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Physical-chemical analyses of contaminations and internal holes in dental implants of pure commercial titanium

N. PENHA[1], S. GROISMAN[2], J. NG[3], O. DIAS GONÇALVES[4], M. FERREIRA KUNRATH[5]

[1] Department of Dentistry, University of the State of Rio de Janeiro (UERJ), Rio de Janeiro, Brazil
[2] Department of Dentistry, Federal University of Rio de Janeiro, Rio de Janeiro (UFRJ), Brazil
[3] Queensland Alliance for Environmental Health Sciences, the University of Queensland, Brisbane, Australia.
[4] Department of Physics of University of Rio de Janeiro(IF-UFRJ), Rio de Janeiro, Brazil
[5] Department of Oral Implantology and Research, Odontology Faculty, Pontifical Catholic University of Rio Grande do Sul (PUCRS), Porto Alegre, Brazil

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ABSTRACT

Aim Titanium implants are one of the main forms of tooth recovery in today's dentistry. Its form of packaging, quality control and properties vary greatly by the large number of companies. The objective of this study was to analyze four different commercial brands in their stage of sale for clinical use, according to their physicochemical properties in comparison to the international ASTM (American Society for Testing and Materials) standards.
Materials and Methods Twelve implants were used and samples were prepared for analyses using SEM (scanning electron microscopy) and EDS (energy dispersive x-ray detector).
Results The results showed impurities and contaminations in most samples as well as different amounts of holes within the physical structure of the implants, in threads, body and apex.
Conclusions The contaminations and holes found suggest some quality control failure at some stage of implant production, this failure can compromise both implant resistance and its purity rating.

KEYWORDS Implants, Impurities, Titanium, Structure, Quality

INTRODUCTION

Titanium over the years and subsequent studies has been proven as the best biomaterial for implantology. However, with the evolution of implant systems, several methodologies for the preparation of implants and treatment of their surfaces were adopted by the different companies (1-4).
Titanium in its commercial form is available as pure titanium (cpTi) or alloy (Ti-6Al-4V) and more currently, in alloy TiZr, all of which are widely used in the manufacture of dental implants, with a significant success rate (5-6). These metals are classified according to their level of purity by ASTM: cpTi grade I has the highest purity due to its low oxygen and iron content, while cpTi grade IV presents a higher percentage of oxygen and iron. ASTM grade V is a titanium alloy with 6% aluminum and 4% vanadium (Ti-6Al-4V). Even so, some authors believe that there is a low level corrosion and released metal ions may remain in the peri-implant tissue or disseminate systematically with the potential to evoke immune response and hypersensitivity (7).
When a metal implant is in contact with human tissues, the body reacts and a corrosion process is initiated. As a consequence, we can observe the release of metal debris due to wear (8). The post mortem analysis of tissues adjacent to the implant evidenced the presence of metallic elements, and that these types of elements depend on the implant (8). In addition, the literature shows several studies on corrosion (9-10) and contaminations (11-12) in body fluids.
The different methods of manufacturing an implant as well as its surfaces can alter its physical structure, or associate some contamination with other chemical elements (3,13,14). The quality control of the material in the preparation of an implant is of paramount importance in all its phases, failing this point, the titanium implant may have a modified degree of purity,

FIG. 1 Samples prepared.

as well as weakening of the physical-chemical structure of the material (15-16) and some possible later clinical involvement when this material is used (17).

The aim of this study was to show the internal physical structure of the implants by Scanning Electron Microscopy (SEM) and the chemical structure by qualitative analysis in dispersive energy spectroscopy (EDS) analyzing possible modifications in the titanium structure of four different commercial systems and verifying possible impurities, contaminations, fragilities or deformities in the physical structure. Comparing the presence of chemical elements with international standards, pure titanium implants that are regulated by the international standard ASTM F67 for pure titanium and should contain only nitrogen, carbon, hydrogen, iron, oxygen and titanium elements in pre-defined maximum percentages.

MATERIALS AND METHODS

Samples

Initially, four commercial brands were chosen (SIN, Brazil; Emfils, Brazil; Derig, Brazil; Pross, Brazil). The implants used were purchased packaged after their complete manufacture and sterilization for commercial sale.

- SIN lots: 0090146582, 0090147028 and 0090147830;
- Emfils lots: 009470, 009767 and 009470;
- Derig lots: 15/7823, 15/7958 and 15/8182;
- Pross lots: 000000000000483357, 000000000000496377 and 000000000000511587.

Three samples of each marker were used (n = 3). All samples were recorded as pure grade IV titanium (ASTM F67 standard).

The samples were fixed in acrylic resin in a polyvinyl chloride cylinder with sufficient diameter for insertion of the whole implant, this step occurred in the Mineral Technology Center (CETEM - Brazil), being made by the same technical professional in the field of characterization of the research unit.

After polymerization, the samples were sectioned sagittally (Struers TegraPol-15) using a diamond disk (125 µm, 200 mm, 8 inches) until the threads appeared on the long axis of the implant body as shown in Figure 1.

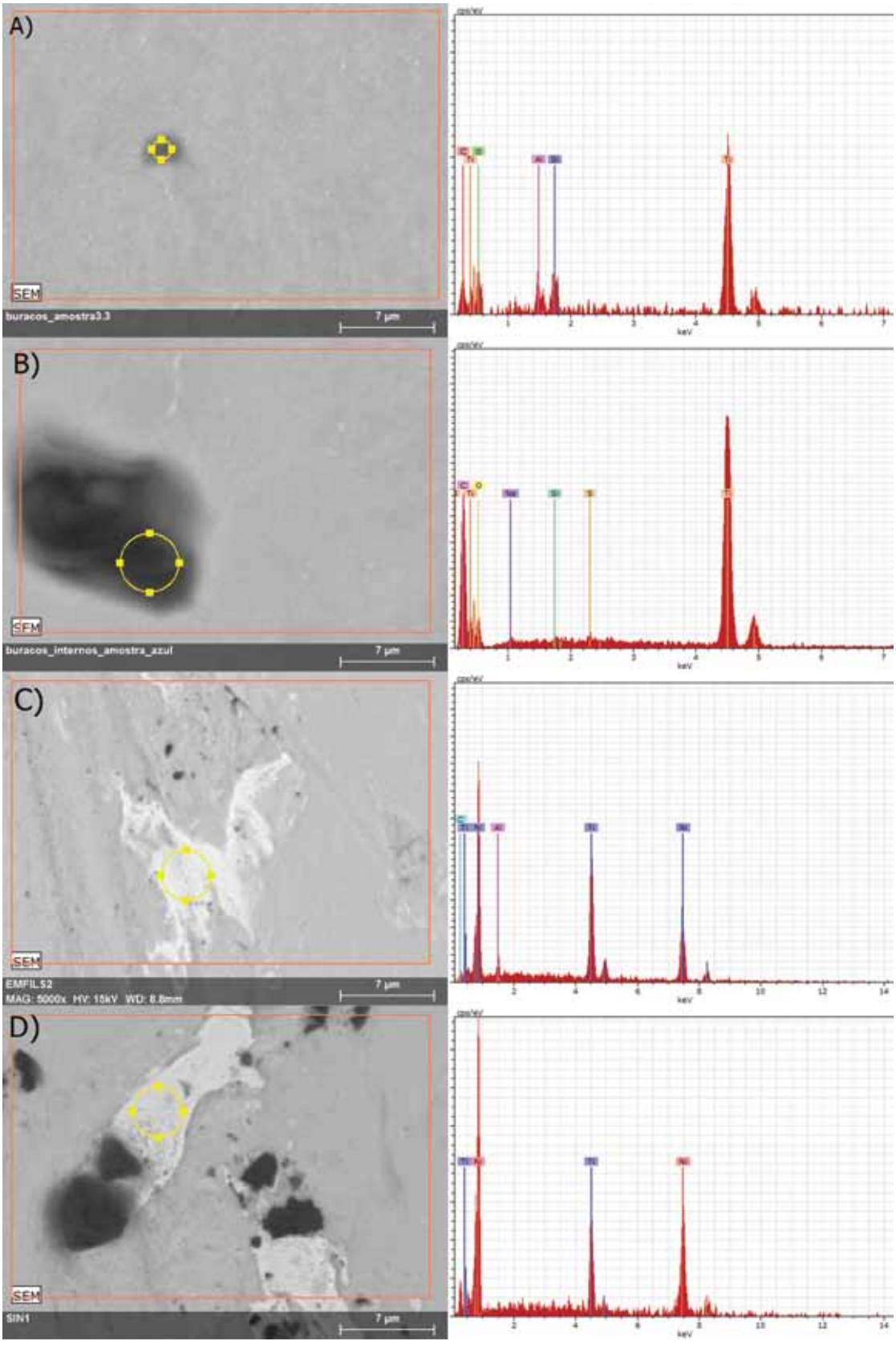

FIG. 2 A) Derig implant, SEM and EDS analyses; B) Pross implant, SEM and EDS analyses; C) Emfils implant, SEM and EDS analyses show Ni and Al; D) SIN implant, SEM and EDS analyses show Ni.

	N (max.)	C (Max.)	H (Max.)	Fe (Max.)	O (Max.)	Ti
ASTM F67 Grade I	0,03%	0,08%	0,015%	0,20%	0,18%	(Bal.)
ASTM F67 Grade II	0,03%	0,08%	0,015%	0,30%	0,25%	(Bal.)
ASTM F67 Grade III	0,05%	0,08%	0,015%	0,30%	0,35%	(Bal.)
ASTM F67 Grade I	0,03%	0,08%	0,015%	0,50%	0,40%	(Bal.)

TABLE 1 Variation of titanium grades according to ASTM international standards.

SEM Analyses

After the initial preparation, the samples were analyzed using scanning electron microscopes (FEI Quanta 400 and TM 3030 Plus Tablestop Microscope Hitachi), using the parameters of 20 kilovolts.

EDS Analyses

The EDS system test (dispersive energy spectroscopy) automatically identifies which chemical elements are present in the sweep performed by the system of each microscope. After the presence of elements in different Asher's scales was visualized, the EDS system identified them, and in the norm ASTM F67 the elements nitrogen, carbon, hydrogen, iron, oxygen and titanium are registered. All implants were analyzed throughout their structure, head, body, internal, external and apex threads. Contamination was considered as any chemical element present in the alloy, except those standardized by ASTM F67 (nitrogen, carbon, hydrogen, iron, oxygen and titanium).

RESULTS

In Table 1, we can verify standardization F67 of ASTM (International Standards Worldwide Organization) and the elements allowed in the different degrees of purity of the titanium. Figure 2 (A, B, C, D) shows the results obtained with scanning electron microscopy and the respective EDS results for samples of each implant system mentioned in the methodology.

Of the 12 samples analyzed, 8 had the presence of nickel in more than one point. Whereas nickel was not detected in all three Emfils and SIN brand implants, two of the Pross brand and all Derig implants tested.

The nickel peaks with the Titanium observed in Figure 2 (C, D) in the EDS analysis, as well as the peak of aluminum with the titanium observed in Figure 2 A, suggest impurities in the analysis of the physical-chemical structure of these implants.

Regarding the physical structure, some findings were important as the presence of holes in a large proportion in the implant bodies. In some samples, the presence of carbon and oxygen holes is intense as can be seen in Figures 3 and 4. The holes in the samples were found in all regions of the implants, with variations of presence throughout their bodies, heads, apexes and threads. The appearance of the holes varied from small to large sizes as shown by the scanning electron microscopy.

The sizes, measurements and proportions of the holes found are quite diverse as can be seen in Figure 4, where the longitudinal measurement was made. With more expressive sizes and presence in locations of fragility of the implants, as in Figure 4 A, several holes in a thread can be observed.

The focus of SEM analysis in the region of the implant threads showed fragility of the material at some important points of the implants as can be seen in Figure 5 A and 5 B), where a sectioned implant with the integral and symmetrical threads is shown, and in Figure 5 C and 5 D, where threads of deformed or nearly fractured as well as asymmetric implants appear.

DISCUSSION

The manufacture of an implant goes through several stages and production sites, from its extraction, bar making, machining, sterilization and sale by commercial means. All of these processes or locations are likely to contaminate titanium because of a lack of quality control or oversight, which may cause a later clinical problem. An analysis of titanium distributors found nickel concentrations ranging in weight from 0.0% in titanium grade IV and from 0.001% to 0.031% in titanium grades I, II and III, suggesting the presence of this element in the initial phase of production of a titanium bar (16). The present study showed only analyses of the final phase of the implant after its complete package and sale.

Different qualities of titanium and alloys are currently commercially available, in different degrees of purity and alloys such as Ti6Al4V (18) and TiZr (6) are also found, these variations of physico-chemical structures must be very well evaluated in terms of biocompatibility and cytotoxicity, because adverse effects may not be immediate, depending on the type of inflammatory response. Every medicine needs a route of administration, then go through a concentration/time curve then go through the speed and extent of absorption to be distributed, metabolized and everything that the excretory system cannot eliminate,

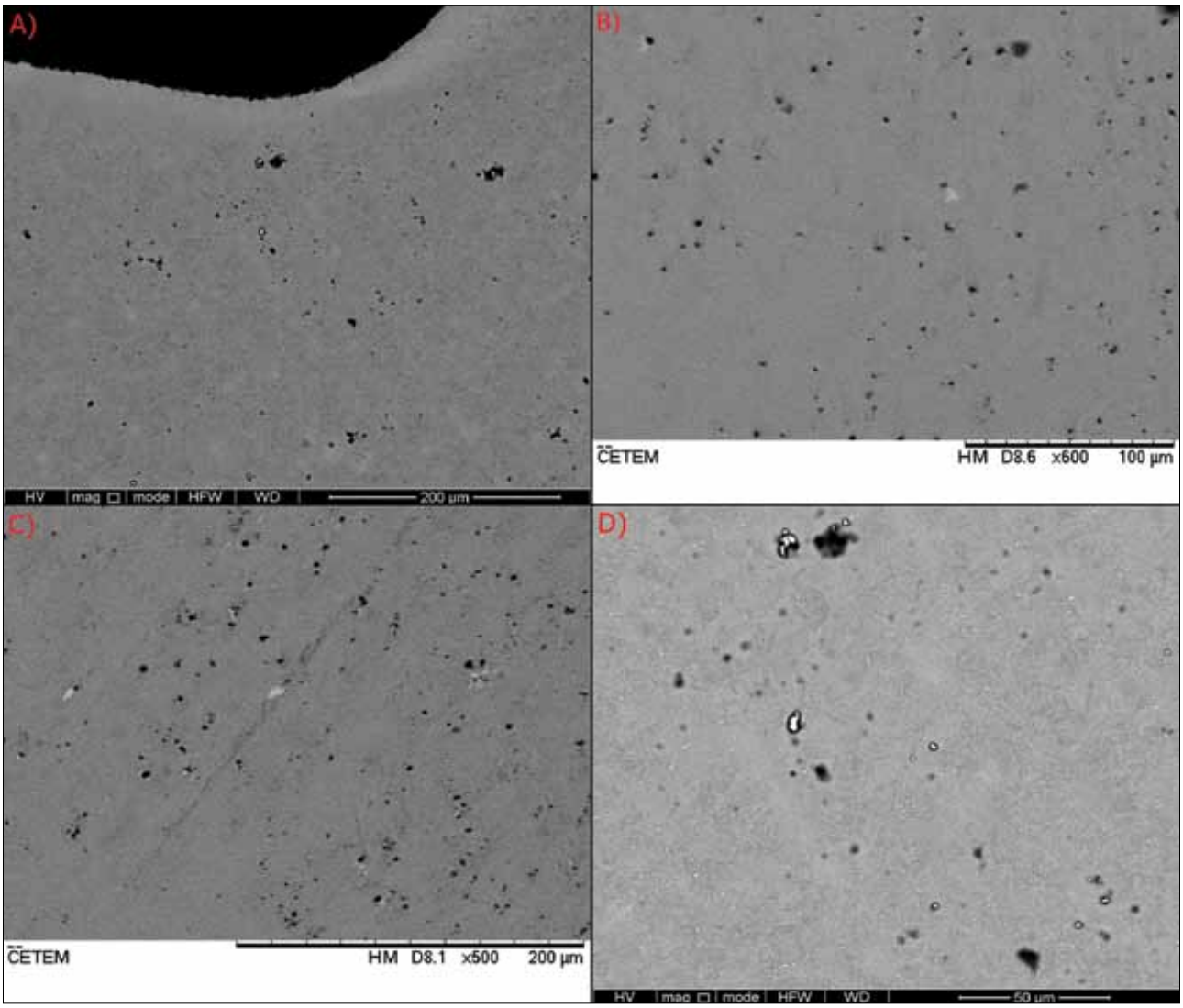

FIG. 3 A) Pross implant; B) Emfils implant; C) SIN implant; D) Derig implant.

will be stored in some tissue of the body, which can travel through the bloodstream and even demonstrate side effects and adverse effects in more than one organ, such as aluminum (19). In this study aluminum peaks were found in some samples, in addition many global industries use sandblasting on the surface of implants (3). Studies show that the altered concentration of Vanadium or Zirconium can be cytotoxic to the human body (11), as well as zirconia implants, in fact they are implants with the chemical formulation of Y-TZP, that is, it contains yttrium. This study focused only on implants commercially presented as Pure Grade IV Ti (ASTM F67 standard).

The EDS results presented in this work showed samples where the concentration of both aluminum and nickel were exceeded in some parts of the implants, contrary to the classification referred to by the international standard. Studies show that the contamination by these elements can happen in their surface treatment where they would have an impregnation of these elements as in surfaces blasted (14,16,20). In turn, this suggests the need for greater quality control in the last stages of implants manufacturing. In contrast, an *in vitro* study that tested surfaces with aluminum shows that the concentration of this element to some extent does not generate cytotoxicity and damage to the body (21).

The SEM findings of the holes of various sizes in most of the samples suggest a weakening of the physical structure of the implants in several critical points of the implants such as head, body, threads and apex. Studies show that the insertion torque of an implant can culminate with deformation or even fracture of the implant (22-23). These internal holes increase the fragility of the implant and favor possible clinical defects when submitted to higher torques or in very cortical bone areas. In this way a control from the mineral choices is necessary, since minerals like rutile, anatase and brookite have above 95% of titanium oxide, whereas titanite has 0 to 6%,

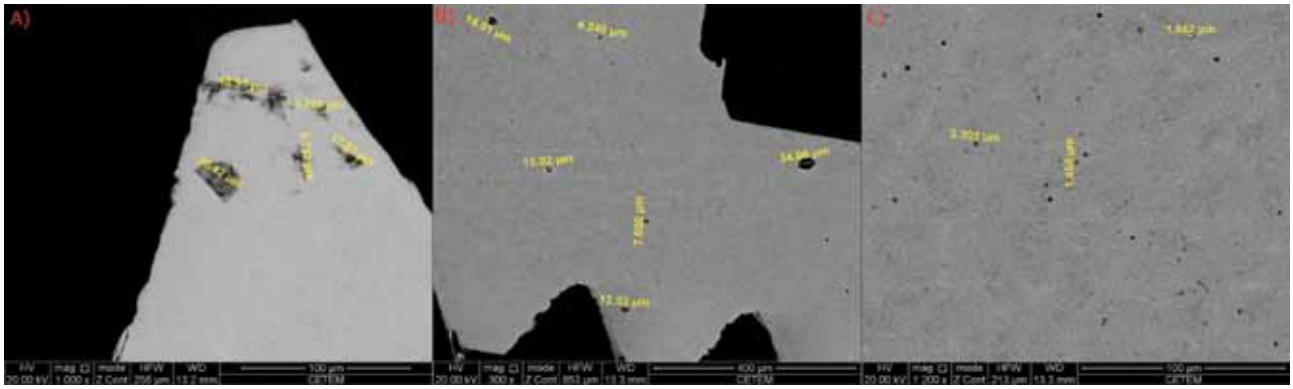

FIG. 4 A) Holes near the implant thread; B) Holes near the thread head; C) Holes in the body.

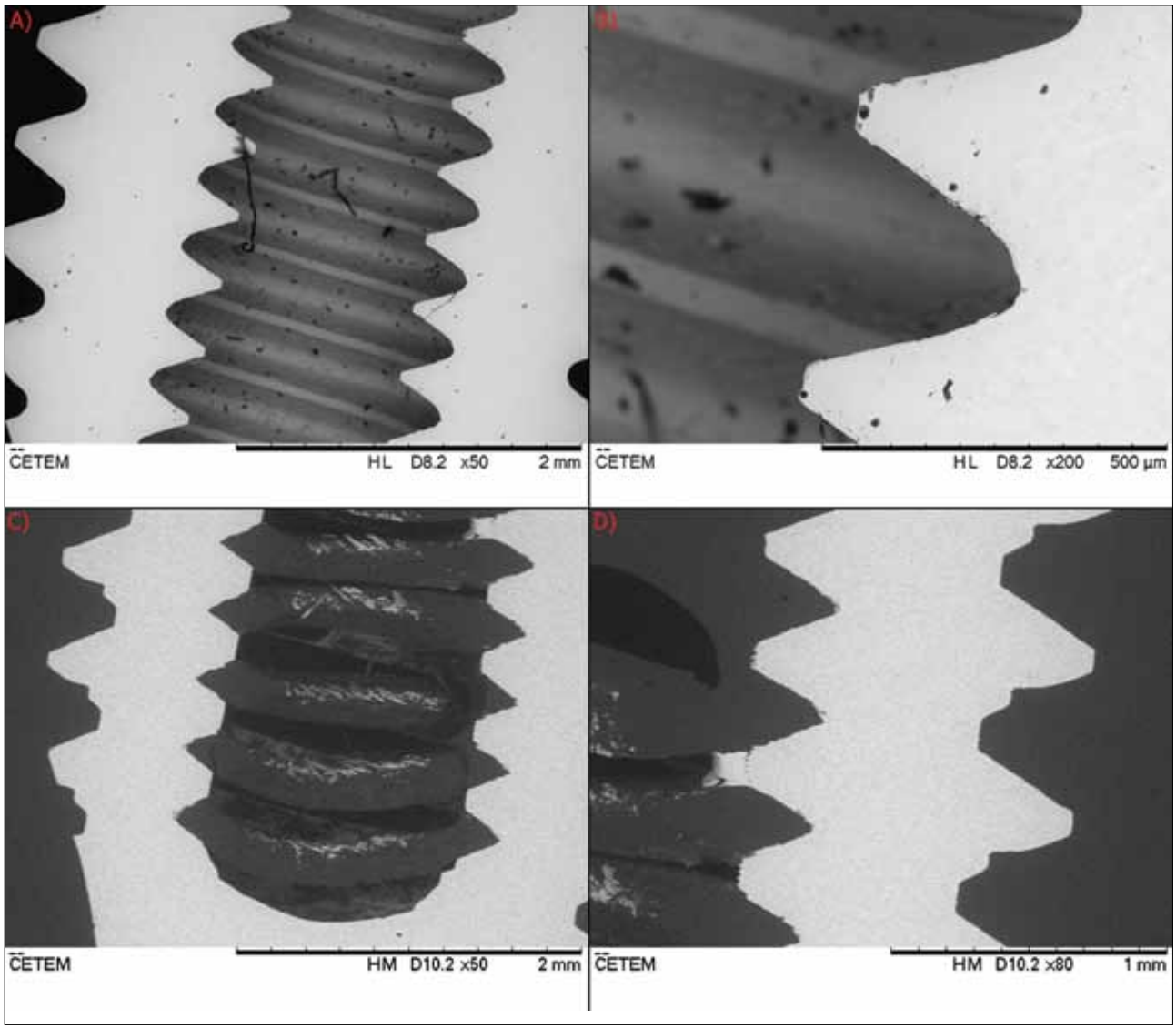

FIG. 5 Pross implant (A and B) at lower and higher magnification at SEM, Derig implant (C and D)at lower and higher magnification at SEM showing fragile threads.

augite of 0 to 9% and magnetite from 0 to 15% of titanium oxide. In addition to the minerals, the different processes such as Kroll, Hunter and Van Arkel de Boer to obtain titanium, must be controlled before processing into bars for dental implants (24).

The degree of purity and quality of the implant depends on several factors as previously reported, the results presented showed contaminations, impurities and fragilities in the physicochemical structure of the chosen implants. However, the limitations of the work do not allow to discover in what stage of implant preparation the defects were created, needing more complex studies of analysis of the physical-chemical structure in all stages of production, as well as studies on the bioaccumulating and biomagnificant effects in relation to all the elements found in the implants, that is, the expected elements and the contaminants in each stage of the different processes.

Based on the information described above and on the limits of this study, it was concluded that the majority of the samples presented impurities in their preparation after the commercial sale contrary to the international standardization ASTM and internal holes in the titanium can weaken the physical structure and increase the risk of deformation and immediate/early fracture of the titanium if not controlled in the manufacturing of the implants.

The experimental findings of this work show the need for manufacturing control in all the phases of implant making. New studies are required to analyze the harmful degree of nickel and aluminum elements and in what stage of preparation of an implant can these contaminations occur. Moreover, further studies are needed to quantify the titanium resistance damage according to the number of holes.

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