# Appearance of a Hard Layer ("α-case") on the Surface of Two Different Titanium-based Alloys

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**Abstract.** In spite of all applied precautions during casting of two titanium-based alloys which involved the application of a vacuum furnace, argon protective atmosphere and ceramic shell molds with very high chemical and thermal-shocks stability, appearance of the hard surface layer (also known as "α-case") could not be avoided. X-ray diffraction analysis, scanning electron microscopy, and microhardness measurements were performed for the microstructural and mechanical characterization of the hard layer.

## Introduction

Beside good mechanical properties, high corrosion resistance and good biocompatibility with the human tissue are of the primary importance in the biomediacal application of implant material [1]. Among many different materials titanium based alloys showed the best performance in the human body. The most used alloy Ti-6Al-4V (α + β) as well as the recently developed TiAl (γ) alloy are at the present time actively used for the the production of the variety of products, such as hip, shoulder and knee implants, screws, plates, *etc*. [1]. However, processing of this material presents a great problem due to very high reactivity of titanium at high temperatures during melting and solidification. Therefore, production of surgical implants by precision casting process has to be performed in vacuum, argon protective atmosphere, and use of specific shell molds is required. Even though mentioned precautions are applied, the metal in the liquid state reacts with the ceramic mold and, as a result of this reaction, the local increase in oxygen content in the metal near the surface promotes the formation of an oxygen-rich titanium c.p.h. solid solution known as "α-case". This reaction occurs at temperature where the bulk alloy would be the single β phase (b.c.c.) and also alters the (α + β) structure near the surface during cooling to room temperature [2]. "α-case" is a brittle and hard surface acting as a crack initiator, and since cracks propagate easily through most titanium alloys, the embrittled "α case" may cause rapid mechanical failure in clinical service. In order to remove this brittle surface (by chemical pickling or machining) it is important to determine the excess thickness of castings.

In view of these facts, an attempt was made to examine the caracteristics of "α case" (composition, thickness, hardness *etc*.), with the idea to find adequate process of its removal.

**Experimental**

Two materials were the object of this investigation: a commercial Ti-6Al-4V alloy (designated as Ti6Al4V) and an intermetallic compound 65Ti-33Al-2V* (designated as TiAl) produced in "Vinča". Ti6Al4V was used for the production of the prototypes of surgical implants, whereas TiAl was processed in the form of a rod with 10 mm in radius and 150 mm in height.

Centrifugal precision casting was performed for the production of surgical implants and TiAl rods. Graphite crucibles with the inner surface sprayed with $Y_2O_3$ layer were used for melting of both alloys.

Considering very high chemical reactivity of titanium and its alloys the conventional ceramic molds of $SiO_2$ and $ZrO_2$ (silica and zirconia) are unsuitable for use. Therefore, a special attention was paid to the development of a new kind of ceramic shell molds.

A conventional precision casting "lost-wax" procedure was performed using proprietary "self-supporting" $ZrO_2$-based ceramic shell molds [3]. Detailed processing of "self-supporting" molds and conditions during melting and casting were described in a previous paper [4]. Ceramic shell molds for shoulder implant consisting of a stem and a socket are shown in Fig. 1a, while corresponding precision castings can be observed in Fig. 1b. A cross-section of a mold showing wax pattern inside the mold surrounded by "primary" ($ZrO_2$) and "secondary" (mullite – $3Al_2O_3{\cdot}2SiO_2$) coatings is represented in Fig. 1c.

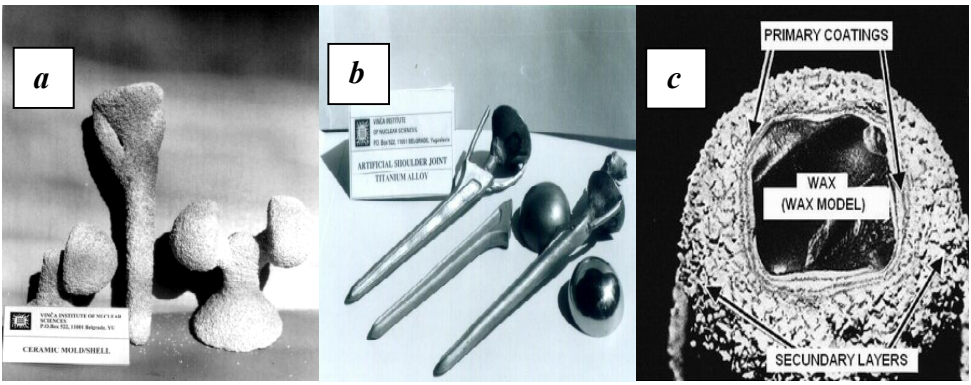


Fig. 1. *A Ti6Al4V shoulder implant consisting of a stem and socket. a) ceramic shell molds, b) precision castings and c) cross-section of mold.*

X-ray diffraction analysis with Ni-filtered $CuK_\alpha$ radiation and scanning (SEM) microscopy were used for microstructural characterization. Specimens for these examinations were cut out from the stem and shoulder socket.

Kroll's reagent (a mixture of 6 ml nitric acid, 3 ml 40% hydrofluoric acid and 100 ml of distilled water) was used as an etchant for microscopy examinations. Vickers hardness ($HV_{30}$) was measured applying load of 30 kg. Microhardness (with 100 g load) was measured in the area starting from the surface to aproximately center of the specimen.

* chemical composition is given in *wt.%*

**Results and discussion**

It should be noted that the first castings showed some defects such as a rough surface, micro and macro porosity when the preheating temperature of the shell mold was lower. However, applying higher preheating temperature these macro defects were successfully eliminated and a smooth surface was obtained .

SEM examinations revealed a surface layer ("α case") with the very coarse grains (Fig. 2). This structure largely differs from the structure of the inner part of the specimen in the case of both considered alloys. While the Ti6Al4V alloy structure consists mainly of the α phase plates showing a characteristic Widmanstätten structure and a small fraction of the β phase (Fig. 2a), TiAl alloy exibits the equiaxed grains whith a fully lamellar microstructure where the γ lamellae are mostly intermixed with dark $\alpha_2$ lamellae (Fig. 2b). The "α case" layer spreads between 150 and 200μm into the inner part of the both specimens .

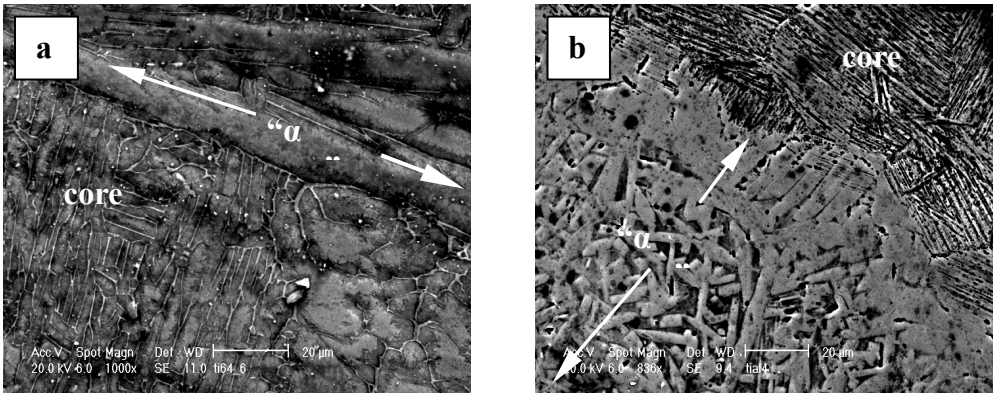


Fig. 2. *SEM micrographs. Microstructures of a) Ti6Al4V alloy, and b)TiAl alloy in the as-cast condition.*

X-ray diffraction analysis (Fig. 3a) of as-cast Ti6Al4V specimens from which the surface layer was removed proved the existence of the α phase with c.p.h. lattice (a = 0.29230 nm and c = 0.4672 nm, with c/a ratio of 1.59), β phase with b.c.c lattice (a = 0.3221 nm) and retained f.c.c. TiC phase. However, examining surface layer of this alloy significant changes in the X-ray diffraction patterns appeared (Fig. 3b). Beside the presence of the α phase, a few peaks of carbide and nitride phase (TiC and TiN) were detected together with a new phase that was not able to define. Curiosity was that the pattern did not reveal the presence of the β phase, which is the one of the constituents of this alloy.

Considering the patterns of the TiAl alloy it can be noticed that, while the pattern of the specimen with removed surface layer (Fig. 3c) exhibits the existance of $\alpha_2$ ordered $Ti_3Al$ phase with c.p.h. lattice (a = 0.5753 nm and c = 0.4644 nm), γ ordered TiAl phase with tetragonal lattice (a = 0.4016 nm and c = 0.4073 nm) with c/a ratio of 1.014 and a few peaks of retained ordered β (B2) phase (b.c.c), different phases appear to be stable on the surface. As can it be seen (Fig. 3d), surface of the TiAl retains all previous phases, except for the β phase, and shows a presence of a combined $Al_2Ti_4C_2$ and a few peaks of the unknown phase previously noticed on the surface of Ti6Al4V alloy.

The appearance of carbon in castings of both alloys originate from the carbon crucible indicating that $Y_2O_3$ coating was not efficient in preventing the reaction between this element and aggressive melt.

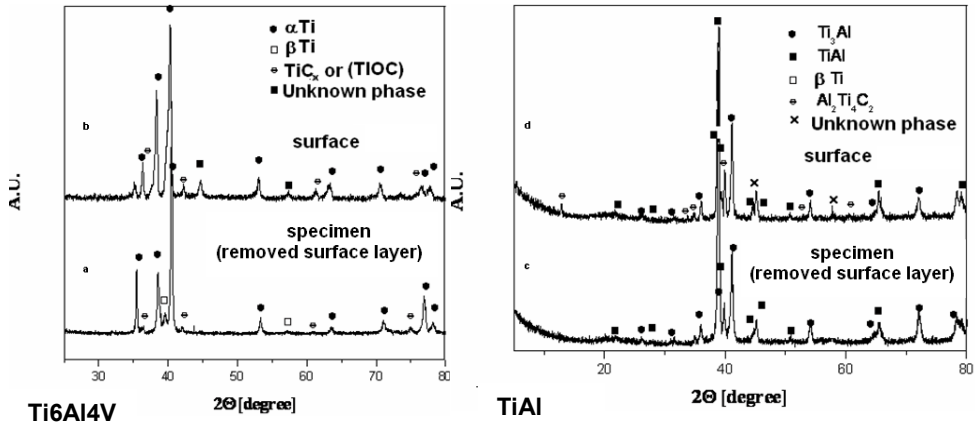


Fig. 3. *X-ray diffraction patterns of Ti6Al4Vand TiAl alloy representing the specimen without the surface layer (a), (c), and the surface of the specimen with the "α case" layer (b) and (d).*

The microhardness profile measured from the surface in contact with $ZrO_2$ "primary coating" into the interior of the specimen shows an abrupt decrease as the distance from the surface increases (Fig. 4). At about 200μm from the surface, which is the limit of the "α-case" region, the value of microhardness reaches a value of 340 and 380HV for Ti6Al4V and TiAl respectivelly, and remains constant. These values correspond to macrohardness measured in the core of the specimen. Hardness of 650HV and 750HV approximately 50μm from the surface of the specimens is nearly twice as that in the core of both alloys.

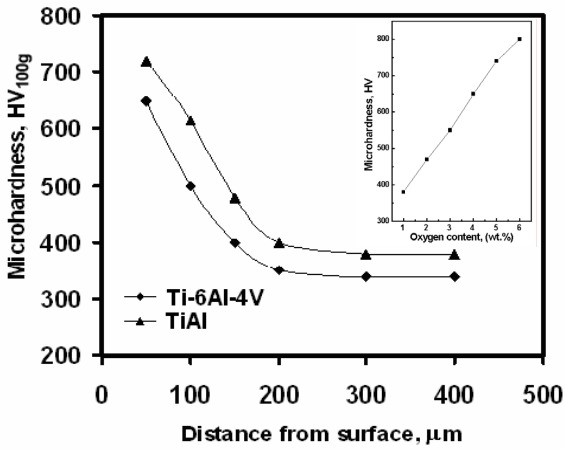


Fig. 4. *Plot of microhardness vs. distance from the surface in contact with $ZrO_2$. Inserted diagram illustrates the effect of oxygen content on microhardness [5].*

The value of 200μm for the "α-case" thickness is in fairly good agreement with SEM investigations. The fact that dissolved oxygen significantly increases hardness of titanium based alloys [5] (see inserted diagram in Fig. 4) together with the absence of the β phase leads to the conclusion that the hard surface layer with approximate thickness of 200μm

corresponds to "α-case". According to the values of hardness it may be supposed that the concentration of the dissolved oxygen near the surface approaches the value of 4 wt.% in the case of Ti6Al4V and around 5 wt.% for TiAl.

These results strongly suggest that for the reliable and safe application of titanium-based alloys processed by precision casting the "α-case" surface layer must be removed.

## Conclusions

1. Microhardness measurements showed that the amount of dissolved oxygen in titanium could be around 5 and 4 wt.% yielding hardness of about 750 and 650 HV for TiAl and Ti6Al4V, respectively, at 50μm from the surface inside "α-case". Although quantitative measurements have not been performed, the results of this paper suggest that "α-case" is most probably oxygen stabilized α phase.
2. Scanning electron microscopy revealed a surface layer ("α-case") which largerly differs from the remainder of the structure in the case of both titanium based alloys.The thickness of "α-case" is approximatelly 200μm.
3. Hardness of "α-case" is approximately two times higher than the core structure of two alloys.
4. X-ray diffraction analysis proved that $Y_2O_3$ coating was not efficient in preventing the reaction between carbon and aggressive melt.
5. The removal of hard "α-case" is essential for the reliable application of precision cast Ti6Al4V and TiAl surgical implants.

## Acknowledgement

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