-Mo-Ti.

Conclusion: It can be concluded that both alloys present the requirements to be used in prosthetic abutments.

Key words: Ti-6Al-4V; Ni-Cr-Mo-Ti; dental alloy; microstructure; hardness; abutment

Resumo

Objetivo: As ligas de titânio são comumente usadas para a fabricação de componentes protéticos, entretanto apresentam alto custo e dificuldade de manuseio laboratorial. Ligas alternativas a base de Ni-Cr combinadas com Mo e Ti também tem sido propostas com o mesmo objeto. Este estudo comparou as ligas Ti-6Al-4V e Ni-Cr-Ti-Mo pela análise de suas propriedades de superfície como dureza, morfologia e caracterização da microestrutura.

Metodologia: Cinco discos (5×2 mm) das ligas Ti-6Al-4V e Ni-Cr-Ti-Mo foram utilizados para a avaliação da dureza Vickers, análise de morfologia de superfície por meio da microscopia eletrônica de varredura (MEV) e análise da microestrutura pela análise metalográfica. Os dados da dureza de superfície foram analisados pela Análise de Variância a um nível seguida do teste de Tukey ($\alpha = 0{,}05$).

Resultados: A liga Ni-Cr-Mo-Ti apresentou os maiores valores de dureza Vickers (kg/mm^2) ($452{,}2 \pm 3{,}9$) comparada a liga Ti-6Al-4V ($375{,}7 \pm 15{,}2$) A morfologia de superfície avaliada por MEV revelou características distintas entre as ligas. A análise metalográfica para ambas as ligas mostrou uma microestrutura com equilíbrio de duas fases, com a presença de fase $\alpha + \beta$ para Ti-6Al-4V; e fase gamma primária (γ) e fase gamma-prime (γ') como secundária para Ni-Cr-Mo-Ti.

Conclusão: Ambas as ligas podem ser utilizadas para fabricação de pilares protéticos.

Palavras-chave: Ti-6Al-4V; Ni-Cr-Mo-Ti; ligas metálicas; microestrutura; dureza; pilar protético

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Introduction

Surface properties and biocompatibility of the implant and its prosthetic abutments, as well as, satisfactory fit and marginal adaptation provide an important condition for the success of implant procedures (1). Nowadays, there is a large number of commercial implant systems available with different biomaterials, connections and their own indications.

However, regardless the abutment type, it is known that there is a positive correlation between the surface and joint characteristics of prosthetic implant components and plaque colonization (2,3). In an attempt to solve these problems, implant manufacturers have launched not only new types of abutment connections but also new biocompatible materials, mainly based on titanium due to its low toxicity, physiological biocompatibility and corrosion resistance (4,5).

Despite Ti-6Al-4V alloy being the most used alloy due to its low density and outstanding mechanical properties (6), the effect of its components aluminum and vanadium in the oral mucosa is still under discussion (5). Furthermore, its high melting point, reactivity and characteristics, such as, low capacity to reproduce details, interaction of the surface with the investment and the development of porosities are responsible for difficulties in its adaptation, besides the need for the use of plastic calcinable cylinders (7-9).

In addition to titanium alloys, a Ni-Cr-Mo-Ti alloy became commercially available as an alternative option for machined implant abutments and as a casting alloy. Advantages claimed by the manufacturers for its use, in special, because of the titanium addition are: integrity and strength in solder joints, castability, easy finishing, oxide formation, good comprehensive strength and strong porcelain-to-metal strength.

Some studies (10-12) about the Ni-Cr-Mo-Ti alloy had already been conducted, but they are still inconclusive to justify the benefits of the replacement of the dental alloys commonly used. Among the current studies, Costa et al. (11) found that Ni-Cr-Mo-Ti alloy showed superior marginal adaptation of superstructure for one-piece implant-supported dentures compared to Pd-Ag alloys. Also, its surface characteristics showed an acceptable roughness and morphology (12). However, only one study discussed its microstructure regarding the equilibrium phases occurring in the solidification process of this alloy (10).

Faced to the few data that clarify and discuss the Ni-Cr-Mo-Ti alloy surface properties, the aim of this study was to characterize the Ni-Cr-Mo-Ti alloy microstructure as well as to analyze its surface morphology by scanning electron microscopy (SEM), comparing it with a Ti-6Al-4V alloy used for dental implant abutments manufacturer.

Methods

Hardness test

Five discs measuring 5 mm in diameter and 2 mm in thickness of Ti-6Al-4V (Sandinox, São Paulo, Brazil) and Ni-Cr-Mo-Ti alloy (Talladium Inc., Valencia, CA, USA), which has in its composition 76% Ni, 13.5% Cr, 6% Mo, 4%Ti, were evaluated for Vickers hardness (kg/mm²), as received by the manufacturer without any surface treatment, in a micro hardness tester (HMV-2, Shimadzu, Tokyo, Japan). The mean values were calculated by means of three indentations with a distance of 150 µm between each of them, with a load of 100 g for 10 s. Data were analyzed using one-way ANOVA followed by Tukey test. The significance level was set at 5% ($\alpha = 0.05$).

Scanning Electronic Microscopy

The surface morphology of each material was examined by scanning electron microscopy with LEO 435 VP (Carl Zeiss SMT, Oberkochen, Germany). The beam acceleration voltage was 15 kV and the SEM observation was set at 500× magnification (12).

Metallographic analysis

For microstructural analysis two randomly chosen specimens of each material were mounted by a semi-automatic mounting press for hot compression (LaboPress 1, Struers, Ballerup, Denmark) with phenolic resin (MultiFast, Struers, Ballerup, Denmark). The basic steps for metallographic specimen preparation included: mounting, planar grinding, rough polishing, final polishing, etching followed by optical microscopic analysis. The plane grinding was performed with silicone carbide paper of 220- to 1000-grit (Struers, Ballerup, Denmark) under water cooling in a LaboPol-21 grinding/polishing machine (Struers, Ballerup, Denmark). The rough polishing was performed with a LaboPol-5 polishing machine (Struers, Ballerup, Denmark) and 6 µm diamond suspension (Struers, Ballerup, Denmark), and the final polishing with 3 and 1 µm diamond pastes (Arotec, São Paulo, Brazil) at 200 rpm without refrigeration. To prevent any pollution between abrasives, the surfaces were washed with propyl alcohol. In order to have a shiny surface, the alloys were chemically-mechanically polished using a mixture of colloidal silica (OP-S, Struers, Ballerup, Denmark) and hydrogen peroxide. The polishing pattern was produced by dipping the samples for 20 seconds into an acid mixture of Kroll's reagent (100 mL water, 6 mL nitric acid, 3 mL hydrofluoric acid), and the reaction was broken with 70% alcohol. After drying, the surface microstructure was examined by light microscope (Olympus BX60, Hamburg, Germany) at 50× and 250× magnifications and photographed by a digital camera (Olympus SC35 Type 12, Hamburg, Germany).

Results

Statistically significant differences for hardness between alloys were found. Ni-Cr-Mo-Ti alloy showed higher values (452.20 ± 3.88) than Ti-6Al-4V (375.67 ± 15.18) (Table 1).

Surface microstructure observed by SEM (Fig. 1A-B) showed a homogeneous matrix characterized by clear, well-defined, unidirectional structure, seeming typical for machined parts without any specific surface treatment. Furthermore, the density of the local defects (slight deviation from a uniform surface structure) appeared to be higher on the Ti-6Al-4V surface compared to the Ni-Cr-Mo-Ti alloy surface, but no quantitative comparison was undertaken. Also, irregular scratches, small pits (characteristic of grains microstructure) and turning marks could be observed and were more evident in the Ti-6Al-4V specimens.

Metallographic microstructural analysis of Ni-Cr-Mo-Ti alloy (Fig. 2A-B) showed two-phase equilibrium microstructure, consisting of gamma (γ) primary phase and gamma-prime (γ') (Fig. 2A) in which the second phase (light phase) is consistently located at the grain boundaries and finely distributed within bulk grains. The Ni-Cr eutectoid structure and the columnar dendritic growth (Fig. 2B) can also be observed through the presence of dendrite cores (light) and interdendritic regions (dark). In contrast, Ti-6Al-4V alloy (Fig. 3A-B) showed an equiaxed acicular grain structure with the presence of $\alpha+\beta$ phase, in which the fine black lines represent the β phase and the white acicular spaces the α phase formed in the β matrix.

Table 1. Vickers Hardness (kg/mm²; Mean ± SD) of the evaluated alloys.

Alloy	Vickers Hardness
Ni-Cr-Mo-Ti	452.2 ± 3.9 [(a)]
Ti-6Al-4V	375.7 ± 15.2 [(b)]

Distinct letters show statistically significant differences between alloys ($P < 0.0001$).

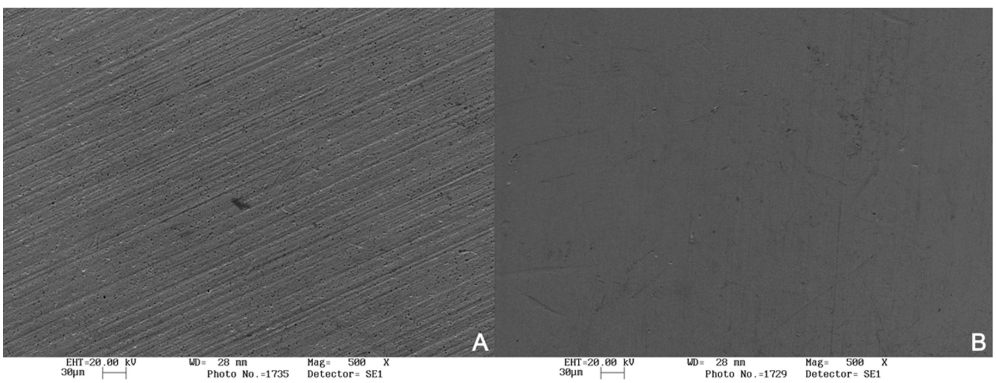

Fig. 1. (A) SEM of Ti-6Al-4V surface at 500x magnification: defects of machining results: small pits, irregular scratches. **(B)** SEM of Ni-Cr-Mo-Ti alloy surface at 500x magnification. Equally smooth surface structure and texture, minor irregularities result of machining and light scratches.

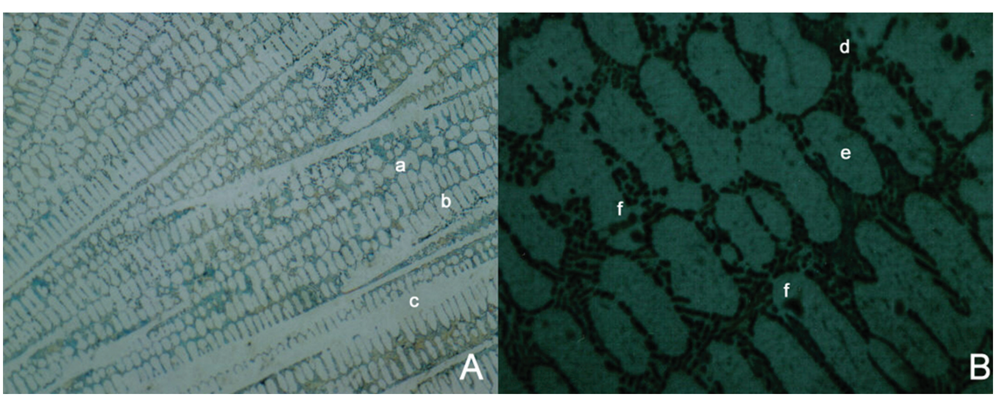

Fig. 2. Microstructure of Ni-Cr-Mo-Ti alloy surface at 50x **(A)** and 250x **(B)** magnification. **(A)** gamma (γ) primary phase and gamma-prime (γ') second phase (light region). **(B)** d) interdendritic regions; e) gamma (γ) grains; f) Precipitates (Mo or Ti) in the dendritic cores.

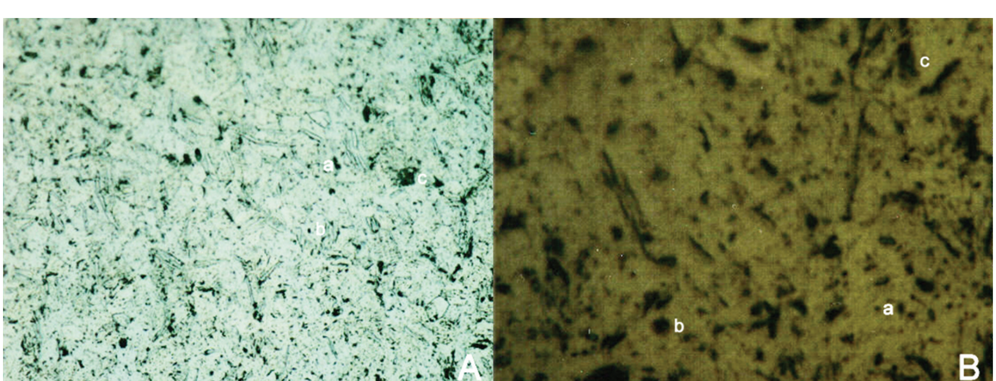

Fig. 3. Microstructure of Ti-6Al-4V. surface at 50x **(A)** and 250x **(B)** magnification. **(A)** binary (alpha+beta) structure was revealed. a) α grains; b) precipitates; c) β grains.

Discussion

Ni-Cr-Mo-Ti alloy is a nickel based superalloy, a non-precious metallic alloy which can be used at high temperatures, with 76% Ni, 13.5% Cr, 6% Mo and 4% Ti, available on the market for medical and dental use. These small quantities of Cr, Mo and Ti could alter the surface hardness, bulk composition (13,14), microstructure and the formation and composition of passive films over the alloy surface (14).

Regarding its surface hardness, in the present study, Ni-Cr-Mo-Ti alloy showed higher values for Vickers hardness than Ti-6Al-4V alloy. These values were superior to those related in previous studies (10,12,15) and similar to those described by Bauer et al. (2006) (10), who evaluated the alloy in the as received condition. However, when they compared Ni-Cr-Mo-Ti alloy in the as-received condition with groups submitted to different casting conditions, such as, in flame/air, induction/Argon, induction/vacuum, induction air, higher values were found, varying from 416 ± 1.6 to 433 ± 2.3. Also, da Rocha et al. (15) described that Ti-6Al-4V alloy after heat treatment showed higher values of hardness (before 340.5 ± 6.2 and after 369.1 ± 10.4).

The knowledge about surface hardness differences is important not only to explain the risk for surface roughening of the abutments during the professional cleaning or even during habitual oral hygiene procedures (3), but also because this surface property can reveal the necessity of heat treatments to optimize specific properties such tensile, fatigue and hardness (16). In addition, higher hardness can lead to difficulties in the metal alloy polishing during the handling, spending more time and altering the routine of the prosthodontics laboratory (7,10,15).

Differences between the two materials regarding surface morphologies were observed by SEM; few surface defects could be observed in the Ni-Cr-Mo-Ti alloy (Fig. 1A), indicating that the specimens consisted of homogeneous matrix that can be due to two reasons: a) the amount of alloying elements was sufficiently low so that all these elements were incorporated in the nickel solid solution and b) the reduction in titanium content causes reduced inclusion sizes and distribution of grains and consequently better surface finishing (17).

Adversely, the Ti-6Al-4V (Fig.1B) showed defects with an organized orientation, which may have resulted from machining process, small pits and irregular scratches. These patterns of surface morphology were similar to those described by Massaro et al. (1), when they analyzed machined (Branemark, Nobel Biocare; 3i ICE, 3i, Implant Innovation Inc) and special micro texture (3i Osseotite, Implant Innovation Inc.) implant surfaces.

The metallographic analysis of a material microstructure is a critical step in determining the reliability of metallic alloys and its correct casting process, and also to investigate why a material failed (10,18-20). The Ni-Cr-Mo-Ti alloy, as all Ni-Cr based alloy, presented a two-phase equilibrium microstructure as observed in Figures 2A-B, consisting of gamma (γ) and gamma-prime (γ') phases and resulting in a transitional zone between the matrix and the interdendritic euthetic formations (21). The γ', an intermetallic phase, is responsible for the elevated-temperature resistance of the material and its strength to creep deformation. The amount of γ' depends on the chemical composition and temperature, as illustrated in the quaternary phase diagrams (19).

The uniform Cr incorporation to the Ni in the gamma (γ) grain phase formation, resulting in Ni-Cr dendrites, is essential for an oxidation resistance due to the formation of a Cr-rich, passive oxide film which is highly resistant to acid attack; while Mo addition to the NiCr based alloy increases the resistance to localized corrosion (14). Mo and Ti, carbide formers, and also the presence of Cr are important to touch off the alloy precipitation process at grain boundaries and reduce the tendency for grain boundary sliding (20-22).

These elements (Cr and Mo) are also solid-solution strengtheners both in γ and γ' (17,19) phase as a dendritic brute fusion microstructure with precipitates dispersed in the entire matrix (19-21), that can be observed through of a columnar dendritic growth and the eutectoid element formation, which shows extensive solid solubility of chromium in nickel, and as a result of binary alloys hardened. (19,22)

In the microstructure analysis of Ti-6Al-4V, two crystallographic forms were observed, a hexagonal closed-packed crystal structure (hcp) with equiaxed α structure referred to as (α) phase and a body centered cubic (bcc) structure of small particles of spheroidal β known as (β) phase (Fig. 3A-B). In the titanium cp the equiaxed grain structures are principally developed by cold work followed by annealing above the recrystalization temperatures (17,18).

About the different chemical composition of the Ni-Cr base alloy studied, some scientific findings are important to be related for a critical interpretation. For general applications in dentistry, the Ni-Cr-based dental alloys added with 12% Cr and 2-5% Mo are well recommended for the improvement of corrosion resistance (14). Regarding to Ti and its reactive and protective oxide layer, normally TiO_2-based oxide, an optimal range of Ti in the passive film on NiCr-based alloy is still unknown (14,16).

As a limitation of this study, the specimens were not submitted to an aging process or a simulated oral environment exposition. Thus, further investigation for exploring the biocompatibility of the Ni-Cr-Mo-Ti alloy and its corrosion resistance and microorganism adherence should be conducted.

Conclusions

Within the limitations of this study, it was concluded that Ni-Cr-Mo-Ti alloy can be used to fabricate prosthetic abutments with appropriate physical and microstructural surface properties.

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References

1. Massaro C, Rotolo P, De Riccardis F, Milella E, Napoli A, Wieland M, et al. Comparative investigation of the surface properties of commercial titanium dental implants. Part I: chemical composition. J Mater Sci Mater Med 2002 June;13:535-48.
2. Piattelli A, Scarano A, Paolantonio M, Assenza B, Leghissa GC, Di Bonaventura G, et al. Fluids and microbial penetration in the internal part of cement-retained versus screw-retained implant-abutment connections. J Periodontol 2001;72:1146-50.
3. Quirynen M, Bollen CM, Willems G, van Steenberghe D. Comparison of surface characteristics of six commercially pure titanium abutments. Int J Oral Maxillofac Implants 1994;9:71-6.
4. Haag P, Nilner K. Questions and answers on titanium-ceramic dental restorative systems: a literature study. Quintessence Int 2007 Jan;38:5-13.
5. Kasemo B. Biocompatibility of titanium implants: surface science aspects. J Prosthet Dent 1983;49:832-7.
6. Aoki T, Okafor IC, Watanabe I, Hattori M, Oda Y, Okabe T. Mechanical properties of cast Ti-6Al-4V-XCu alloys. J Oral Rehabil 2004;31:1109-14.
7. Paulino SM, Leal MB, Pagnano VO, Bezzon OL. The castability of pure titanium compared with Ni-Cr and Ni-Cr-Be alloys. J Prosthet Dent 2007;98:445-54.
8. Wataha JC. Biocompatibility of dental casting alloys: a review. J Prosthet Dent 2000;83:223-34.
9. Wee AG, Aquilino SA, Schneider RL. Strategies to achieve fit in implant prosthodontics: a review of the literature. Int J Prosthodont 1999r;12:167-78.
10. Bauer JR, Loguercio AD, Reis A, Rodrigues Filho LE. Microhardness of Ni-Cr alloys under different casting conditions. Braz Oral Res 2006;20:40-6.
11. Costa HM, Rodrigues RC, Mattos MG, Ribeiro RF. Evaluation of the adaptation interface of one-piece implant-supported superstructures obtained in Ni-Cr-Ti and Pd-Ag alloys. Braz Dent J 2003;14: 197-202.
12. Lima EM, Silva WJ, Moura JS, Faot F, Del Bel Cury AA. Evaluation of surface characteristics of Ti-6Al-4V and Tilite alloys used for implant abutments. Braz Oral Res 2006;20:307-11.
13. Baumgardner JD, Lucas LC. Cellular response to metallic ions released from nickel-chromium dental alloys. J Dent Res 1995;74:1521-7.
14. Huang HH. Surface characterization of passive film on NiCr-based dental casting alloys. Biomaterials 2003;24:1575-82.
15. da Rocha SS, Adabo GL, Henriques GE, Nobilo MA. Vickers hardness of cast commercially pure titanium and Ti-6Al-4V alloy submitted to heat treatments. Braz Dent J 2006;17:126-9.
16. Huang HH. Effect of chemical composition on the corrosion behavior of Ni-Cr-Mo dental casting alloys. J Biomed Mater Res 2002;60:458-65.
17. Smith WF. Structure and properties of engineering alloys. 2nd ed. New York: McGraw-Hill; 1993.
18. Boyer R, Welsch G, Collings E. Materials properties handbook: titanium alloys. 2.ed. Materials Park: ASM International; 1994.
19. Davis JR. Materials properties handbook: titanium alloys. 2.ed. Materials Park: ASM International; 2000.
20. Lewis AJ. The mechanism of tensile failure in a nickel-base casting alloy. J Dent Res 1977;56:631-4.
21. Lewis AJ. The metallography of a nickel base casting alloy. Aust Dent J 1975;20:298-303.
22. Baran GR. The metallurgy of Ni-Cr alloys for fixed prosthodontics. J Prosthet Dent 1983;50:639-50.