

# CHEMICAL AND METALLOGRAPHIC CHARACTERIZATION OF STAINLESS STEEL IN IMPLANTS REMOVED FROM PATIENTS

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## ABSTRACT

**Objective:** This study examines the chemical and metallographic composition (microstructure, grain size, inclusion content) of austenitic stainless steel developed as biomaterials for used in the manufacture of orthopedic implants. **Method:** An analysis was carried out of twelve implants removed from patients affected by inflammation. Chemical analyses were carried out using Optical Emission Spectrometry and Energy Dispersive Microanalysis (EDS), and the grain size was determined by optical microscopy and scanning electron microscopy (SEM) according to ASTM

Standard E 1382 97. **Results:** It was observed that all the implants had a larger grain size than is recommended by the Standard. The presence of delta ferrite was also observed in ten of the twelve implants removed, which according to ASTM Standard F138-92, should not be perceived microscopically under magnification of 100x. **Conclusions:** In eight cases, there is a strong indication that the inflammation was triggered by pitting corrosion. **Level of Evidence:** Level III, Systematic review of studies.

**Keywords:** Stainless steel; Prostheses and implants; Biocompatible materials; Corrosion.

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## INTRODUCTION

Austenitic stainless steel for surgical implant is the material used most in the production of orthopedic implants in Brazil. Two reasons contribute to this domain over non-ferrous materials: mechanical resistance and its lower cost, when compared to other materials such as titanium and cobalt-based alloys, which as they are imported have a far higher cost than stainless steel. An imported part manufactured with one of these alloys has an approximate cost of 8 times that of stainless steel.<sup>1</sup>

Austenitic stainless steels classified as AISI 316L by the American Iron and Steel Institute were for several years those most frequently used in orthopedic implants as fracture and joint fixation components. Austenitic stainless steels are not magnetic and their basic composition includes 18% of Cr, 14% of Ni and 2.8% of Mo, which confers good mechanical properties and corrosion resistance.<sup>2</sup>

Among the possible forms of corrosion affecting stainless steels special emphasis is placed on pitting corrosion, which is undoubtedly the most worrying. Body fluids promote an extremely localized corrosion attack, which starts with the breakage of the protective film of chromium oxide (denominated passive layer). With thickness between 30Å and 50Å, the passive film

is strongly adherent to the stainless steel, is non-porous, self-regenerative and has its resistance increased as chromium is added to the steel.

The microstructure of steel is composed of grains, whose contour separates two small grains or crystals with different crystallographic orientations. Since the grain contour is chemically active, through physical and chemical mechanisms, impurity atoms segregate preferentially along these contours, as they present higher energy states. In order to reduce the energy of the total grain contours in the microstructure, these grow when submitted to high temperatures. In other words, the growth of the grain size is a physicochemical phenomenon that can be controlled during the implant production process. There are several kinds of microstructures in steels and they are the ones that will define their properties, characterizing them. There can also be a combination of different structures with diversified physicochemical properties. Among the possible microstructures in steels, the so-called austenitic steels are the most indicated for the stainless steels designed for prostheses, due to their mechanical and chemical properties.

Stainless steel implants should not contain other microstructural phases in addition to the austenite. There are international standards that specify the steels for such applications and

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determine that their microstructure should not contain delta ferrite when examined under the microscope, with 100X of magnification. Delta ferrite is a secondary phase detrimental to the physicochemical properties of stainless steel, decreasing its corrosion resistance when compared to austenitic matrix. Moreover, as it presents ferromagnetic characteristics, ferrite causes the increase of the magnetic permeability of stainless steel.<sup>1</sup> There are cases reported in which patients using prostheses of austenitic stainless steel, submitted to magnetic resonance imaging (MRI), had interaction with the magnetic field of this equipment, altering the results of the analysis even though this alloy is not magnetic. These effects depend on the size and on the format of the implant, besides the magnetic permeability and the degree of ferromagnetism of the material provoked by different microstructures of austenite.<sup>3</sup>

The need to find metallic materials with more appropriate physicochemical characteristics for orthopedic implants has prompted researchers to develop several compositions of stainless steels, whose properties minimize faults of a physiological, mechanical and chemical nature.

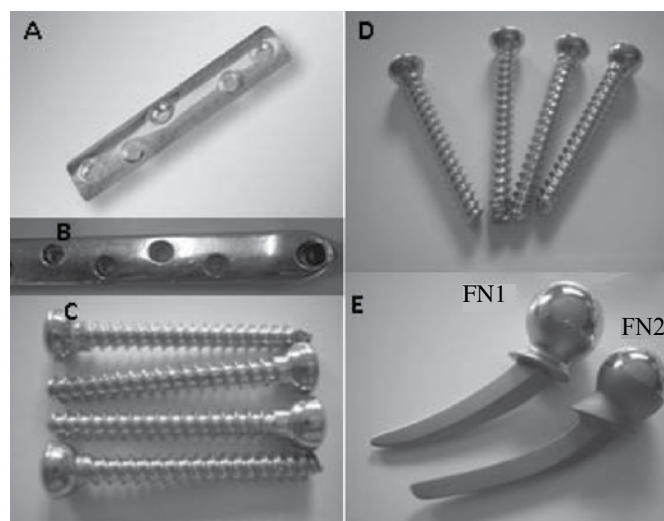
According to Soares,<sup>1</sup> the expenditures of the Brazilian Unified Health System - SUS with orthopedics totaled about R\$ 60 million, with 6,337 items (except inputs) supplied by 39 companies. The total hip arthroplasty procedure alone generated - in the sphere of SUS - almost 10 thousand hospitalizations and a total expenditure of almost R\$ 30 million earmarked for the purchase of prostheses. These amounts, although not yet updated in the DATASUS portal, certainly present higher figures. Studies conducted in the United States in the last decade reveal that about 10% of osteosynthesis devices removed from patients were outside of the specifications determined by the American Society for Testing and Materials - ASTM standard then in force.<sup>3</sup> In Brazil, there have been few studies on the metallurgical characteristics of faults that have led to the removal of implants from patients, aiming to verify the compliance of steels that constitute these removed prostheses with international standards. The lack of regulations defining technical criteria concerning the production of orthopedic implants in stainless steel, has led the Brazilian Sanitary Surveillance Agency - ANVISA of the Health Department to mobilize to the effect of creating a Technical Regulation that preserves the quality of these products. According to data from this entity there are 12 registered national manufacturers serving the area of arthroplasty, one in Paraná state and the rest in São Paulo. Revision surgeries, according to data from SUS, added up to the amount of R\$ 7 million in 2004 to cover 1500 surgeries.<sup>3</sup> The durability of an implant depends on inherent factors of the patient (quality of the bone matrix, biological age, clinical conditions), of the surgical technique and of the quality of the implants.

This study is aimed at characterizing the stainless steels of the prostheses removed from patients affected by irritation, analyzing the metallurgical and chemical properties of the material used in their production, in order to evidence possible unconformities between these properties and those required by the ASTM standard. Twelve implants removed from patients operated in public hospitals were studied for this purpose.

## MATERIAL AND METHODS

The materials studied were implants removed from patients being grouped as follows: 1 self-compression plate (SP) removed 44 months after implantation (Figure 1A); 1 autodynamic plate (AP) removed 18 after implantation (Figure 1B); 4 fully threaded Ø4.5mm malleolar screws (MS) removed 18 months after implantation (Figure 1C); 4 fully threaded Ø6.5 spongy screws (SS) without identification of the time of use (Figure 1D); 2 total hip prosthesis femoral nails (FN) removed 24 months (FN1) and 18 months (FN2) after implantation (Figure 1E). In all 12 implants it was not possible to identify their origins as they did not present the manufacturer's specification, batch and date of manufacture. The removed implants were cleaned under ultrasound with acetone for eight hours to remove organic material adhering to the surface of the steel. The samples were sectioned lengthwise and crosswise, in a metallographic cutting machine than inlaid cold in self-curing acrylic. The samples were sanded with a hand-held polisher, using common silicon carbide (SiC) abrasive paper with granulometries of 120, 240, 320, 400, 500, 600, 800, 1200, 2000 and diamond folder of 1µ diamond paste. Afterwards they were washed with distilled water and ethyl alcohol then dried in hot air. The chemical attack to reveal the grain contours was executed in aqua regia with added glycerin.

The methods used to analyze these implants followed these procedures: chemical analyses according to the standards of the American Society for Testing and Materials ASTM F138<sup>4</sup> and of the International Organization is Standardization - ISO 5832-9<sup>5</sup> for Emission Spectrometry; for the metallographic examinations the participants used standards ASTM E3-95<sup>6</sup> - "Standard Practice for Preparation of Metallographic Specimens" and ASTM E 407-93<sup>7</sup> - "Standard Practice for Microetching Metals and Alloys" to specify the microstructure; and standards ASTM E 1382-97<sup>8</sup> - "Standard Test Methods for Determining Average Grain Size Using Semiautomatic and Au-



**Figure 1.** Material analyzed. A - Self-compression plate. (PC), B - Autodynamic plate. (PA), C - 4 Ø4.5mm malleolar screws (MS), D - 4 fully threaded Ø6.5 spongy screws (SS), E - 2 total hip prosthesis femoral nails (FN) and (FN1).

tomatic Image Analysis” to calculate grain size and lastly, to determine the content of the inclusions, standards ISO 4967 - 1998<sup>9</sup> - “Steel - Determination of Content of Non-Metallic Inclusion - Micrographic Method using Standard Diagrams” and standard ASTM E-45<sup>10</sup>, Method A, Plate III.

## RESULTS AND DISCUSSION

### Chemical analysis

The chemical composition described as ideal by the adopted standards that specify the steels studied in this survey, establishes parameters for the various chemical elements that should be present in them in the steels under analysis.<sup>4,5</sup> The maximum percentile values defined with a basis on these standards are shown in Table 1. The analyses were executed at the Laboratory of Centro Tecnológico de Fundação “Marcelino Corradi - CETEF - Itauna, to characterize the chemical composition of implant steels, through optical emission spectroscopy. According to the guidelines specified by standards ASTM F138-92<sup>4</sup> and ISO 5832-9<sup>5</sup>, steels should present a percentage of the alloying elements in maximum contents and concentration ranges that characterize them, whereas these percentile values are shown in Table 1. These standards are concerned with ensuring, in stainless steels designed for implantology, greater resistance to corrosion, with special emphasis on pitting corrosion. They also guarantee a good stability of their austenitic structure against the formation of the undesirable ferrite phase. This stability is reached when

the nickel content appears with minimum value of 13%. When the molybdenum content is above 2.25% it ensures greater corrosion resistance, notably localized. The combination of chromium, nickel and molybdenum contents also increases the stability of austenite and guarantees the decrease of the growth tendency of magnetic permeability ( $\mu$ ) due to deformation.

The percentile values of the elements found in each one of the samples are also presented in Table 1. The carbon contents that are lower than the maximum values established by the standards indicate the unlikelihood of formation, on the grain contour, of the compound  $Cr_{23}C_6$  responsible for chromium loss in this region, with consequent impoverishment of this element and the loss of the characteristics of corrosion resistance offered by chromium. Lower silicon contents also improve the properties of stainless steel, which also applies to the elements manganese, phosphorus and sulfur. Nickel is an element of addition to stainless steel that besides improving corrosion resistance, also stabilizes austenite. In the studied parts, the nickel contents shown in Table 1, were presented in the range under consideration, by the standards adopted for chemical composition, as ideal. A similar result is also valid for chromium and molybdenum contents, whose values were presented in conformity with the standards. The values observed for chromium ensure good properties for formation of the passive layer with thickness and characteristics appropriate for use as a biomaterial. Molybdenum is a chemical element that, in the proportion indicated by the standards presented in Table 1, confers an increase in the localized cor-

**Table 1.** Chemical composition established by the standards for steels F138 and ISO5832-9. Chemical composition of the studied parts obtained by optical emission spectroscopy.

Element	Standards		Chemical composition observed in the parts					
	ASTM F138-92	ISO 5832-9	SP	AP	MS	SS	FN1	FN2
Carbon	0.03 max.	0.08 max.	0.011	0.017	0.03	0.011	0.011	0.017
Silicon	0.75 max.	0.75 max.	0.190	0.16	0.53	0.47	0.25	0.16
Manganese	2.00 max.	2.00 - 4.25	1.890	1.98	1.83	1.92	1.89	1.79
Phosphorus	0.025 max.	0.025 max.	0.025	0.013	0.023	0.024	0.025	0.013
Sulfur	0.01 max.	0.010 max.	0.002	0.0018	0.002	0.002	0.009	0.001
Copper	0.50 max.	0.25 max.	0.049	0.06	0.05	0.057	0.048	0.06
Nickel	13.00 - 15.00	9.00 - 11.0	14.50	10.98	13.00	14.19	14.40	14.30
Chromium	17.00 - 19.00	19.50 - 22.00	17.60	20.55	17.60	17.48	17.51	17.31
Molybdenum	2.00 to 3.00	2.0 to 3.0	2.200	2.44	2.40	2.18	2.11	2.80
Iron	Balance	Balance	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Nitrogen	0.10 max.	0.25 - 0.50.	NM	NM	NM	NM	NM	NM

SP - Self-compression plate; AP - Autodynamic plate; MS - Ø4.5mm malleolar screws; SS - fully threaded Ø6.5 spongy screws; FN 1 and 2 - Femoral nails.

rosion resistance. As can also be seen in this Table, the molybdenum values presented in all the parts are in compliance with the standards. Ultimately, the stainless steels used in the production of the studied parts presented chemical composition within the ranges established by the standards of reference for chemical composition.

### Metallographic analysis

Standards ASTM E 3-95<sup>6</sup> and ASTM E 407-93<sup>7</sup> describe the metallographic analysis methods, ASTM E 138-2-97<sup>8</sup> describes the grain size and standard ISO 4967-98 specifies the content of non-metallic inclusions.<sup>9</sup> As established by the standards adopted in this survey, the microstructure should appear 100% austenitic and free of delta ferrite so that the physical and corrosion resistance properties are guaranteed. The grain size should not be below number 4 and the percentage of non-metallic inclusions such as aluminates, oxides, silicates and sulfides should not exceed the percentile values established in these standards.

The metallographic testing of the samples was conducted at the laboratory of the Technological Characterization Sector of Centro de Tecnologia Mineral – CETEM (Mineral Technology Center), through a LEO S440 scanning electron microscope (SEM), equipped with a backscattered electron and secondary electron detector and the optical microscopy was done with a TOPCON metallographic microscope from the Metallography Laboratory (LABMETA) of Instituto Federal de Educação Ciência e Tecnologia - IFET - Juiz de Fora Campus.

Grain size determination complied with standardized techniques in which the area, volume and mean diameter of the grains were observed. Standard ASTM E 112-96<sup>11</sup> uses standardized comparative charts with the different mean sizes of the grains that receive a number designated “grain size number”. This scaling ranges from 0 to 18, and it is considered that the higher the number, the smaller the grain size.

The surface of the sample was adequately prepared through sanding, polishing and chemical attack so as to reveal the grain contours. This procedure is standardized by ASTM E 407-93 - “Standard Practice for Microetching Metals and Alloys”.<sup>7</sup> Grain size determination was accomplished by comparing the photograph with 100X increase, with the charts expressed in terms of the grain size number. Through this relatively simple procedure it was possible to visually determine the grain size. When in the presence of mediums such as the organic fluids existing in the human body, stainless steels suffer progressively accentuated corrosion with the increase in the content of inclusions. Pitting corrosion is the main form of attack on stainless steels and may be related to the presence of non-metallic inclusions in the residual form, in order to preserve the physical and chemical characteristics of the stainless steel implant.<sup>12,13</sup> Standard ISO 4967-1998<sup>9</sup> establishes the methods for determination of the content of non-metallic inclusions using standard diagrams in micrographic techniques.

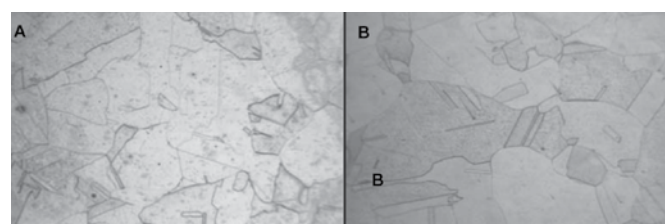
The 12 implants were submitted to the metallographic analysis consisting of microstructure evaluation; grain size measurement and determination of the content of non-metallic inclusions. All the implants presented microstructural heterogeneity in relation to grain size (Figures 2A, 2B and 3D). Figure 2 also

shows that the grains exhibited values above those indicated by the ASTM standard, which establishes number 4 sizes as an acceptable maximum limit, in order to preserve the physical and chemical properties of the implant.

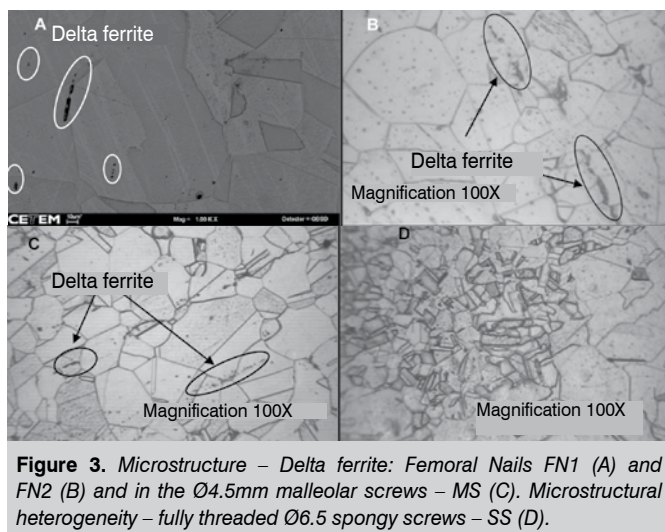
The microstructures observed in the self-compression plate - SP and in the autodynamic plate - AP were completely austenitic (Figure 2), while the delta ferrite phase was detected in femoral nails FN1 and FN2 and in the malleolar (MS) and spongy (SS) screws. (Figure 3)

Chromium carbides precipitation on the grain contours was not detected in any of the implants, demonstrating that the steels under analysis do not exhibit susceptibility to intergranular corrosion.

The two nails, the malleolar screws and the spongy screws exhibited pitting corrosion. (Figure 4) Figure 5A shows the region of nail FN1 where a cross-section was made, signaling the development of pitting corrosion. Nail FN2 exhibited pitting corrosion in articulation regions (head) shown in Figures 5B and 5C. Figure 5D also shows pitting corrosion on one of the spongy screws.



**Figure 2.** Optical micrography. (Zoom 100X). A – Self-compression plate (SP), B – Autodynamic plate (AP). Austenitic microstructures. Microstructural heterogeneity and size of grains above those indicated by the ASTM standard.

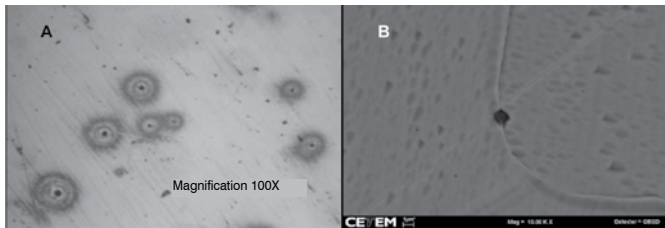


**Figure 3.** Microstructure – Delta ferrite: Femoral Nails FN1 (A) and FN2 (B) and in the Ø4.5mm malleolar screws – MS (C). Microstructural heterogeneity – fully threaded Ø6.5 spongy screws – SS (D).

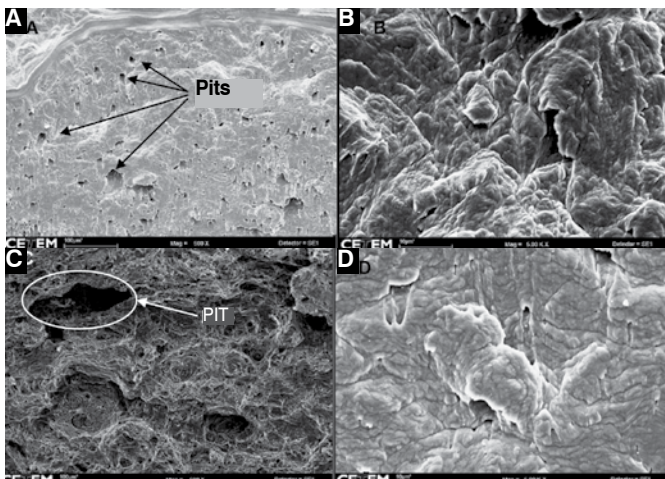
The presence of non-metallic inclusions was not indicated in any of the prostheses. Table 2 shows the nonconformities observed according to the adopted standards.

Standard NBR ISO 5832-9:2008 of the Brazilian Association of Technical Standards establishes precepts for orthopedic implants of stainless steel, also serving as a reference in the





**Figure 4.** Pitting corrosion in samples FN (A) and PE (B).



**Figure 5.** (A) region of nail FN1 where there was a fracture. Presence of pits. (B) and (C) nail FN2 presented pitting corrosion in articulation regions (head). (D) pitting corrosion on one of the spongy screws.

certification of implants of this material by the Brazilian Sanitary Surveillance Agency. The studied implants were produced in stainless steel in chemical composition within the specifications of standards ASTM F138-92 and ISO 5832-9. However, the analyses carried out on this material demonstrate that the production processes of these implants were not in accordance with some specifications established by the standards of reference: ASTM E 407-93 and ASTM E 407-93. These conclusions are evidenced in the nonconformities found in the microstructures (delta ferrite) and in the grain sizes (heterogeneous and above number 4). The

presence of delta ferrite observed in the total hip prosthesis femoral nails (FN) and in the screws (MS) and (SS) where localized corrosion appears, is highlighted as one of the important factors that cause pitting in stainless steels, whereas this type of chemical degradation is a strong indication that the conditions of irritation were brought about by the release of metallic ions in the patients' body. The micrograph from Figure 4B shows that the pits formed probably started on the grain contours, indicating that these regions where the passive film probably exhibits defects originating from the crystallographic differences, are preferential sites for the localized breakage of the passive film and subsequent pit nucleation.

In relation to the self-compression (SP) and autodynamic (AD) plates that did not exhibit pitting or intergranular corrosion, but where larger than indicated grain sizes were observed, it was not possible to associate the irritative processes, developed by the patients, with this microstructural irregularity presented by the steel of the parts.

The growth process of the grains occurs after recrystallization and depends on the temperature, the time and the chemical composition of the steel. Since control over grain size is very important in the determination of the physical and chemical properties of stainless steel, the manufacturing process of prostheses in materials of this nature should be discerning in order to ensure grain size that is consistent with the standard, as well as the nonexistence of delta ferrite.<sup>7</sup> Nonconformities exhibited by the steels of the studied prosthesis demonstrate that during the manufacturing process of the implants covered here, some metallurgical technological procedures were not properly considered. Therefore, the surgical procedures of implantation of prostheses may be compromised by physical and chemical faults presented by the material, but that can be minimized when these products comply with international standards, notably regarding manufacturing techniques. In considering the implant selection criteria, it is recommended that hospitals make sure that the quality of these steels is demonstrably in conformity with standards NBR ISO 5832-9:2008 or ASTM F138-92, by means of appropriate certificates.

**Table 2.** Nonconformities observed according to the standards adopted.

Parameter	Standard	Result –samples						Technique adopted
		SP	AP	MS	SS	FN1	FN2	
Chemical analysis	ISO 5832-9:2008	C	C	C	C	C	C	Optical emission spectroscopy
Microstructure	ASTM E 407-93	C	C	NC	NC	NC	NC	Optical microscopy and scanning electron microscopy
Grain size	ASTM E 1382-97	NC	NC	NC	NC	NC	NC	Optical microscopy
Content of inclusions	ISO 4967 - 1998	C	C	C	C	C	C	Optical microscopy and scanning electron microscopy

C – Compliant; NC – Non-compliant

The absence of specific legislation in our country determining that implants, in stainless steel, must be accompanied by these documents attesting to their quality, through the specification of chemical and metallographic analyses, has contributed to the neglect of their metallurgical and chemical properties.

Accordingly, hospitals from our country, in opting for a particular stainless steel alloy, urgently need to become aware of the need to establish as another methodology to be adopted: the requirement that these prostheses be accompanied by their respective manufacturing quality certificates, provided by the manufacturers or technical expert, a procedure that will be able to significantly reduce the risks of undesirable biological reactions to an implant, besides minimizing the chance of mechanical faults in these parts.

## CONCLUSIONS

The technology used in the production of the studied implants took the growth of grains from the austenitic microstructure to values above that recommended by the international standards of reference, as well as to the appearance of delta ferrite, which is provenly harmful to a biomaterial of this nature. As regards the production metallurgy of the steels employed as the raw material of these implants, no chemical nonconformity was detected and all the elements presented composition within the limits established by the standards.

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