A metallurgical study of the contamination zone at the surface of dental Ti castings, due to the phosphate-bonded investment material: the protection efficacy of a ceramic coating

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Commercial pure (cp) titanium exhibits remarkable advantages compared to conventional dental alloys, mostly in the fields of biocompatibility and corrosion resistance. Today there exist very optimistic perspectives for the use of titanium as an ideal alternative for the conventional dental alloys. However, titanium casting procedure shows some serious difficulties related mainly with its high melting point and its great chemical reactivity at high temperatures. As a result, an extensive contamination is observed in Ti castings when SiO_2-based investment materials are used (phosphate-bonded or silica-bonded). In the present work, a detailed metallurgical study of the contamination zone of Ti castings due to Si, P and O, was performed. The new phases which formed, were investigated and analyzed using mainly light and scanning electron microscopy, as well as energy dispersion spectrometry. These phases were found to be: α-Ti, β-Ti and a Ti-Si compound. An attempt was done to prevent the contamination of cast Ti by using a wax pattern coating technique. The protection efficacy of a ZrO_2 coating was proven. Ti castings without contamination were obtained in this way. © *1999 Kluwer Academic Publishers*

1. Introduction

Titanium was firstly used in Dentistry almost thirty years ago as a machinable material for implant manufacturing. Since early 80s, titanium was introduced also as a castable material for the construction of dental prostheses. Commercial pure (cp) titanium exhibits remarkable advantages compared to conventional dental alloys, mostly in the fields of biocompatibility and corrosion resistance. In addition, the abundance of this element in nature, as well as the fact that it is a cost effective raw material, created very optimistic perspectives for the use of titanium as an ideal alternative for the conventional dental alloys.

However, titanium casting procedure shows some serious difficulties related mainly with its high melting point and its great chemical reactivity at high temperatures. The latter is the reason for the problems which dental laboratories meet when using conventional investment materials for the casting of titanium. Ti reduces many oxides and oxidizes itself easily. Moreover,

Ti has high chemical affinity with Si and forms a series of Ti-Si compounds. As a result, an extensive contamination is observed in Ti castings when SiO_2-based investment materials are used (phosphate-bonded or silica-bonded). This contamination leads to microstructure modification and new compound formation, with consequent influence on the corrosion and mechanical properties of the cast work, especially within the depressive and corrosive oral environment. It has been reported [1, 2] that many elements from the investment material (Si, Al, P, O) were found in important contents in a depth of some tenths of microns from the outer surface of Ti castings. The contaminated zone showed increased microhardness [3, 4], while the reactions between the liquid metal and the investment material gave rise to subsurface internal porosity [5]. From the clinical point of view, the contaminated zone is undesirable because (a) it reduces the fatigue limit and the elongation of the cast parts [6], (b) it increases the surface roughness of the castings [7] resulting in non proper fit of the

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appliance in the oral cavity. In a recent study [2] it was reported that the thickness of the contamination zone is affected by the mold temperature and the cast volume and this renders very difficult the removal of this zone during the grinding and polishing procedures.

During the last ten years, an effort has been done to replace the conventional SiO_2-based investments by materials non containing the above mentioned contaminating elements. Therefore, MgO-based investment materials were developed [8], in which Si and P were replaced by inert to Ti elements such as Mg, Zr etc. However, although these materials do not contaminate Ti cast works, they do not exhibit the good combination of properties of the conventional investment materials (expansion coefficient, air permeability, mechanical properties) [9]. In addition, their high cost increases dramatically the total cost of the dental prosthetic work. The idea of using the successful and cost effective SiO_2-based dental investments with a simultaneous avoidance of the contamination of the cast Ti has risen recently and some authors have tried to apply barriers between the cast metal and the investment material [8, 10].

In the present work, a detailed metallurgical study of the contamination zone of Ti castings due to Si, P and O, was performed. The new phases which formed, were investigated and analyzed using mainly light and scanning electron microscopy, as well as energy dispersion spectrometry. An attempt was done to prevent the contamination of cast Ti by using a wax pattern coating technique. The protection efficacy of a ZrO_2 coating was proven.

2. Materials and methods

Two series of wax patterns (A, B) were prepared for the casting of cp Ti (Krupp, grade 2, chemical composition in Table I). Each pattern was a cylinder of 3 mm in diameter and 15 mm in length. The patterns of the series A were directly invested with a conventional SiO_2-based, phosphate-bonded investment material (Neoloy, Neoloy Product Co. Posen, ILL, USA), which was first submitted in chemical analysis (atomic absorption) and XRD analysis. The patterns of the series B were coated with a thin layer of ZrO_2 before being invested with the same investment material. The coating material was produced by mixing ZrO_2 powder with the liquid Kleen Cast (Belle de St. Claire, Chatsworth, CA, USA) and then it was applied on the patterns. The particle size distribution of the ZrO_2 powder was studied using laser granulometry. After the removal of the wax, the ZrO_2 coating was practically transferred to the investment material, on the internal surface of the mold.

After the investment procedure, the molds were fired according to the manufacturer's instructions, allowed to cool at $450\,°C$ and transferred into a two chamber electric arc vacuum/gas pressure machine (Cyclarc, J. Morita Co., Kyoto, Japan), where Ti casting took place. The investment material was then removed from the surface of the Ti samples using sandblasting (alumina grains of 150–200 μm in size). The samples of both series A, B were prepared for metallographic observation of the cross section which is perpendicular to the length axis, in order to study the penetration of the investment elements into the castings. The metallographic preparation included (a) embedding in epoxy resin, (b) grinding using SiC papers from 220 up to 1200 grit, (c) diamond paste (3 μm, DP paste M, Struers, Copenhagen, Denmark) polishing, (d) ultrasonic cleaning for five minutes (T-14B, L&R Manuf. Co. NJ, USA), (e) etching (2 ml HF, 98 ml oxalic acid). An optical microscope (Nikon Microphot, Nikon-Kogaku, Tokyo, Japan) was used for the metallographic study of the samples. In addition, the Ti castings were investigated in a scanning electron microscope equipped with energy dispersion spectrometry system. The new phases which formed, were studied by means of spot analysis and X-ray mapping.

3. Results

The results of chemical analysis and X-ray diffraction of the investment material are presented in Table II. It is a conventional SiO_2-based, phosphate-bonded material, used for the casting of all types of dental alloys. Its high content in Si, P and O was expected to create contamination problems to the cast Ti samples of the series A. The ceramic powder used for wax pattern coating was a monoclinic ZrO_2 powder with very fine particles in the range of -6 μm according to the laser granulometry results. More than 50% of the particles were below 1.2 μm in size.

Secondary electron images (SEI) of the two series of samples A and B in low magnification are presented in Fig. 1. It is of great interest the difference in surface roughness between the two samples, which is related with the reactivity appearing in the interface between the cast Ti and the investment material. In the case of direct contact between Ti and investment, a high reactivity between the two materials took place. This was not the case when a thin ZrO_2 layer existed between the two materials. The micrographs in Fig. 2 confirm this observation. These back-scattering electron images (BEI) reveal the existence of various phases in sample A, as the result of reactivity between Ti and the investment material, in a depth of about 100 μm (Fig. 2a and b).

TABLE I Chemical composition of the cp Ti (Krupp, grade 2)

Element	Ti	Fe	O	N	C	H
wt %	>99.40	<0.25	<0.20	<0.06	<0.08	<0.013

TABLE II Chemical analysis and XRD results for the investment material Neoloy

Phases	wt %
SiO_2 (quartz)	47.4
SiO_2 (cristobalite)	28.1
MgO	12.2
$NH_4H_2PO_4$	8.1
Fe_2O_3	0.35
CaO	0.25
Al_2O_3	0.25
Organic materials	Bal.

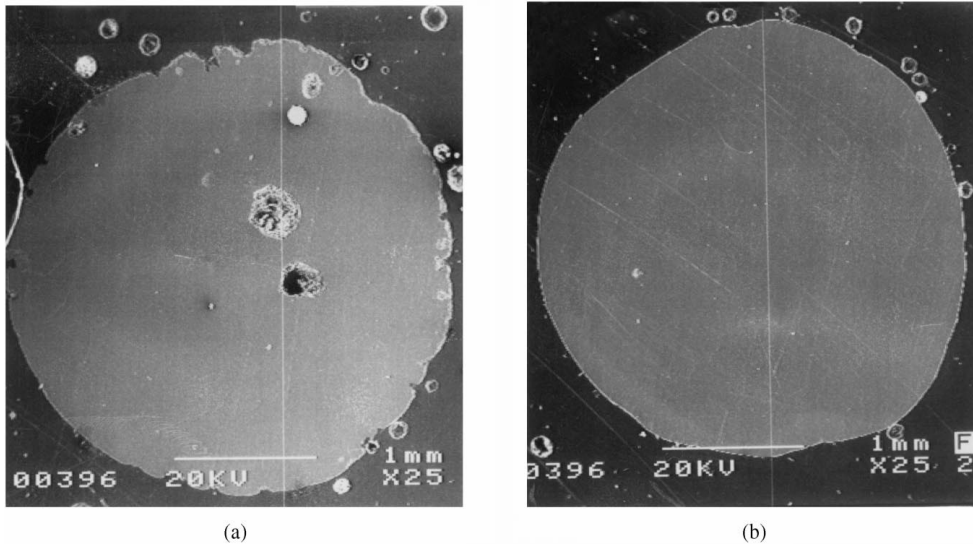(a)   (b)

Figure 1 Secondary electron images (SEI) of the two Ti samples, showing the difference in surface roughness: (a) Ti casting from conventional investment and (b) Ti casting from investment with ZrO_2 coating.
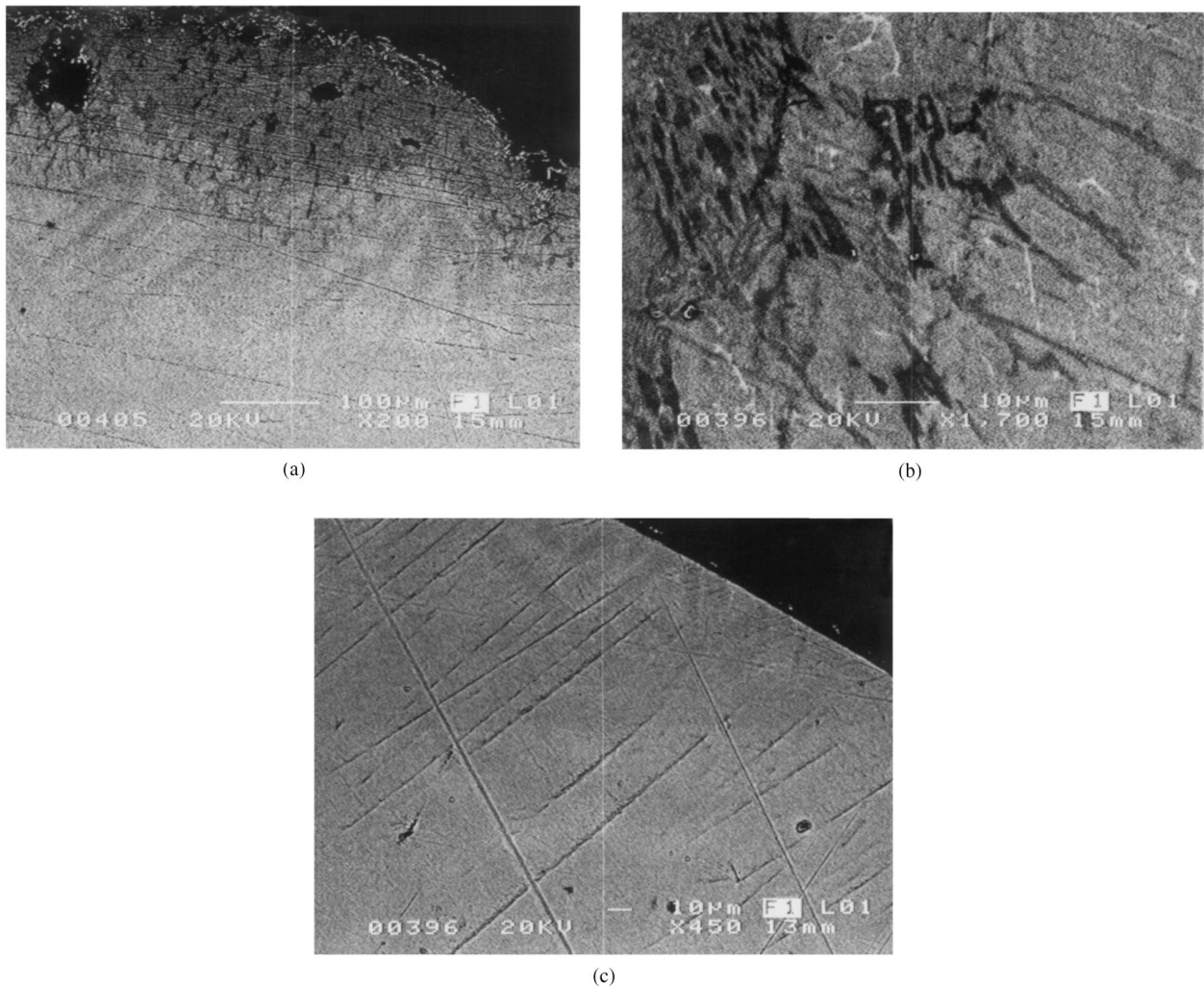

(a)   (b)

(c)

Figure 2 Back-scattering electron images (BEI) of the two Ti samples: (a) Ti casting from conventional investment showing the contamination zone with various phases; (b) the same sample as in (a) in higher magnification; and (c) Ti casting from investment with ZrO_2 coating, where no contamination is present.

No presence of such phases in sample B was shown (Fig. 2c). In Fig. 3, characteristic optical micrographs of the contaminated sample A are presented. One can observe the corrugated surface and the contamination layer just below the surface, where various phases have formed in a depth of about 100 μm. Below this layer it appears the characteristic structure of *as cast* metal, showing macrosegragation due to dentrite formation.
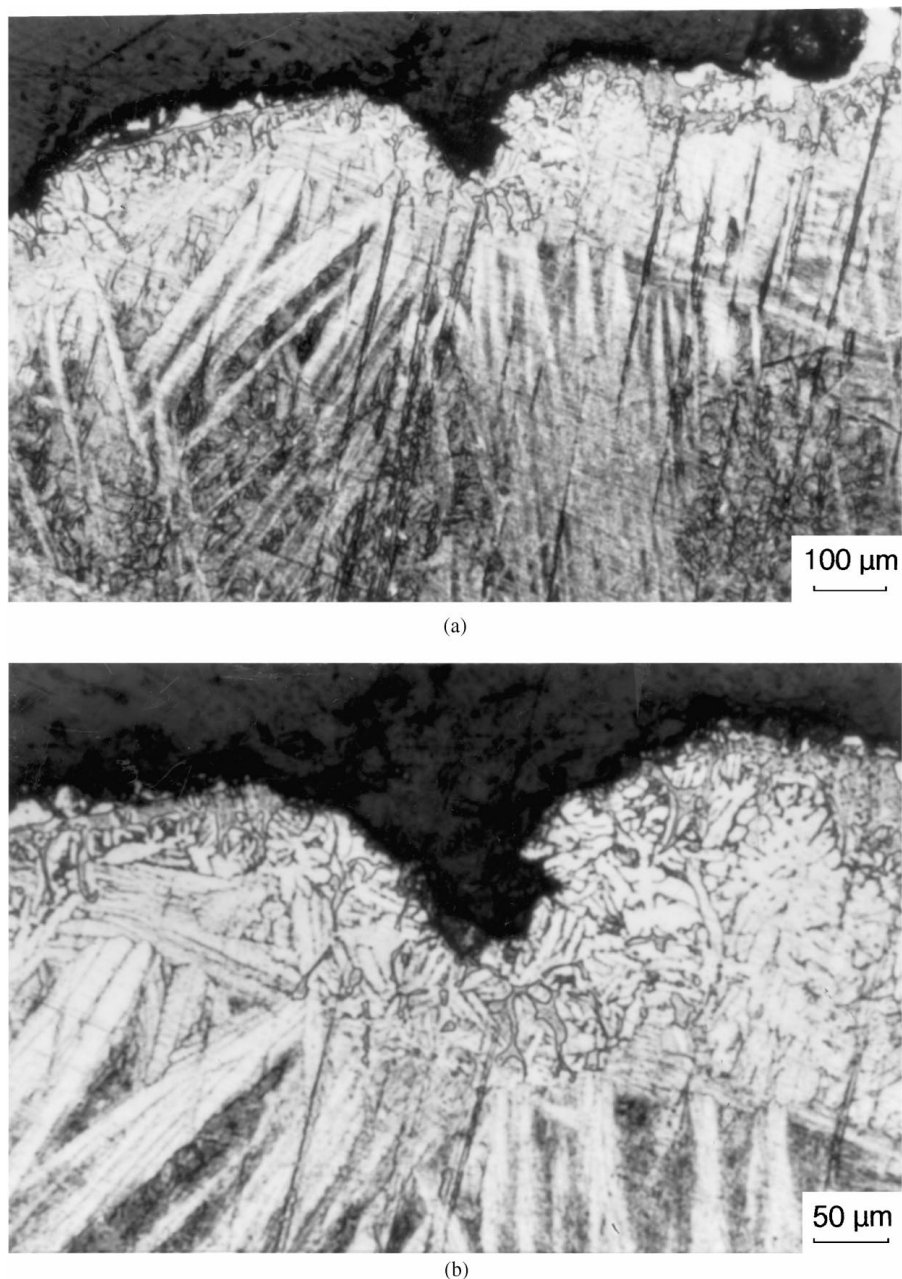
(a)

(b)

Figure 3 (a) Optical micrograph of the Ti casting from conventional investment, showing the contamination surface layer and the characteristic cast structure and (b) the same sample as in (a) in higher magnification.

TABLE III Chemical compositions (at %) of the detected phases (EDS) in the contamination layer

Phases of present study	Corresponding phases from phase diagram [11]	Ti	O	Si	P	Fe	Cr
a	α-Ti	76.7	22.4	0.9			
b	β-Ti	88.5	1.4	2.4		6.7	1.0
c	Ti_5Si_3-Ti_3Si	65.7		31.8	2.5		

The phases which formed in sample A, were analyzed using spot analysis and X-ray mapping. The results are presented in Fig. 4 and Table III. Fig. 4a shows a BEI micrograph of the contaminated zone in a depth of 10 μm from the outer surface. Fig. 4b shows the corresponding X-ray maps for the elements Ti, Si, P and O. In general, three distinct phases can be observed: (i) phase **a**, the gray phase in majority, (ii) phase **b**, the white phase, (iii) phase **c**, the black phase. The at % compositions of these phases are shown in Table III. It seems that the elements Ti and O exhibit common distribution in these phases, while P follows Si's distribution.

4. Discussion

According to the results presented in the previous paragraphs, a contamination layer with an average thickness of 100 μm formed at the Ti casting's surface when casting took place in a mold without protective coating (sample A). On the other hand, when a ZrO_2 coating was applied on the investment, no contamination layer was observed (sample B). The mechanism for the formation of this reaction zone in sample A is very probably related with the capability of Ti to reduce many oxides and with its high chemical affinity with Si. When
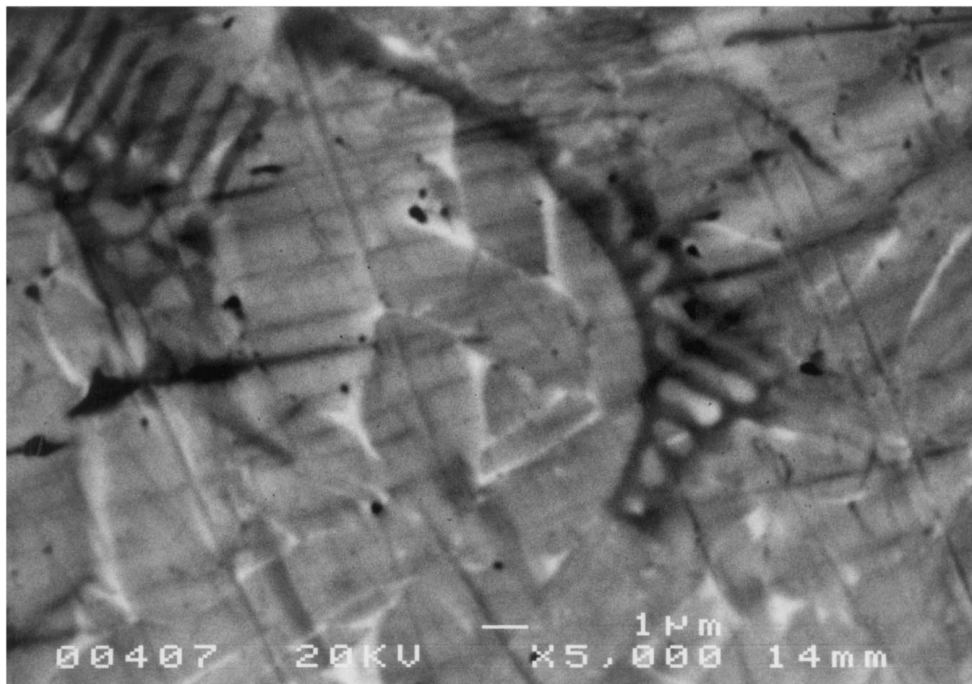
(a)
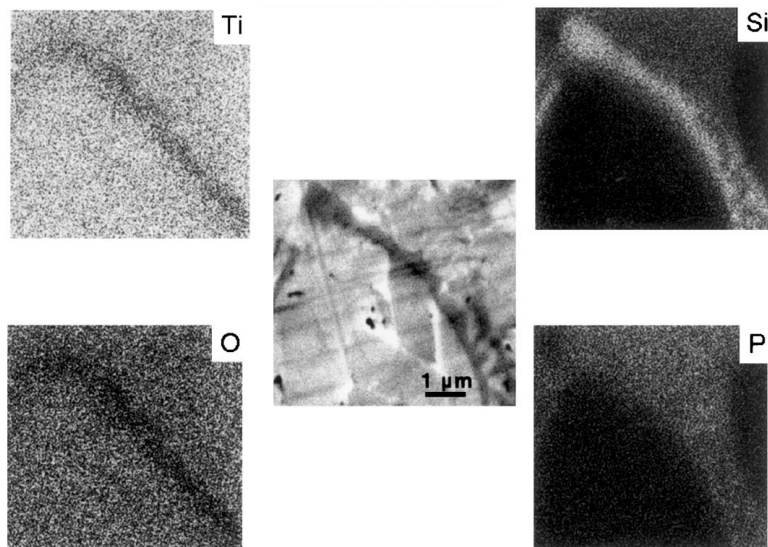
(b)

Figure 4 (a) Back-scattering electron image (BEI) of the contamination zone at a depth of 10 μm from the outer surface and (b) X-ray maps for the elements Ti, Si, P and O.

molten Ti comes in contact with the mold surface, it reduces the oxides of the investment material and liberates elements such as Si, O, P, Fe etc. These elements either form various compounds with Ti (e.g., Si, P), or remain in solid solution after solidification (e.g., O). Similar results concerning the diffusion of elements (Si, P, Al, Mg) from SiO$_2$-based investment materials to Ti castings have been reported also by other investigators [1, 2].

In the present study, the elements Si, P, O, Fe and Cr were detected in the three distinct phases **a**, **b**, **c**. The chemical compositions of these phases are given in Table III. In order to understand the heterogeneous distribution of the dissolved elements and the formation of the phases observed, it is essential to consider the at % solubility limits of the above elements in α and β

TABLE IV Maximum solubilities (at %) in α and β Ti of the elements detected in the contamination layer [11]

Elements	α-Ti	β-Ti
O	31.9	8
Si	0.5	3.5
P	—	0.3
Fe	0.04	22
Cr	0.2	100

Ti. These values are shown in Table IV according to the binary phase diagrams [11]. Except P, which is actually insoluble in α Ti, all the other elements exhibit great differences in their maximum solubility values in the two Ti phases. O is an α Ti stabilizer, while the other elements stabilize β Ti.

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Based on the values presented in Tables III and IV, the following hypotheses can be done concerning the detected phases within the contamination zone: Phase **a** corresponds to α Ti, since it retains in solution 22.4 at % O. This value is lower than the maximum solubility limit of O in α Ti (31.9 at %) and higher than its maximum solubility limit in β Ti (8 at %). In addition, the Si content is low (0.9 at %) and close to the maximum solubility limit (0.5 at %). Phase **b** corresponds to β Ti. Its contents in O, Si, Fe and Cr are within the solubility limits of β Ti, and for Si, Fe and Cr much higher than the solubility limits of α Ti. Finally, phase **c** corresponds to a Ti-Si intermetallic phase with a Si content of 31.8 at %. This value is lower but close to the content in Si of the phase Ti_5Si_3 (37.5 at %). According to the Ti-Si binary diagram shown in Fig. 5 [11], the phase Ti_5Si_3 has a very high melting point (2130 °C), much higher than the casting temperature which is about 1800 °C. However, this phase can form as a proeutectic phase in the temperature range 1330–2130 °C. In lower temperatures it can be transformed in Ti_3Si according to the peritectoid reaction occuring at 1170 °C:

$$4Ti(\beta) + Ti_5Si_3 \Leftrightarrow 3Ti_3Si$$

This reaction can take place at the interface between **b** and **c** phases. Consequently, both compounds (Ti_5Si_3, Ti_3Si) may coexist in the detected **c** phase which contains 31.8 at % Si, a value between 37.5 at % for Ti_5Si_3 and 25 at % for Ti_3Si. Ti_5Si_3 is characterized as an intermetallic compound with hexagonal symmetry and Ti_3Si as a chemical compound which crystallizes in the tetragonal system [11]. The results of the present investigation are in agreement with those reported in a previous study [2], where O was found as a solute and Si both as a solute and as an intermetallic compound. Phosphorous was detected only in **c** phase in limited concentration. It could be assumed that P behaves like Si, since it forms with Ti several compounds (Ti_3P, Ti_2P, Ti_5P_3, etc.) [11].

In summarizing, the solidification process of the contamination layer has as follows: Ti melts at 1670 °C, but the casting temperature is at least 100 ° higher (about 1800 °C) to avoid premature solidification of liquid metal before filling the mold. At this high temperature the liquid Ti reduces some of the oxides of the investment material (SiO_2, Fe_2O_3 etc.) and the free elements (mainly Si, O, P, Fe,) dissolve into the molten metal. Their presence there affects strongly the solidification process and therefore the final microstructure of the casting. When molten Ti first solidifies, it forms the β phase which transforms into α phase at lower temperatures (882 °C for pure Ti according to the phase diagram [11]). However, if the molten Ti contains high O percentages (more than 15 at %) it solidifies directly in the α phase (Fig. 6). On the other hand, the solidification temperature of Ti_5Si_3 is 2130 °C, but it can also form as a proeutectic phase in the temperature range 1330–2130 °C. These two phases—α Ti and Ti_5Si_3—very probably form simultaneously. The phase of α Ti (**a** phase in the present study) grows by consuming mainly O from the liquid metal and pushing there Si P, Fe and Cr which all have a limited solubility in α Ti. The phase Ti_5Si_3 (**c** phase in the present study) grows by consuming mainly Si and P from the liquid and pushing there O, Fe and Cr. Therefore the contents of Fe and Cr in
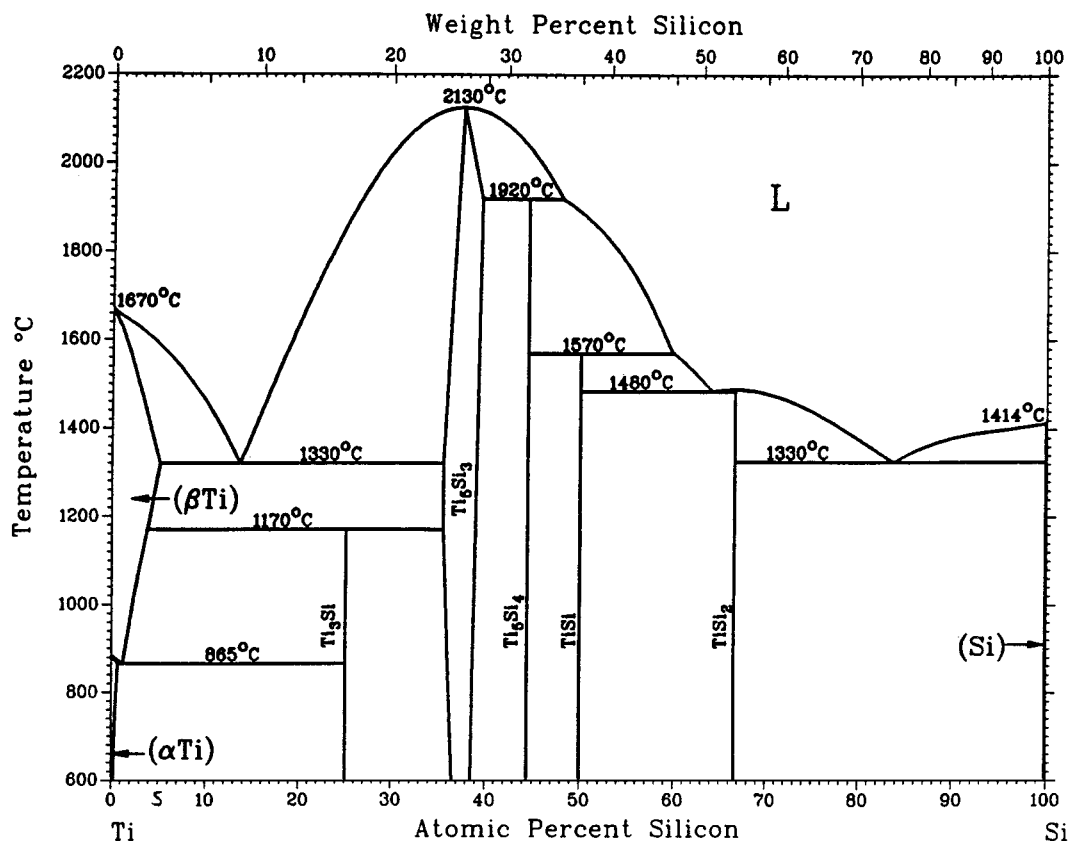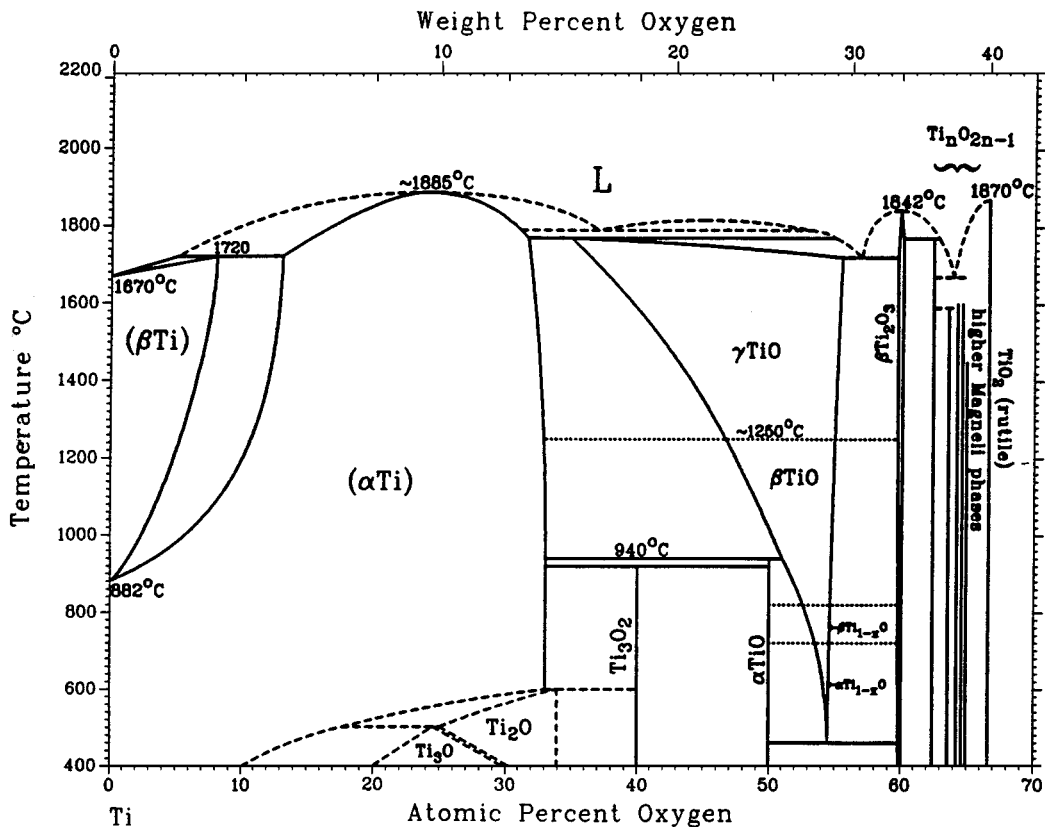

Figure 5 Ti-Si phase diagram [11].

Figure 6 Ti-O phase diagram [11].

the remaining liquid increase. This liquid solidifies at the end as β Ti (**b** phase in the present study), rich in Fe and Cr (Table III).

Other authors who have performed similar investigations using the same materials and methods [1], found that the thickness of the contamination zone was about 150 μm, higher than the thickness measured in the present study. In that previous study, the mold temperature was kept at 950 °C during casting, while in the present study the mold temperature was kept at 450 °C. The difference in mold temperatures provides the explanation for the difference in the thickness of the contamination zone. When the difference in temperature between the molten metal and the investment material increases, the heat transfer is accelerated and the solidification time decreases. This results in the decrease of the available time for the diffusion within the liquid of the elements coming from the investment material. This is in agreement with Miyakawa *et al.* [2], who mention that the increase in mold temperature increases the depth of the contamination zone. Lower mold temperatures have been proposed for the elimination of the contamination of cp Ti from SiO$_2$-based investments [9], but other severe problems concerned with final castings accuracy arise in this case. It is very probable that molten Ti solidifies before filling the mold. This results in incomplete casting which is quite unacceptable in commercial production.

In another study [2], it was found that the contamination zone had a layered structure and consisted of distinct layers with different microstructures. In that case, a Al$_2$O$_3$/SiO$_2$ investment material was used, while in this study the investment material contains practically

no Al$_2$O$_3$ (Table II). Al stabilizes the α-Ti phase. Its dissolution in molten Ti probably affected the solidification process in the contamination zone and resulted in the formation of an outer α-Ti phase layer.

From a clinical point of view, Ti castings with surface contamination are unacceptable, because various phases with unknown biocompatibility—instead of pure Ti—come in direct contact with oral tissues and thus severe biological hazards can occur. In addition, the contaminated surface of the Ti cast dental works could be problematic in applications when a metal-ceramic bond has to be applied (e.g. crowns). Finally, castings with contaminated surface exhibit reduced fatigue and elongation characteristics [6].

All the above mentioned considerations are concerned with cast Ti coming from conventional casting procedure with the use of an uncoated wax pattern and a mold made of SiO$_2$-based investment material (sample A). When the same investment material was coated by a protective ZrO$_2$ layer (sample B), the final Ti castings were clean, without traces of contamination at the surface neither from the investment material, nor from the coating material. The protective coating prevented the contamination of the casting from the of SiO$_2$-based investment material. ZrO$_2$, as well as Y$_2$O$_3$ and CaO, cannot be reduced by Ti and play the role of a diffusion barrier between the cast Ti and the investment. In addition, the fact that no Zr was detected at the casting's surface layer, means that the ZrO$_2$ particles were not detached from the mold walls by the liquid metal during casting and that the bonding between the investment material and the coating was strong and adequate for dental casting. The possible mechanisms of bonding

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between the investment material and the coating are currently under investigation by the same authors and the results will be published in a next paper.

An additional noteworthy result of the present study is the great difference in surface roughness that castings from coated and uncoated investments exhibited. The high roughness of sample A (uncoated investment), which has also been reported by other investigators [7], could be attributed to the two following reasons: (a) The liquid metal reduces some oxides from the investment material roughening its surface. Then the metal solidification starts onto the investment surface due to the heterogeneous nucleation and therefore, the cast metal copies the roughness of the investment surface. (b) The contamination zone shows high hardness and brittleness compared to the pure cast Ti. Consequently, during the sandblasting procedure for the removal of the investment material from the cast metal, small pieces of this brittle zone could also be removed.

5. Conclusion

When casting of cp Ti for dental applications takes place in molds made of conventional SiO_2-based, phosphate-bonded investment materials, a contamination zone with a thickness of about 100 μm forms at the casting's surface, due to the high chemical affinity of Ti and its capability to reduce many oxides. This zone is consisted of three distinct phases: (i) α-Ti phase with high O content (about 22 at %), (ii) β-Ti phase with remarkable Fe, Si and Cr contents (6.7, 2.4 and 1.0 at % respectively) and (iii) a Ti-Si compound with a mixed formula between Ti_5Si_3 and Ti_3Si. From a clinical point of view, this contamination zone is unacceptable. To eliminate contamination, a ZrO_2 coating was deposited on the investment's surface with the help of a wax pattern coating technique. This coating operated as a barrier between the investment material and the liquid metal. Clean castings without contamination were obtained in this way.

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