Effect of pickling solution on the surface morphology of Ti6Al4V alloy investment cast

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Abstract

Ti6Al4V alloy interacted with yttria fully stabilized zirconia face-coat to generate the alpha-case layer during the investment casting. The alpha-case mainly contained Al_2O_3, TiO_2, $TiO_{0.48}$, VO_2, ZrO_2 and Ti_2ZrAl as revealed by the Energy dispersive X-ray and X-ray diffraction analyses.
The chemical milling of this outer layer, using a mixture of hydrofluoric acid and nitric acid, removed contaminating phases and led to lower hardness of the free surface of the investment casting. The roughness as well as the glossiness of the chemically milled surface decrease as the hydrofluoric acid concentration decreases. Mixing the hydrofluoric acid with phosphoric acid affects the surface morphology.

Keywords: Alpha-case, yttria stabilized zirconia face-coat, investment casting and chemical milling, surface roughness

Introduction

Titanium and its alloys are extensively used in the new generation of commercial aircrafts and biomedical applications, because of their advantages, such as high specific strength, excellent fatigue property, good corrosion resistance and excellent biocompatibility. However the high melting point and high reactivity of titanium and its alloys with ceramic crucibles and ceramic moulds lead to the formation of alpha-case layer, in spite of the thermodynamic stability of ceramic refractories such yttria stabilized zirconia and yttria.

Hydrofluoric acid offers a fast pickling rate for removing this alpha-case layer from the surface. Although the chemical milling process has been investigated, the effect of the pickling solution on the surface quality after the alpha-case removal still needs to be addressed.

The commercially pure Ti (cp Ti) and its alloys may possibly interact with the ceramic materials such as Al_2O_3, $ZrSiO_4$, ZrO_2 and CaO or Y_2O_3 stabilized ZrO_2 during melting or investment casting processes. The α-case layer generated thereby seems to be the result of both interstitially dissolved elements such as O, N, and C and substitutionally dissolved elements such as Si, Ca, Fe, Zr and Y [1, 2, 3, 4].

Hydrofluoric acid offers a fast pickling rate for removing this alpha-case layer from the surface. Although the optimal ratio of nitric-hydrofluoric solution and the mechanism of the etching have been investigated by Say et al.[5], the optimal time and temperature, and the effect of the chemically milling solution on the free surface after the alpha-case removal still needs to be addressed.

This study, mainly investigated the effect of pickling solution on the surface roughness and the removal of the alpha-case layer generated by yttria fully stabilized zirconia/Ti-6Al-4V interaction during investment casting.

Experimental Procedure

The Ti-6Al-4V alloy was investment cast, after induction melting, using fully yttria stabilized zirconia (Y_2O_3-ZrO_2) face-coat. The ceramic shell mould was made by alternate dipping of wax patterns into a colloidal ZrO_2 and subsequent stuccoing with ZrO_2 stucco. The entire tree mould was first dried for 24 hours at 22°C, then de-waxed using a LBBC steam boiler clave at 200°C and 8 bars for 15 minutes and fired at 800^{o}C for 2 hours.

The free surface and the cross section of the as cast was chemically analyzed using the Scanning Electron Microscope (SEM) equipped with Energy dispersive X-Ray (EDS) and X-ray diffraction (XRD). The Vickers microhardness was measured from the surface according to the ASTM E92 [6].

Ti-6Al-4V samples were chemically milled in nitric-hydrofluoric acid solution ($HF+HNO_3$). Cylindrical specimens of 15mm diameter and 10mm thick were used. Hydrofluoric acid (70%) and nitric acid (55%) were mixed with distilled water to make up the pickling solutions. Subsequently, specimens were immersed, washed with pressured water and then ultrasonically clean in ethanol.

The loss of weight and the seize reduction were determined for chemical milling rate evaluation purposes.

A Talyform surface texture measuring machine with a 2µm probe radius was used for the surface roughness measurement.

Results and Discussion

Microstructural examination of the cross section of Ti6Al4V investment cast, using the stereo and optical dark field micrographs (Figure 1) showed a darkish area at the edge of the cast, as sign of the presence of contaminating elements.

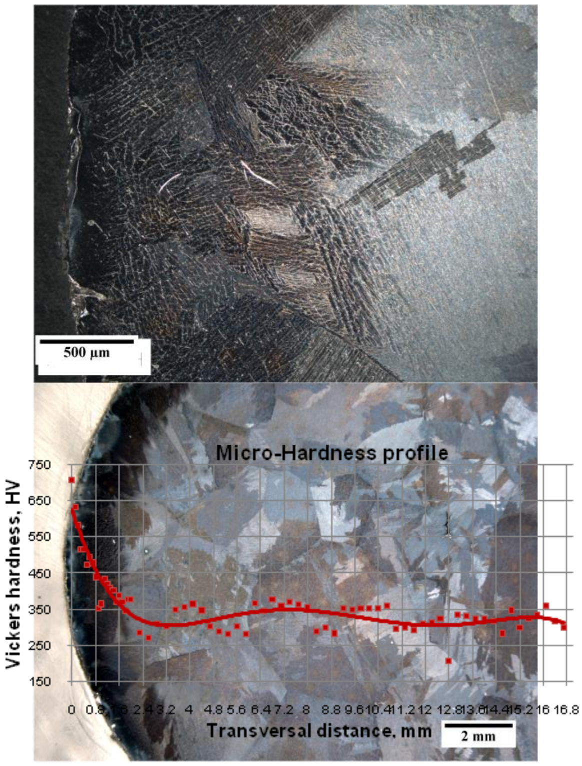


Figure 1. Alpha-case layer after investment casting of Ti6Al4V alloy, and the microhardness profile from the edge into the core of cast.

The microhardness profile of the as cast Ti6Al4V is shown on Figure 1. The outer layer seems harder than the core of the casting. The hardness in the core averaged 325 Hv (with Stdv=75), however the outer layer reached about 700 Hv.

The SEM microstructural analysis, performed on the as cast free surface, revealed black and white spots, rough surface and cracks on the castings, Figure 2.

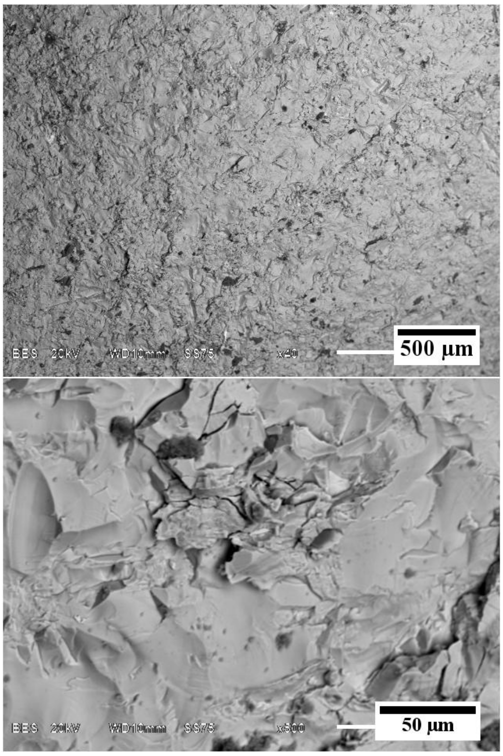
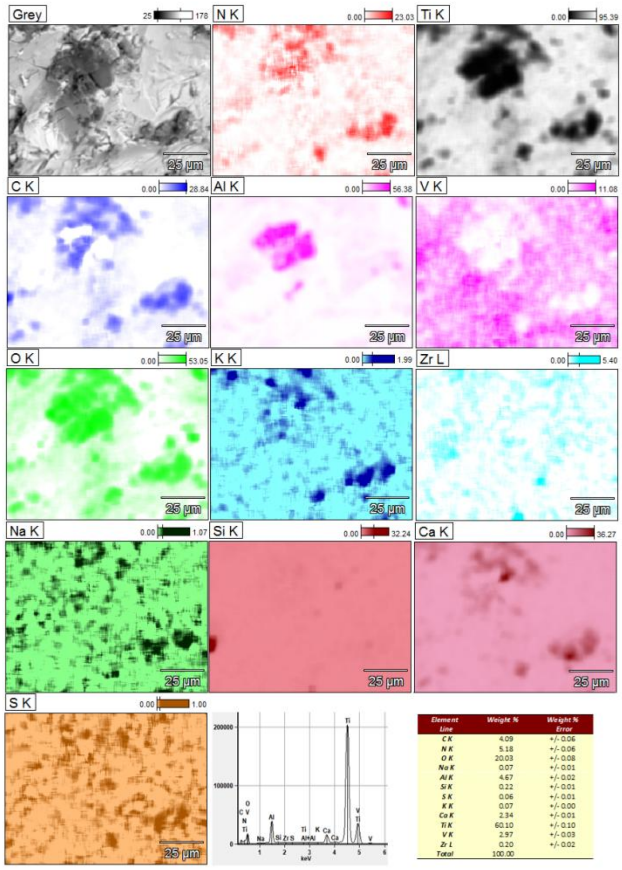


Figure 2. Black and white spots on the on the free rough surface of the as cast Ti6Al4V alloy.



Element Line	Weight %	Weight % Error
C K	4.09	+/- 0.06
N K	5.18	+/- 0.06
O K	20.03	+/- 0.08
Na K	0.07	+/- 0.01
Al K	4.67	+/- 0.02
Si K	0.22	+/- 0.01
S K	0.06	+/- 0.01
K K	0.07	+/- 0.00
Ca K	2.34	+/- 0.01
Ti K	60.10	+/- 0.10
V K	2.97	+/- 0.03
Zr L	0.20	+/- 0.02
Total	100.00	

Figure 3. EDS spectrum imaging of the free surface of Ti6Al4V investment cast.

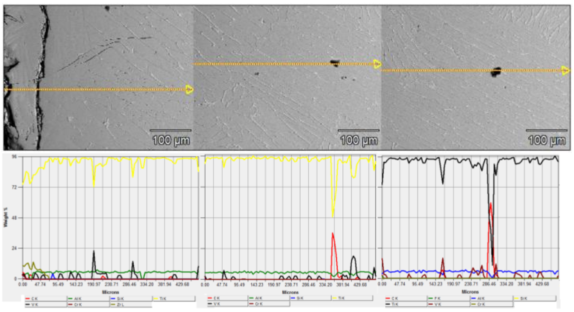


Figure 4. Edge EDS line scanning of the investment cast Ti6Al4V alloy.

The X-ray diffraction analysis made on the as cast free surface revealed the presence of Ti oxides, Al_2O_3, $CaCO_3$, FeO and V_8C_7, as represented on the XRD spectrum, Figure 5.

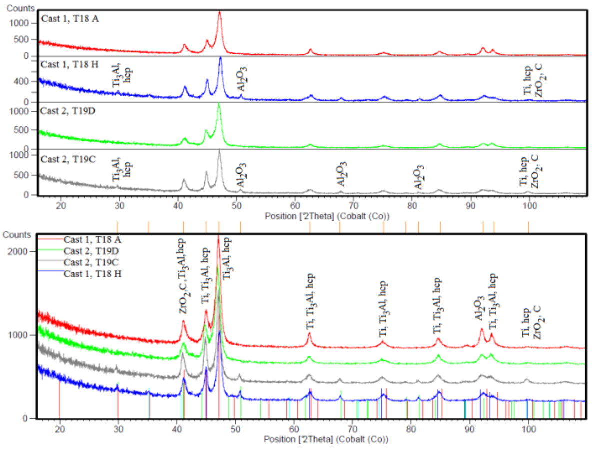


Figure 5. XRD spectrum of the cross-sections of Ti6Al4V investment cast.

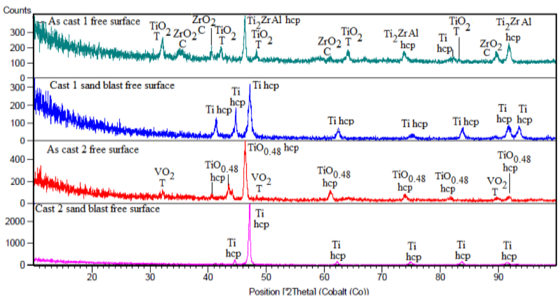


Figure 6. XRD spectrums of the as cast and sand blast free surface of Ti6Al4V investment cast 1 and cast 2.

The depth profile of the microhardness, after chemical milling, decreased from 700 HV (Figure 1, as cast Ti6A4V), to about 330 HV (stdv=55) (Figure 7).

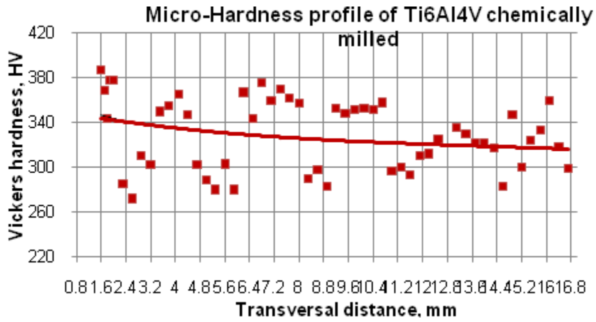


Figure 7. Hardness profile of the chemically milled Ti6Al4V with 3%HF+20%HNO_3 solution.

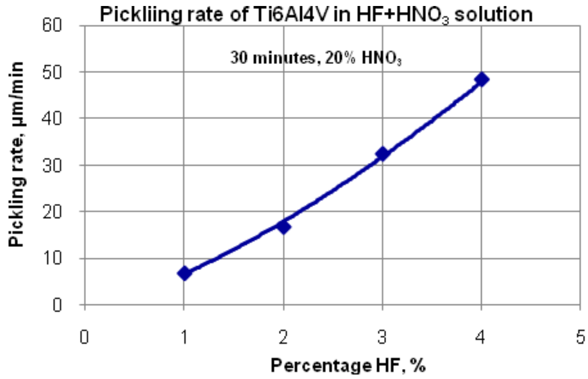


Figure 8. Pickling rate of Ti6Al4V HF+20% HNO_3 solution for 30 minutes

The influence of the hydrofluoric acid (HF) in 20% (volume) of nitric acid (HNO_3) is shown in the Figure 8. The pickling rate of Ti6Al4V in 20% volume of HNO_3, for 30 minutes, increases as the volume percent of HF increases. The 4% HF etching solution revealed less contaminating elements on the free surface, comparatively to that of 2 and 3% HF, Table 1, however the presence of fluorine (F) was detected for 4% HF. The solution of 3%HF+20% HNO_3 produced the acceptable results for the chemical milling process.

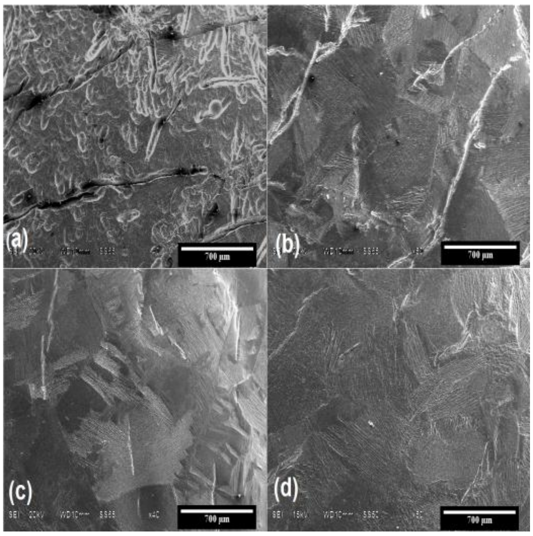


Figure 9. Free surface after chemical milling, (a) 1%HF, (b) 2%HF, (c) 3%HF and (d) 4%HF.

Table 1. Chemical composition of the as cast and chemically milled Ti6Al4V alloy using HF and 20% HNO_3 solution.

Element, Wt %	As cast	1% HF	2% HF	3% HF	4% HF
C	1.24	2.70	<0.01	<0.01	<0.01
N	4.52	ND	ND	ND	ND
O	6.61	ND	ND	ND	ND
F	ND	ND	ND	ND	1.13
Na	0.07	ND	0.02	ND	ND
Mg	0.01	ND	ND	ND	ND
Al	3.72	5.89	5.60	6.18	6.19
Si	0.09	0.05	0.02	0.04	ND
P	0.11	ND	ND	ND	ND
S	0.06	ND	ND	ND	ND
K	0.07	ND	ND	ND	ND
Ca	1.08	0.21	0.02	ND	ND
Ti	71.60	86.05	88.98	88.48	88.16
V	3.57	4.36	4.20	4.16	4.76
Cr	0.01	<0.01	<0.01	<0.01	ND
Fe	0.14	0.06	0.11	0.11	ND
As	0.06	ND	ND	ND	ND
Zr	0.39	0.23	0.16	0.09	0.04

The pickling rate is seriously affected by the chemical milling temperature; the highest rate is reached at temperature range of 60-70°C in 3% HF and 20% HNO_3 etchant solution, for 30 minutes, Figure 10. The optimum milling rate and efficiency was revealed to be about 40 minutes, in the same range, Figure 11. Milling the Ti6Al4V at temperature above 70°C and for longer than 40 minutes resulted in fluorine contamination and rougher surface after chemical milling process.

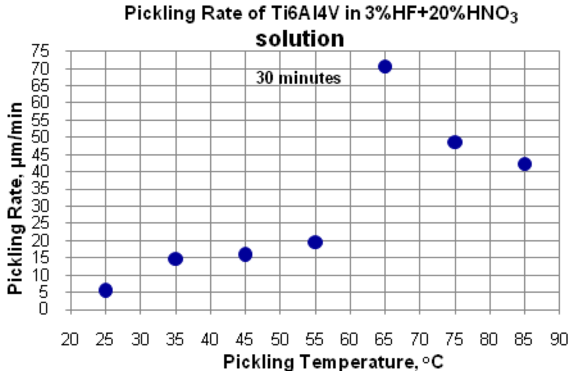


Figure 10. Change of pickling rate with temperature of Ti6Al4V in 3% HF + 20% HNO_3.

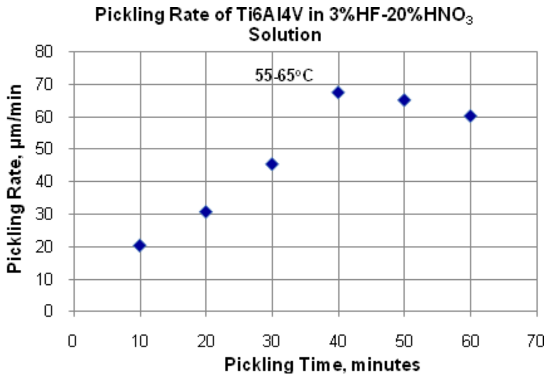


Figure 11. Optimal time for etching Ti6Al4V with 3% HF+20% HNO_3 in the temperature range of 55-65°C.

The surface roughness of Ti6Al4V investment cast, chemically milled using HF+20% HNO_3 is shown on Figures 12, 13, 14, 15 and 16 for 1, 2, 3, 4, and 5% HF. The maximum height of the Profile (R_t), the arithmetic average of absolute values (R_a), and the average distance between the highest peak and lowest valley (R_z), are given in Table 2.

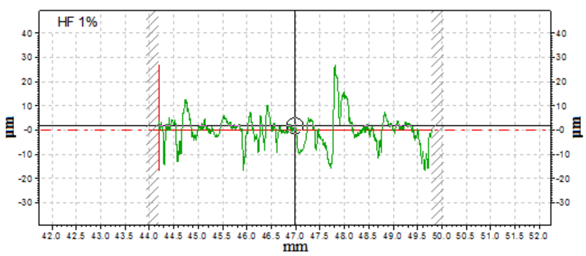


Figure 12. Roughness of Ti6Al4V investment cast, chemically milled using 1% HF +20% HNO_3 solution.

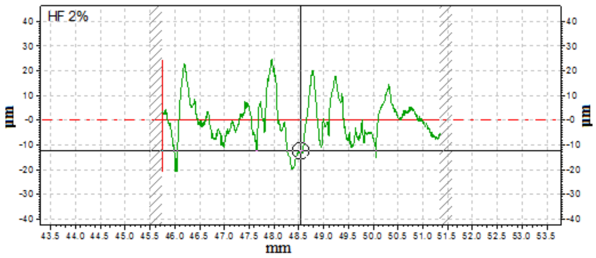


Figure 13. Roughness of the chemically Ti6Al4V investment cast, using 2% HF +20% HNO_3 solution.

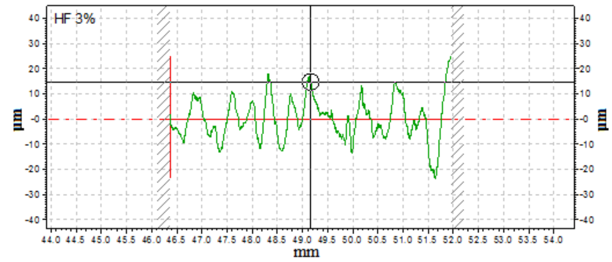


Figure 14. Roughness of the chemically Ti6Al4V investment cast, using 3% HF +20% HNO_3 solution.

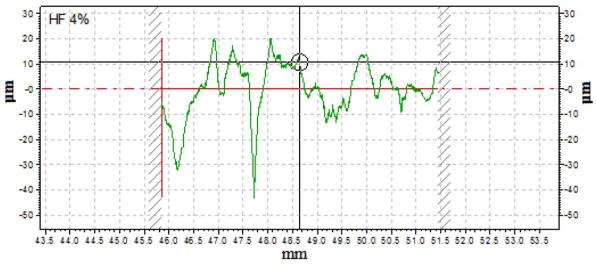


Figure 15. Roughness of the chemically Ti6Al4V investment cast, using 4% HF +20% HNO_3 solution.

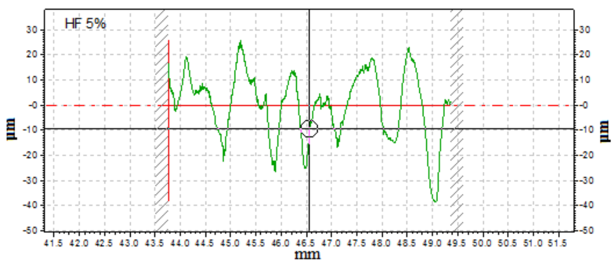


Figure 16. Roughness of the chemically Ti6Al4V investment cast, using 5% HF +20% HNO_3 solution.

Table 2. Ra, Rt and Rz values of the chemically milled Ti6Al4V investment cast

	Chemical milled surface Roughness		
HF, (%)	*Ra, µm*	*Rt, µm*	*Rz, µm*
1	4.272	43.866	22.938
2	6.873	45.424	29.587
3	6.603	48.744	27.875
4	7.920	63.482	28.217
5	10.498	64.289	39.597

The surface roughness of the Ti6Al4V investment cast, chemically milled using HF+ 20% HNO_3 solution, increases as the HF content increases in the pickling solution, Figure 17.

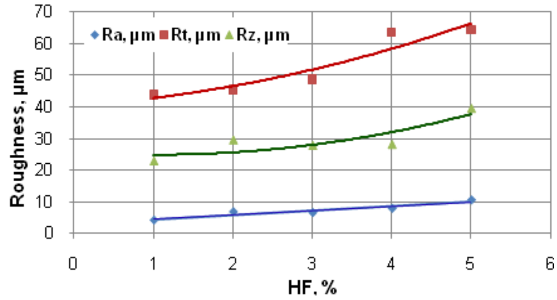


Figure 17. The increase of surface roughness with HF content in the pickling solution.

The surface roughness of the Ti6Al4V investment cast and chemically milled using the mixture of HF+H_3PO_4 solution is shown on Figures 18, 19, 20 and 21.

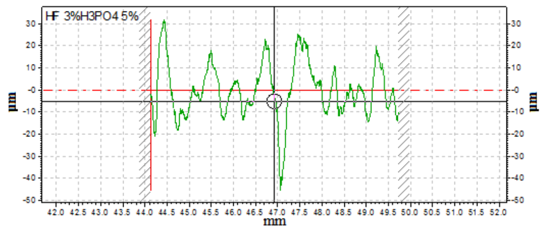


Figure 18. Roughness of the chemically Ti6Al4V investment cast, using 3% HF+5% H_3PO_4 solution.

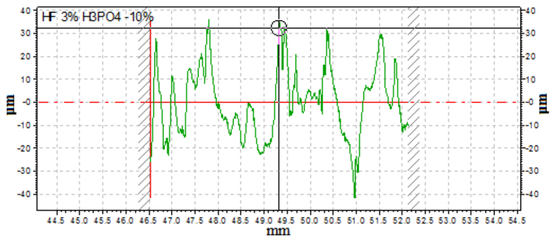


Figure 19. Roughness of the chemically Ti6Al4V investment cast, using 3% HF+10% H_3PO_4 solution.

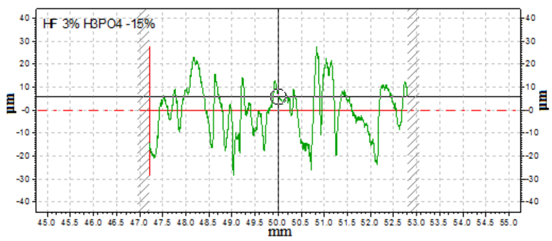


Figure 20. Roughness of the chemically Ti6Al4V investment cast, using 3% HF+15% H_3PO_4 solution.

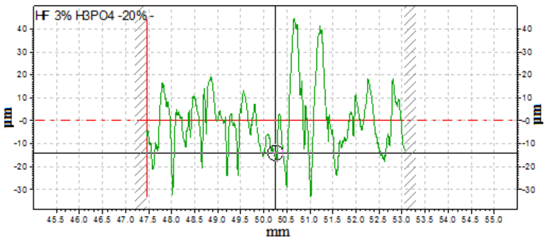


Figure 21. Roughness of the chemically Ti6Al4V investment cast, using 3% HF+20% H_3PO_4 solution.

The arithmetic average of absolute values (R_a) and the maximum height of the Profile (R_t), remain unchanged with the increase of H_3PO_4 content in the pickling solution, however the average distance between the highest peak and lowest valley (R_z), is negatively affected with 20% H_3PO_4 content in the solution, Figure 22 and Table 3.

Table 3. Ra, Rt and Rz values of the chemically milled Ti6Al4V investment cast.

	Chemical milled surface Roughness		
H_3PO_4, %	*Ra, µm*	*Rt, µm*	*Rz, µm*
5	9.466	77.457	37.907
10	12.108	77.849	38.49
15	8.752	56.189	37.277
20	10.556	77.720	50.718

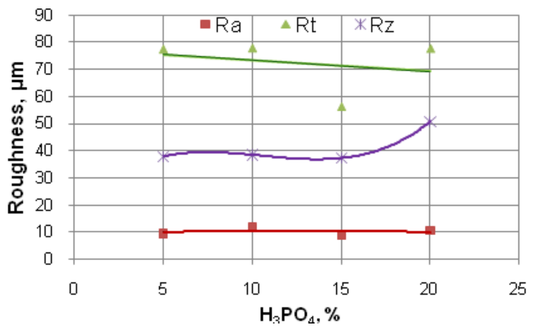


Figure 22. Effect of H_3PO_4 content on the surface roughness of Ti6Al4V investment cast.

Conclusions

The alpha-case was efficiently removed using the optimal ratio of hydrofluoric/nitric acid solution.

The surface finished and its subsequent chemical contamination were affected by hydrofluoric/nitric acid ratio, and the pickling time and temperature. High hydrofluoric acid content increases the surface roughness.

The phosphoric acid may be used to attenuate the negative effect of the hydrofluoric/nitric acid solution on the surface roughness.

Acknowledgments

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