Optimization of the chemical milling of investment cast titanium alloys

Silvia Gaiani[1,2], Elena Colombini[2], Paolo Veronesi[2], Uroš Rosa[1]
[1] Akrapovič d.d. – Ivančna Gorica, Slovenia
[2] University of Modena & Reggio Emilia – Dept. of Materials Engineering – Italy

Abstract
Investment casting is a popular casting technique for manufacturing of several titanium alloy components dedicated to different industrial applications, as aerospace and automotive. This manufacturing process could be an economic net-shape technology, since the investment casting allows obtaining complex shapes, accurate geometries and reduced thicknesses. However, the reactions between titanium in liquid state and ceramic shell result in the formation of the so called *alpha case*, a brittle layer developed by the interstitial elements such as carbon, nitrogen and especially oxygen dissolved from mold materials. The alpha case layer will deteriorate the surface of titanium castings, but it can be eliminated using chemical milling processes.
This paper describes the work developed by the authors to investigate the effects of chemical milling on two of the most used titanium alloys: Ti6Al4V and CP Ti grade 2. The aim of this study is finding a reliable industrial method for performing chemical milling on titanium casting which can be efficient in terms of metal removal rate, repeatable and environmentally safe.

Keywords: titanium investment casting, titanium pickling, chemical milling, alpha case layer

1. Introduction

Investment casting technology is widely used for manufacturing of titanium components. Compared to other forming methods, such as forging or machining, casting presents several benefits; in detail, its biggest advantages over other forming methods are flexibility and possibility to obtain complex components in near to net shape. Especially in case of titanium and its alloys, the high final machining costs greatly limit the number of applications for which these materials are feasible [1]. Due to this reason, net shape techniques as investment casting could be a valuable alternative to conventional forming processes.

On the other hand, the investment casting of Ti alloys has also a drawback. In fact, these materials present a high inherent reactivity with the mold primary materials at elevated temperatures during investment casting [2]. The reactions between liquid titanium and mold materials result in the formation of the so called "*alpha case" (*or *α-case*) [3], a hard and brittle layer which will deteriorate the surface and change the mechanical properties of titanium castings.

The α-case is generally known to be developed by the interstitial elements such as carbon, nitrogen and especially oxygen dissolved from mold materials [4] and diffused further below the surface of the cast at a high temperature. The final depth of α-case layer depends on the cooling rate, casting geometry, and the amount of oxygen at the interface between mold and liquid metal; a thickness in the range of 50 to 500 μm is normally detected for standard Ti castings [5].

The presence of α-case makes the castings difficult to be machined and can promote cracks initiation and propagation, with a significant reduction of fatigue properties. Due to these reasons, is very important find a method which allows preventing, or at least reducing, the α-case formation. In order to avoid this problem, is common praxis to adopt as primary coat layer during mold preparation ceramic materials Zirconia (ZrO_2) or Yttria (Y_2O_3) based, because these oxides present a standard free energy more negative than Titania (TiO_2), so that a minimal reaction occurs between the mold wall and the liquid metal during pouring and solidification.

However, also if the use of Zirconia or especially Yttria, can be helpful in reducing the depth of α-case layer, its formation cannot be completely avoided, and moreover the use of these ceramic materials increases the cost of Ti castings. In order to completely remove the hardened layer, the most efficient industrial method is chemical milling. In detail, all the most common chemical products for titanium pickling available on the market are acid baths containing etching solutions based on sulfuric, hydrofluoric, or nitric acid or their mixtures. Despite the high dissolution rates of titanium alloys in hydrofluoric acid itself, very often HF is used in combination with the aforementioned acids, since its individual solutions rapidly loose their activity and, hence, serviceability because of their buffering with the fluorides formed. Additional introduction of sulfuric or hydrochloric acids slightly increases the initial rate of the process and substantially improves the serviceability of the baths. Nitric acid is less efficient from the viewpoint of the process rate, but provides the smoothest surface relief and diminishes the hydrogen absorption by the alloys [6].

This paper describes the work developed by the authors to investigate the effects of chemical milling on two of the most used titanium alloys: Ti6Al4V and CP Ti Gr. 2. The primary aim of this research is to evaluate the metal removal rate of various chemical baths, presenting different acid mixtures and concentration, in order to define which of them would be the most efficient and stable for industrial scale use.

2.0 Experimental procedure

2.1 Samples preparation

The wax patterns for performing the chemical milling trials were made by wax injection into a simple aluminum mold. The nominal geometry of the wax patterns is shown in Fig. 1.

Fig. 1 – Geometry of the specimen for CM trials

Subsequently, the patterns were assembled in two trees, one for casting CP Ti Gr. 2 and one for casting Ti6Al4V alloy; on every tree 60 specimens were placed. The shelling process started with a primary layer ZrO_2 based, followed by one layer of Al_2O_3. After the first two layers, the backup was applied using molochite (seven layers); the shell molds were dried at a controlled temperature (298±1 K) and a relative humidity (40±1%) for 4 h for every single layer.

The dewaxing process of the shell molds was carried out at around 1123 K for 2 h using flash fire method. Finally, the melting process took place in an induction skull melting vacuum oven using centrifugal casting procedure.

After shell removal, the specimens were cut off from the trees and ball blasted using stainless steel abrasive material.

2.2 Chemical composition & gas content determination

The chemical analyses of the two melts have been performed choosing a sample in as castes condition from both the trees and using a CCD optical spectrometer SpectroLab. The obtained results are shown in Table 1 (average values of four measurements).

	Al (%)	**V** (%)	**Fe** (%)	**Si** (%)	**C** (%)	**Ti** (%)
Gr. 2	0,022	0,052	0,066	0,022	0,014	Bal.
Ti6Al4V	6,123	4,071	0,156	0,021	0,026	Bal.

Table 1 – Chemical composition of the two melts

From the same specimens, other samples for performing gas contentment analyses have been extracted. These measurements have been performed using the analyzer ELTRA ONH 200. The measuring principles used by this instrument are solid state infrared absorption for detecting oxygen and thermal conductivity for detecting nitrogen and hydrogen. According to standard ASTM 1447, for gas content analyses the specimen must be extracted 6 mm below the surface, in order to avoid the influence of α-case layer or other contaminations. Considering that subject of this paper is studying the effect of α-case removals by chemical milling, the analyses have been repeated twice: one extracting a sample from the center of the specimen (according to the standard), and another extracting a sample with three surfaces in as casted condition. The obtained results are summarized in Tab. 2.

	Center			**Surface**		
	O (%)	**N** (ppm)	**H** (ppm)	**O** (%)	**N** (ppm)	**H** (ppm)
Gr. 2	0,148	34,8	35,7	0,289	47,2	99,8
Ti6Al4V	0,219	33,6	50,5	0,316	32,4	95,8

Table 2 – Gas content determination

Observing the data summarized in Table 1 and 2, is visible that the two alloys are accomplishing the requirements of standard ASTM B 367 in terms of chemical composition. Regarding the gas content, the values of O_2 detected on the surface are exceeding the limit value, which is 0,25 %.

2.3 Alpha case depth determination: hardness profile method

The standard EN 2003/9 *"Determination of surface contamination (Method A – Micrographic examinations; Method B – Hardness evaluation)"* specifies two methods of determining surface contamination caused by α-stabilizers elements on titanium and titanium alloys for aerospace applications.

The first method, that is micrographic inspection, establish to observe the etched sample (cross section of the part under testing) using an optic microscope and simply report any appearance of a white layer which indicates the presence of surface contamination (α-phase).

The second method, which is hardness evaluation, prescribe to realize two series of indentations $HV_{0,2}$ in two specific locations:

a) Minimum 3 indentations at a distance < 0,1 mm from the section surface

b) Minimum 3 indentations at about mid-thickness of the section

Afterwards, the average value of these measurements shall be calculated for each location, and if the difference between these values is > 50 $HV_{0,2}$ the surface contamination is present.

Considering that the aim of our studies is detecting the depth of alpha case layer on components obtained by investment casting, the idea is to use the EN 2003/9 standard – Method B as a basic reference, and then standardize a procedure which can allow performing a quantitative determination of the hardened layer.

From two specimens in as cast condition (one Gr.2 one Ti6Al4V), transvers sections of every steps have been extracted, put into phenolic resin, polished and etched in order to reveal the microstructure. After that, a series of micro hardness test have been done using the following procedure:

a) Perform a series of indentations $HV_{0,1}$ (minimum 15) moving perpendicularly from the surface to the center of the specimen. The distance between these indentation is equal to 0,07 mm. In this way the hardness profile of the sample will be detected
b) Perform 10 indentations $HV_{0,1}$ in the center of the section. The distance between these indentations is equal to 1 mm. In this way the hardness of the core is detected; the average value of these measurements will be the cut – off limit used for determining the alpha case depth (see Fig. 3)

The displacement of hardness indentations, as explained in point a) and b), is showed in Fig. 2.

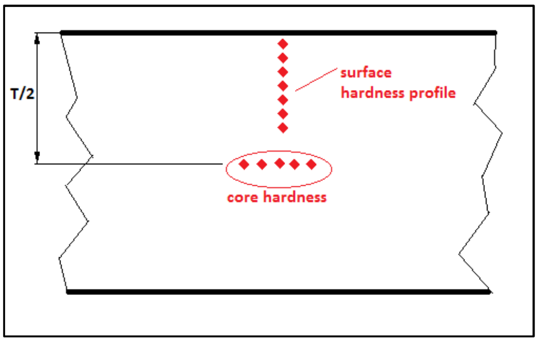

Fig. 2 – Indentations position

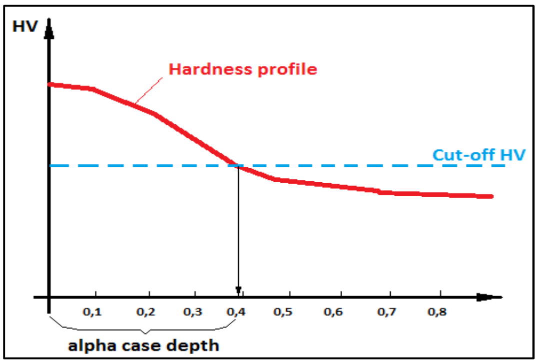

Fig. 3 – Hardness method concept

In titanium components obtained by investment casting, the hardness of the core is strongly influenced from several factors, like:

- type of alloy
- nature of the microstructure (monophasic or biphasic)
- dimension of the grain size (strongly dependent on speed of solidification)
- oxygen content

Due to these reasons, is obvious that the cut-off limits must be evaluated for every single step singularly, and that is not possible to standardize a value which is always valid.

In Fig. 4 and 5 the hardness profile for every single step of the specimens are shown, while Table 3 summarizes the depth of α-case obtained using a specific cut-off value for every hardness profile.

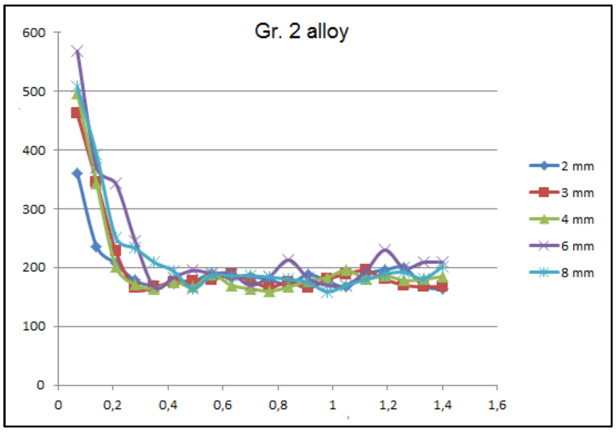

Fig. 4 – Hardness profile of Gr. 2 specimen as cast

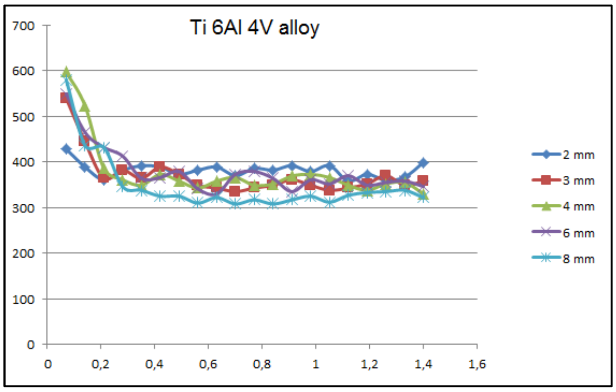

Fig. 5 – Hardness profile of Ti 6Al 4V specimen as cast

	Gr. 2		Ti 6Al 4V	
	Cut - off (HV0,1)	αcase depth (mm)	Cut – off (HV0,1)	αcase depth (mm)
2	183	0,28	355	0,35
3	181	0,35	376	0,28
4	184	0,28	357	0,35
6	181	0,35	361	0,35
8	179	0,42	353	0,42

Table 3 – Alpha case depth determination

The results summarized in Tab. 3 show that the depth of α-case layer is increasing with the thickness of the specimens. This tendency is fully understandable, because the ticker is the wall, the longer will be the solidification time and so the time that the chemical species have for dissolving in the liquid metal. However, considering that the hardness peak is smoothening quite rapidly, we can assume that for both the alloys an average removal of 0,35±0,02 mm could be enough for eliminating the α-case effects. Considering that the total surface of the cast specimens is equal to 60,4 cm^2, the mass of material to be removed by chemical milling can be calculated using a simple equation. The results are summarized in Table 4.

	ρ (g/cm^3)	Min. removal (gr.)	Max. removal (gr.)
Gr. 2	4,54	9,049	10,146
Ti6Al4V	4,42	9,043	10,139

Table 4 – Target for mass removal

2.4 Mass, thickness and roughness measurements

Every specimens used for performing chemical milling trials have been measured before the tests. In detail, the thickness of every step of the specimens has been measured in the center of the step using a micrometer (accuracy 0,001 mm), while the mass has been detected using a precision balance (accuracy 0,0001 gr.). The roughness of the specimens has been measured in the center of two steps: the one of 3 mm thickness and the one of 6 mm thickness. The length of measurement was 0,8mm and a Gaussian filter has been used; the values of R_a and R_z have been estimated.

For better understanding, the data collections of the measurements mentioned above will be presented together with the final results of the chemical milling trials in the following paragraphs 3.2 and 3.3.

3.0 Chemical milling trials

3.1 Acid bath solutions

Since several years, chemical milling is considered as a valuable method for removing the alpha case layer from cast or hot worked titanium components. Historically, the most popular family of chemical milling baths was based on hydrofluoric and nitric acid solutions. In recent times, these baths have been replaced by pickling solution obtained mixing HF and peroxide, with the aim of preventing the formation of hydrogen gas during titanium etching.

Generally, solutions of chemical milling would have strong effects on the surface and mechanical properties for the etched parts. Due to this reason, in order to the detected the best solution for industrial application in terms of efficiency, costs, and environmental safety, several different acid baths has been tested. The trials have been carried out in different laboratories or industrial plants. Anyway, during every test, the specimens have been hold using a polymeric wire, in order to avoid any contact with the basin surface and moreover, a circulation of the pickling baths using compressed air and/or mechanical agitation has been realized. The treatment period on two specimens for every trial has been respectively 30 and 60 minutes. The nature of the solutions used for the chemical milling trails are presented in Table 5.

The efficiency of the bath, however the ability to obtain a metal removal, depends on the concentration of acid, temperature of the solution, and amount of metal dissolved in acid. Obviously, the greater the concentration of the acid and the higher the temperature, the more the removal rate is accelerated. Anyway, in order to obtain a stable process and a constant removal in every area of the treated component, an important role is played just from the amount of titanium dissolved into the bath. In fact, as the concentration of titanium increases in the bath, the reaction proceeds slower. This is because one titanium ion reacts with six fluoride ions.

	Chemicals species	Concentration in H_2O	T (°C)	Correction
S1	HF + H_2SO_4	110g/l S1 + 70 g/l H_2SO_4	36	Standard product H_2O_2 based
S2	HF + H_2O_2 stabilized	20% S2	22	H_2O_2
S3	HF + $Fe_2(SO_4)_3$	56,5% $Fe_2(SO_4)_3$ / 7% HF / 35,5% H_2O	35	None
S4	Various Fluorides + HNO_3	Not diluted in water	56	Addition of new S4 product

Table 5 – Different solutions used for the trials

Approximately 12 gr./liter of titanium will require ten to twenty times longer than one gram per liter of titanium to achieve the same etching [7]. To avoid the increasing titanium concentration, periodic additions of hydrofluoric acid or peroxide has been made to the baths (see Table 5); during every trial, the maximum concentration of dissolved titanium has been kept under 5 gr./liter, with the aim to maintain the etching speed as constant as possible.

The results of the chemical milling trials in terms of weight reduction, thickness distribution, roughness, hardness and hydrogen adsorption are presented and discussed in the following paragraphs.

3.2 Weight reduction evaluation

Every specimen has been weighted before and after the chemical milling treatment. The results are listed in Tables 6 and 7.

	GR. 2			Ti 6Al 4V		
	Before CM (gr.)	After CM (gr.)	Remov. (gr.)	Before CM (gr.)	After CM (gr.)	Remov. (gr.)
S1	51,3280	40,4474	10,8806	53,2552	44,2994	8,9558
S2	52,8821	50,5230	2,3591	50,0402	47,5370	2,5032
S3	51,8390	47,0759	4,7631	52,5094	48,4652	4,0442
S4	49,2884	40,2808	9,0076	50,9353	42,4106	8,5247

Table 6 - Weight reduction after 30 minutes treatment

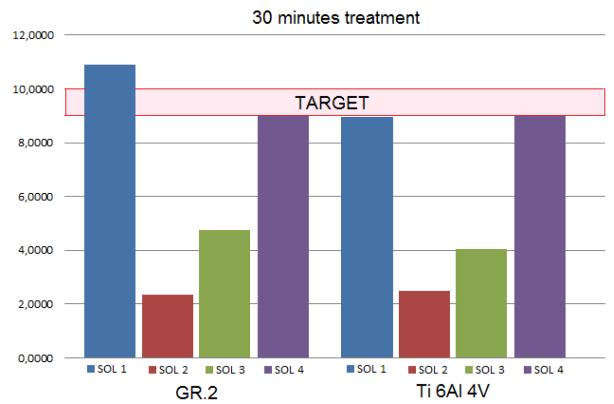

Fig. 6 - Weight reduction after 30 minutes treatment

	GR. 2			Ti 6Al 4V		
	Before CM (gr.)	After CM (gr.)	Remov. (gr.)	Before CM (gr.)	After CM (gr.)	Remov. (gr.)
S1	50,9185	32,7506	18,1679	51,8616	34,7568	17,1048
S2	49,8818	44,8090	5,0728	52,3226	46,6740	5,6486
S3	49,4694	41,2702	8,1992	51,4274	43,8945	7,5329
S4	51,7688	38,6648	13,1040	51,8351	38,4158	13,4193

Table 7 - Weight reduction after 60 minutes treatment

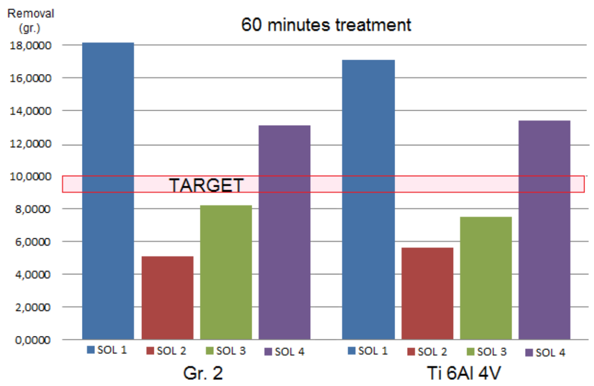

Fig. 7 - Weight reduction after 60 minutes treatment

Knowing the mass reduction obtained after chemical milling allows calculating the metal removal rate of the baths (Table 8).

	GR. 2		Ti 6Al 4V	
	30 min	60 min	30 min	60 min
	Rem. Rate (cm^3/min)	Rem. Rate (cm^3/min)	Rem. Rate (cm^3/min)	Rem. Rate (cm^3/min)
S1	0,0799	0,0667	0,0675	0,0645
S2	0,0173	0,0186	0,0189	0,0213
S3	0,0350	0,0301	0,0305	0,0284
S4	0,0661	0,0481	0,0643	0,0506

Table 8 – Metal removal rate for different acid baths

3.3 Roughness evaluation

Before performing chemical milling trials, the roughness values Ra and Rz have been measured for all the specimens. However, roughness is an extremely punctual value, and it changes substantially from point to point. Due to this reason, it is not possible calculating a real difference before and after milling.

The roughness values detected on a population of more that forty specimens in as cast condition where the following:

- Ra = 2,00 – 2,30 μm
- Rz = 11,00 – 16,50 μm

These values are equal between the specimens cast in Gr.2 or in Ti 6Al 4V alloy.

After chemical milling, the roughness values detected on the specimens are listed in Table 9.

	GR. 2				Ti 6Al 4V			
	Step 3 mm		Step 6 mm		Step 3 mm		Step 6 mm	
	Ra (μm)	Rz (μm)	Ra (μm)	Rz (μm)	Ra (μm)	Rz (μm)	Ra (μm)	Rz (μm)
S1	3,39	16,75	3,46	21,32	2,44	14,21	2,70	16,63
S2	2,22	11,43	2,15	13,07	2,39	14,28	2,05	11,18
S3	3,57	15,92	3,76	22,76	2,82	10,28	2,97	17,28
S4	0,73	5,11	0,41	2,33	0,37	1,97	0,42	2,22

Table 9 – Roughness values after 30 minutes treatment

The roughness measurements listed above, show that the baths S1 and S3 are deteriorating the surface, while the solution S4, which contains nitric acid, is significantly improving the aspect and the surface quality. Moreover, in general, the Gr. 2 specimens are much more etched than Ti 6Al 4V alloy and the microstructure (grain boundaries) is totally revealed. Because of this reason, some of the Gr. 2 specimens pickled for 60 minutes present a surface which is completely unacceptable from an esthetic point of view, and is not relevant to present their roughness values after pickling.

3.4 Hydrogen adsorption

The hydrogen absorption by titanium alloys is one of the main drawbacks of their pickling process. It may result in the degradation of mechanical properties, and can cause embrittlement and reduction of fatigue life of the components. Generally, with a higher concentration of solution, higher immersion temperature or longer immersion time, hydrogen absorption is enhanced. However, the increase in the amount of absorbed hydrogen could become saturated in the longer stages of immersion. The reason for the saturation of hydrogen absorption appears to be the hydride formation in the surface layers of the specimen. This hydride serves as a barrier to further hydrogen absorption [10] and so its pick-up is not following linear relations.

According to the standard ASTM B 367, the highest admissible hydrogen content is equal to 0,015%. Sometimes, especially for aerospace applications, the limit is still lower, and so a vacuum annealing treatment could be required. The results obtained executing the gas content analyses on samples presenting three etched surfaces are listed in Table 10.

	Gr. 2			Ti 6Al 4V		
	O (%)	N (ppm)	H (ppm)	O (%)	N (ppm)	H (ppm)
S1	0,1425	37,5	88,6	0,2064	51,6	140,8
S2	0,1481	34,8	35,7	0,2154	33,6	50,5
S3	0,1546	48,5	105,4	0,2185	55,4	359,1
S4	0,1570	58,2	95,7	0,2309	57,1	139,6

Table 10 – Hydrogen adsorption after 30 minutes treatment

The hydrogenation depends not only on the composition of the etching baths, but also on the chemical and phase composition of titanium alloys, especially on the α/β phases ratio in their microstructure [8]. In detail, the presence of β phase accelerates and deepens the hydrogen penetration into titanium, because the hydrogen diffusivity in it is several times as high as in the α-phase.

Studying the effects of the type of etching solutions on the hydrogen absorption behavior of pure Ti and Ti alloys is complicated, because the chemical reactions occurring on the surface are still unknown, and many of them are following non stoichiometric equations [9].

3.5 Thickness distribution

Table 11 and 12 listed above summarize the data showing the thickness distribution of the specimens before and after chemical milling. The analysis of the results basically confirms the results obtained observing the weight reduction presented at paragraph 3.2. These data also show that all the different solutions under testing present a tendency to remove a bigger quantity of material in the thicker step of the specimens (8 mm). Anyway, generally speaking, the difference in the material removal can be comprised in ± 0,04 mm, which is a good tolerance especially for components obtained by investment casting.

		GR. 2					Ti 6Al 4V				
		2mm	3mm	4mm	6mm	8mm	2mm	3mm	4mm	6mm	8mm
S1	**Before CM (mm)**	1,906	2,831	3,807	5,706	7,538	2,143	3,154	4,082	5,770	7,645
	After CM (mm)	1,121	2,071	3,071	4,938	6,757	1,446	2,562	3,429	5,166	7,016
	Difference (mm)	**0,785**	**0,760**	**0,736**	**0,768**	**0,781**	**0,697**	**0,592**	**0,653**	**0,604**	**0,629**
S2	**Before CM (mm)**	1,899	2,836	3,81	5,724	7,56	1,867	2,782	3,736	5,603	7,459
	After CM (mm)	1,802	2,738	3,705	5,603	7,435	1,753	2,674	3,597	5,467	7,312
	Difference (mm)	**0,097**	**0,098**	**0,105**	**0,121**	**0,125**	**0,114**	**0,108**	**0,139**	**0,136**	**0,147**
S3	**Before CM (mm)**	1,899	2,826	3,784	5,628	7,514	2,069	2,996	3,875	5,599	7,481
	After CM (mm)	1,575	2,526	3,469	5,290	7,176	1,785	2,729	3,593	5,322	7,132
	Difference (mm)	**0,324**	**0,300**	**0,315**	**0,338**	**0,338**	**0,284**	**0,267**	**0,282**	**0,277**	**0,349**
S4	**Before CM (mm)**	1,940	2,811	3,716	5,536	7,342	2,073	2,869	3,764	5,658	7,529
	After CM (mm)	1,317	2,159	3,046	4,893	6,687	1,458	2,291	3,153	4,991	6,880
	Difference (mm)	**0,623**	**0,652**	**0,670**	**0,643**	**0,655**	**0,615**	**0,578**	**0,611**	**0,667**	**0,649**

Table 11 – Thickness distribution after 30 minutes treatment

		GR. 2					Ti 6Al 4V				
		2mm	**3mm**	**4mm**	**6mm**	**8mm**	**2mm**	**3mm**	**4mm**	**6mm**	**8mm**
S1	**Before CM (mm)**	1,886	2,818	3,814	5,722	7,548	1,897	2,832	3,818	5,653	7,517
	After CM (mm)	0,480	1,399	2,434	4,299	6,089	0,666	1,539	2,597	4,354	6,204
	Difference (mm)	**1,406**	**1,419**	**1,380**	**1,423**	**1,459**	**1,231**	**1,293**	**1,221**	**1,299**	**1,313**
S2	**Before CM (mm)**	1,895	2,837	3,778	5,635	7,536	2,001	2,934	3,807	5,560	7,428
	After CM (mm)	1,611	2,531	3,463	5,293	7,185	1,676	2,556	3,441	5,024	7,046
	Difference (mm)	**0,284**	**0,306**	**0,315**	**0,342**	**0,351**	**0,325**	**0,378**	**0,366**	**0,536**	**0,382**
S3	**Before CM (mm)**	1,948	2,782	3,723	5,521	7,453	1,885	2,853	3,798	5,628	7,545
	After CM (mm)	1,358	2,239	3,165	4,980	6,827	1,356	2,336	3,286	5,103	6,951
	Difference (mm)	**0,590**	**0,543**	**0,558**	**0,541**	**0,626**	**0,529**	**0,517**	**0,512**	**0,525**	**0,594**
S4	**Before CM (mm)**	1,901	2,846	3,78	5,638	7,381	1,879	2,838	3,770	5,711	7,489
	After CM (mm)	0,996	1,944	2,873	4,721	6,449	0,950	1,901	2,869	4,726	6,526
	Difference (mm)	**0,905**	**0,902**	**0,907**	**0,917**	**0,932**	**0,929**	**0,937**	**0,901**	**0,985**	**0,963**

Table 12 – Thickness distribution after 60 minutes treatment

3.6 Hardness profiles after chemical milling

The metal removal measured observing the weight reduction and the thickness distribution shows that after 30 minutes of pickling the solutions S1 and S4 are achieving, or almost achieving the target to remove a superficial layer 0,35 mm. Due to this reason, a hardness profile on the thicker step of the specimens (8mm), where in the beginning the α-case layer was deeper, has been done, in order to observe if on the surface are still detectable the effects of mold contamination.

In Fig. 8 and 9 are represented the hardness profile of the specimens after 30 minutes pickling. From the profiles is visible that once again the thickness distribution and especially the weight reduction analyses are useful methods for predicting the α-case removal. In the graphs, a cut-off line respectively at 180 $HV_{0,1}$ and 365 $HV_{0,1}$ has been added as reference of the average hardness of the core.

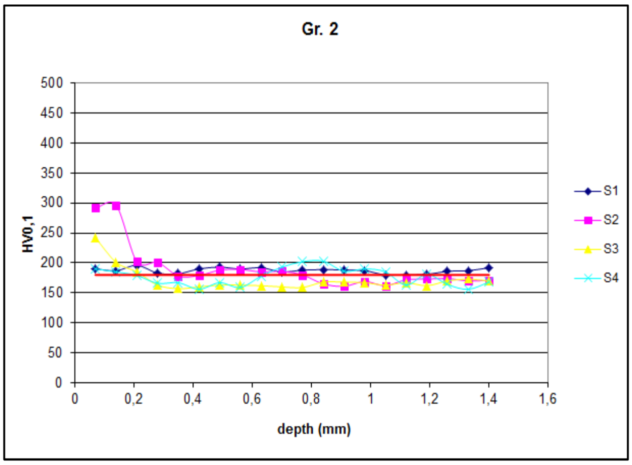

Fig. 8 – Gr.2 specimens hardness profile after C.M.

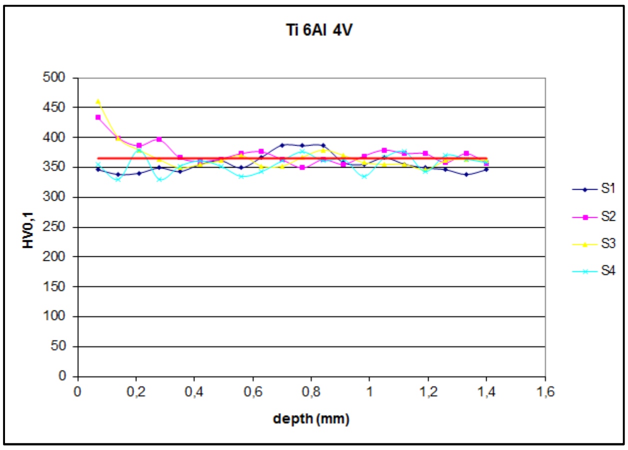

Fig. 9 – Ti 6Al 4V specimens hardness profile after C.M.

4.0 Comments & Conclusions

The series of chemical milling trials executed on Gr. 2 and Ti 6Al 4V alloy specimens using different commercial pickling baths allow getting to the following results:

- The α-case layer which is formed during casting of titanium and its alloys using zirconia mold (thickness 0,3 – 0,4 mm) can be efficiently removed using commercial products as solutions S1 or S4. In relation to the baths service conditions tested during these trials (in terms of concentration, temperature and dissolved Ti into the solution), the cycle time for removing the hardened layer mentioned above is equal to 30 – 40 minutes.

- The removal rate of Gr.2, or generally pure Ti with alpha based structure is approximately 10-15% faster that Ti 6Al 4V alloy. Moreover, pure Ti shows a bigger tendency to be etched and revealing the grain boundaries and its microstructures. This aspect can be problematic from a point of view of superficial aspect, in case of elevated thickness of α-case layers need to be removed.

- Generally, all the tested solutions show a tendency to remove a bigger quantity of material where the wall thickness is higher; in case of cast components with narrow tolerances this aspect should be carefully take into account, in order to fulfill the project requirements of the finished product.

- In order to assure the correct service conditions of the bath on industrial scale, a crucial aspect is maintaining the amount of metallic titanium dissolved into the solution below the limit of 6-7 gr./liter. For achieving this target, is important to know as fundamental input data the exposed surface of the components under treatment, and consequentially the weight reduction required for the α-case removal. With this method is possible calculating the frequencies and the amount of the corrections needed from the pickling solutions and also the maximum number of components which can be treated in a single chemical milling cycle

- The hydrogen adsorption which occurs after chemical milling treatment needs to be controlled carefully, because the trials show that also with relatively short cycle time the possibility to get near the upper limit of 150 ppm stated from ASTM B 367 standard. Generally, In case of solutions containing H_2SO_4 (or the ion SO_4^{--}) the amount of absorbed hydrogen tends to increase.

- The solution S4, which contains HNO_3, allows obtaining a very high level of surface finishing on treated specimens. With this product, the initial roughness of the cast part can be efficiently smoothed (Ra < 1 μm) and also the brightness of the pickled surface is really high (see Fig. 10).

Fig. 10 – Comparison with sample before and after CM

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CONTACTS

Dr. Eng. Silvia Gaiani
Akrapovič d.d.
Malo Hudo 8 – Ivančna Gorica (SLO)
silvia.gaiani@akrapovic.si

Prof. Paolo Veronesi
Materials Eng. Dept. – Modena University
Via Vignolese 905/A - Modena (I)
paolov@unimore.it

OPTIMIZATION OF THE CHEMICAL MILLING OF INVESTMENT CAST TITANIUM ALLOYS

Dr. Eng. Silvia Gaiani
Akrapovič d.d. – Materials & Technologies Consultant

AKRAPOVIČ

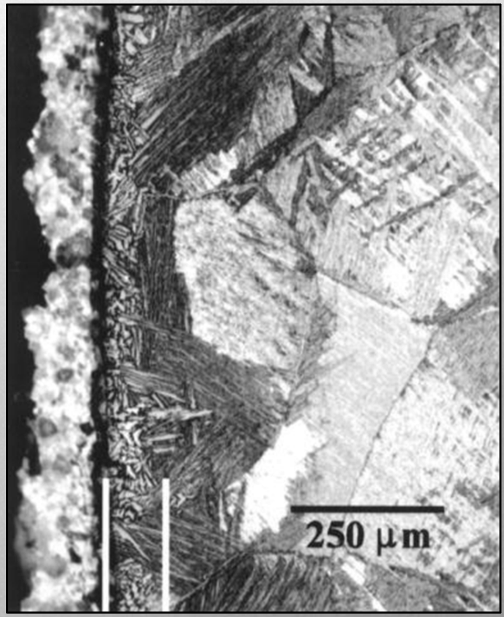
INVESTMENT CASTING TECHNOLOGY is widely used for manufacturing of titanium components.

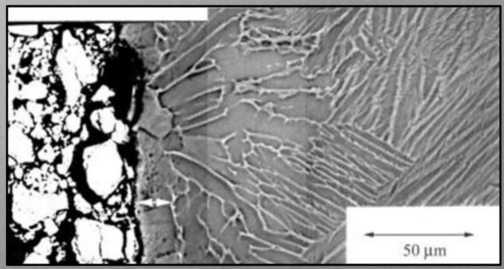
Compared to other forming methods, such as forging or machining, casting presents several benefits:

- Possibility to produce parts with complicated geometries and reduced wall thickness
- Flexibility of the process
- Manufacturing of components in near to net shape

On the other hand, the investment casting of Ti alloys has also a drawback. In fact, these materials present a high inherent reactivity with the mold primary materials at elevated temperatures during investment casting.

The reactions between liquid titanium and mold materials result in the formation of the so called "***ALPHA CASE***" *(*or *α-case*) a hard and brittle layer which will deteriorate the surface and change the mechanical properties of titanium castings





The α-case is generally known to be developed by the interstitial elements such as carbon, nitrogen and especially oxygen dissolved from mold materials and diffused further below the surface of the cast at a high temperature.

The final depth of the layers depends on the following aspects:

- Cooling rate
- Type of molted alloy
- Type of ceramic materials constituents of the mold

Typical depth of **alpha case layer** formed during standard investment casting process is between **200 – 500 μm**

The type of ceramic shelling systems plays a crucial role in determining alpha case formation.

Materials with standard free energy more negative than Titania (TiO_2) can minimize the reaction between the mold wall and the liquid metal during pouring and solidification

ZIRCONIA or YTTRIA based mold are particularry suitable for alpha case reduction

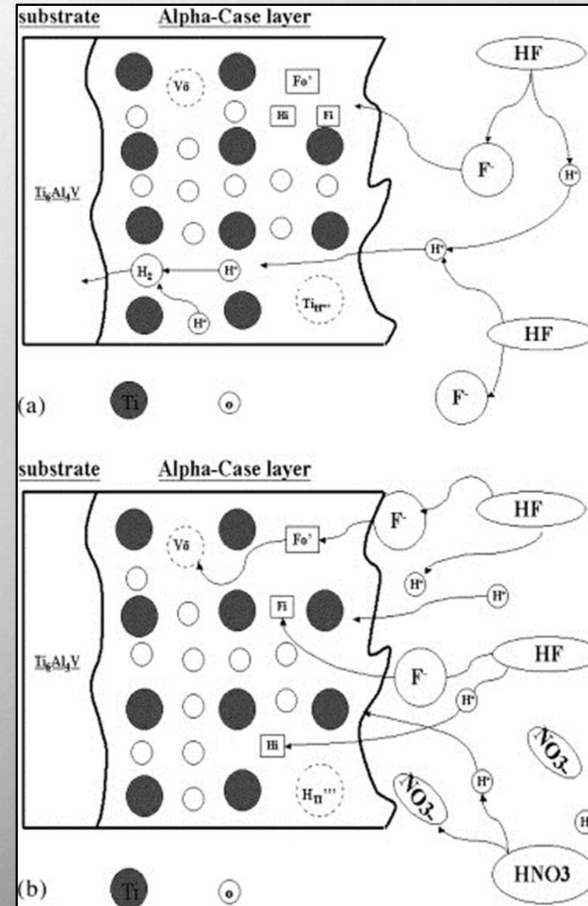
In order to completely remove the hardened layer, the most efficient industrial method is **CHEMICAL MILLING**. All the most common chemical products for titanium pickling available on the market are acid baths containing etching solutions based on hydrofluoric, sulfuric, or nitric acid or their mixtures.

The aim of this study is identifying some **COMMERCIAL CHEMICAL PRODUCTS** suitable for performing chemical milling on two standard titanium alloys:

- Grade 2
- Grade 5 (Ti 6Al 4V)

Grade 2 is a titanium alloy with alpha microstructure, while Ti 6Al 4V presents alpha + beta microstructure.

Their behavior is expected to be different in terms of chemical etching and removal rate

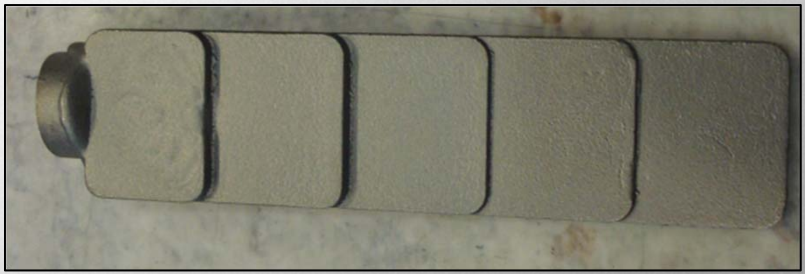


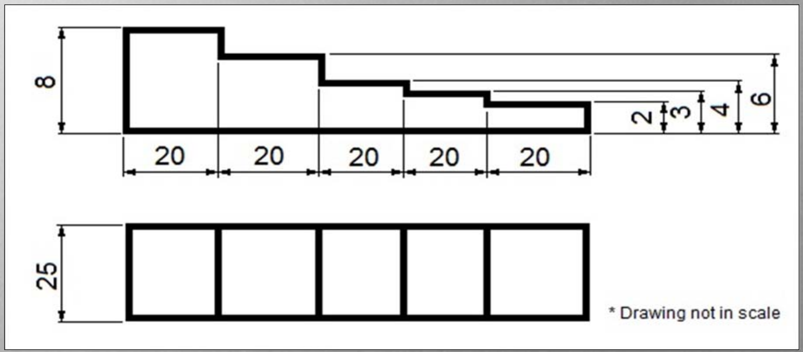
EXPERIMENTAL PROCEDURE

For performing the chemical milling trials few samples were casted in Gr. 2 and Gr. 5.

The samples are shaped like „stairs“ for evaluating the influence of different thicknesses on alpha case formation.

The samples has been cast in an induction skull melting oven using a zirconia based ceramic shell.



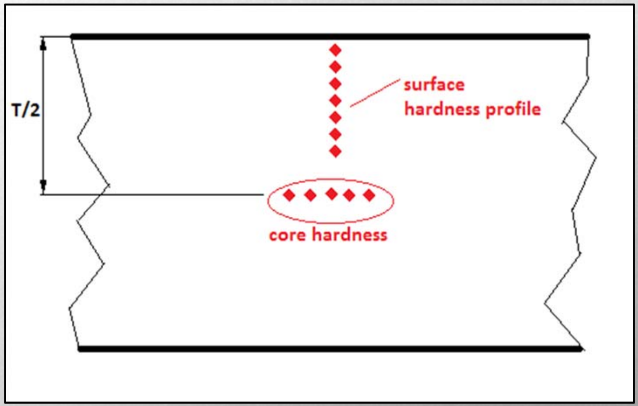


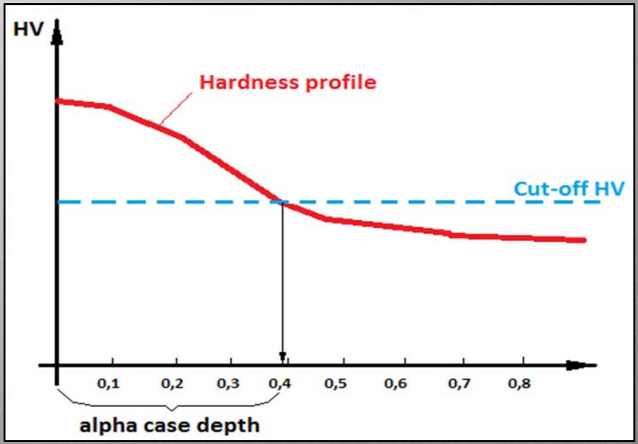
ALPHA CASE PRELIMINARY DETERMINATION

For alpha case depth determination, a method based on hardness profile has been chosen.

a series of micro hardness test have been done using the following procedure:

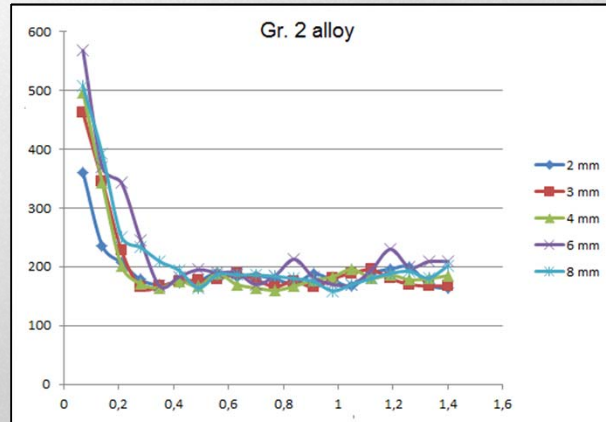
- Perform n°15 indentations $HV_{0,1}$ (distance = 0,07 mm) perpendicular from the surface to the center of the specimen for obtaining the hardness profile
- Perform n°10 indentations $HV_{0,1}$ (distance = 0,07 mm) in the center of the section for obtaining the hardness of the core (cut off value).

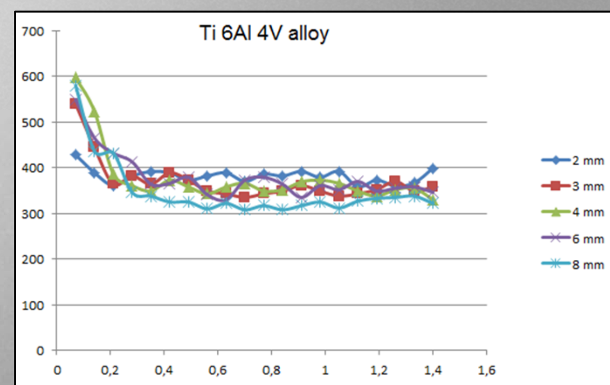




ALPHA CASE DEPTH

	Gr. 2		Ti 6Al 4V	
	Cut - off ($HV_{0,1}$)	αcase depth (mm)	Cut – off ($HV_{0,1}$)	αcase depth (mm)
2 mm	183	0,28	355	0,35
3 mm	181	0,35	376	0,28
4 mm	184	0,28	357	0,35
6 mm	181	0,35	361	0,35
8 mm	179	0,42	353	0,42





MASS REMOVAL TARGET

	ρ (g/cm³)	Min. removal (gr.)	Max. removal (gr.)
Gr. 2	4,54	9,049	10,146
Ti6Al4V	4,42	9,043	10,139

Observing the results of alpha case depth, we can assume that for both the alloys an average removal of 0,35±0,02 mm could be enough for eliminating its effects. Considering that the total surface of the cast specimens is equal to 60,4 cm^2, the mass of material to be removed by chemical milling can be calculated using a simple equation.

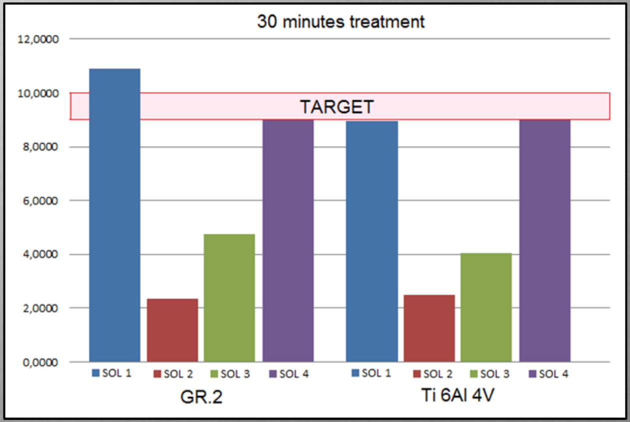
ACID BATH SOLUTIONS

	Chemicals species	Concentration in H_2O	T	Correction
S1	$HF + H_2SO_4$	110g/l S1 + 70 g/l H_2SO_4	36 °C	Standard product H_2O_2 based
S2	$HF + H_2O_2$ stabilized	20% S2	22 °C	H_2O_2
S3	$HF + Fe_2(SO_4)_3$	56,5% $Fe_2(SO_4)_3$ / 7% HF / 35,5% H_2O	35 °C	None
S4	Various Fluorides + HNO_3	Not diluted in water	56 °C	Addition of new S4 product

The efficiency of the bath, however the ability to obtain a metal removal, depends on the concentration of acid, temperature of the solution, and amount of metal dissolved in acid

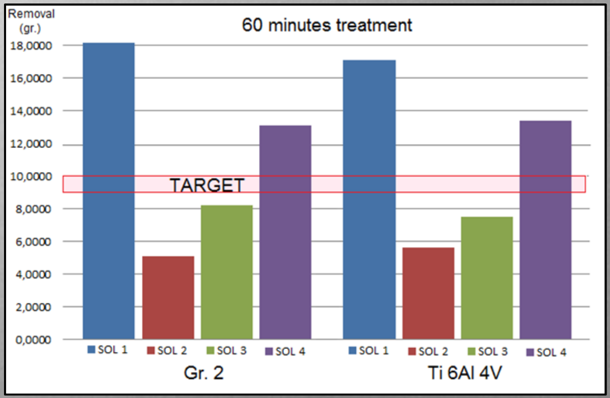
MASS REMOVAL – 30 min

	GR. 2			Ti 6Al 4V		
	Before CM (gr.)	**After CM** (gr.)	**Remov.** (gr.)	**Before CM** (gr.)	**After CM** (gr.)	**Remov.** (gr.)
S1	51,3280	40,4474	10,8806	53,2552	44,2994	8,9558
S2	52,8821	50,5230	2,3591	50,0402	47,5370	2,5032
S3	51,8390	47,0759	4,7631	52,5094	48,4652	4,0442
S4	49,2884	40,2808	9,0076	50,9353	42,4106	8,5247



MASS REMOVAL – 60 min

	GR. 2			Ti 6Al 4V		
	Before CM (gr.)	After CM (gr.)	Remov. (gr.)	Before CM (gr.)	After CM (gr.)	Remov. (gr.)
S1	50,9185	32,7506	18,1679	51,8616	34,7568	17,1048
S2	49,8818	44,8090	5,0728	52,3226	46,6740	5,6486
S3	49,4694	41,2702	8,1992	51,4274	43,8945	7,5329
S4	51,7688	38,6648	13,1040	51,8351	38,4158	13,4193



ROUGHNESS

BEFORE CM

The roughness values detected on a population of more than 40 specimens in as cast condition where the following:

Ra = 2,00 – 2,30 µm

Rz = 11,00 – 16,50 µm

AFTER CM

	GR. 2				Ti 6Al 4V			
	Step 3 mm		Step 6 mm		Step 3 mm		Step 6 mm	
	Ra (µm)	Rz (µm)	Ra (µm)	Rz (µm)	Ra (µm)	Rz (µm)	Ra (µm)	Rz (µm)
S1	3,39	16,75	3,46	21,32	2,44	14,21	2,70	16,63
S2	2,22	11,43	2,15	13,07	2,39	14,28	2,05	11,18
S3	3,57	15,92	3,76	22,76	2,82	10,28	2,97	17,28
S4	0,73	5,11	0,41	2,33	0,37	1,97	0,42	2,22

THICKNESS REDUCTION – 30 min

		GR. 2					Ti 6Al 4V				
		2mm	**3mm**	**4mm**	**6mm**	**8mm**	**2mm**	**3mm**	**4mm**	**6mm**	**8mm**
	Before CM (mm)	1,906	2,831	3,807	5,706	7,538	2,143	3,154	4,082	5,770	7,645
S1	After CM (mm)	1,121	2,071	3,071	4,938	6,757	1,446	2,562	3,429	5,166	7,016
	Diff. (mm)	**0,785**	**0,760**	**0,736**	**0,768**	**0,781**	**0,697**	**0,592**	**0,653**	**0,604**	**0,629**
	Before CM (mm)	1,899	2,836	3,81	5,724	7,56	1,867	2,782	3,736	5,603	7,459
S2	After CM (mm)	1,802	2,738	3,705	5,603	7,435	1,753	2,674	3,597	5,467	7,312
	Diff.(mm)	**0,097**	**0,098**	**0,105**	**0,121**	**0,125**	**0,114**	**0,108**	**0,139**	**0,136**	**0,147**
	Before CM (mm)	1,899	2,826	3,784	5,628	7,514	2,069	2,996	3,875	5,599	7,481
S3	After CM (mm)	1,575	2,526	3,469	5,290	7,176	1,785	2,729	3,593	5,322	7,132
	Diff. (mm)	**0,324**	**0,300**	**0,315**	**0,338**	**0,338**	**0,284**	**0,267**	**0,282**	**0,277**	**0,349**
	Before CM (mm)	1,940	2,811	3,716	5,536	7,342	2,073	2,869	3,764	5,658	7,529
S4	After CM (mm)	1,317	2,159	3,046	4,893	6,687	1,458	2,291	3,153	4,991	6,880
	Diff. (mm)	**0,623**	**0,652**	**0,670**	**0,643**	**0,655**	**0,615**	**0,578**	**0,611**	**0,667**	**0,649**

THICKNESS REDUCTION – 60 min

		GR. 2					Ti 6Al 4V				
		2mm	3mm	4mm	6mm	8mm	2mm	3mm	4mm	6mm	8mm
S1	Before CM (mm)	1,886	2,818	3,814	5,722	7,548	1,897	2,832	3,818	5,653	7,517
	After CM (mm)	0,480	1,399	2,434	4,299	6,089	0,666	1,539	2,597	4,354	6,204
	Diff. (mm)	**1,406**	**1,419**	**1,380**	**1,423**	**1,459**	**1,231**	**1,293**	**1,221**	**1,299**	**1,313**
S2	Before CM (mm)	1,895	2,837	3,778	5,635	7,536	2,001	2,934	3,807	5,560	7,428
	After CM (mm)	1,611	2,531	3,463	5,293	7,185	1,676	2,556	3,441	5,024	7,046
	Diff.(mm)	**0,284**	**0,306**	**0,315**	**0,342**	**0,351**	**0,325**	**0,378**	**0,366**	**0,536**	**0,382**
S3	Before CM (mm)	1,948	2,782	3,723	5,521	7,453	1,885	2,853	3,798	5,628	7,545
	After CM (mm)	1,358	2,239	3,165	4,980	6,827	1,356	2,336	3,286	5,103	6,951
	Diff. (mm)	**0,590**	**0,543**	**0,558**	**0,541**	**0,626**	**0,529**	**0,517**	**0,512**	**0,525**	**0,594**
S4	Before CM (mm)	1,901	2,846	3,78	5,638	7,381	1,879	2,838	3,770	5,711	7,489
	After CM (mm)	0,996	1,944	2,873	4,721	6,449	0,950	1,901	2,869	4,726	6,526
	Diff. (mm)	**0,905**	**0,902**	**0,907**	**0,917**	**0,932**	**0,929**	**0,937**	**0,901**	**0,985**	**0,963**

HYDROGEN PICK UP

	Center			Surface		
	O (%)	N (ppm)	H (ppm)	O (%)	N (ppm)	H (ppm)
Gr. 2	0,148	34,8	35,7	0,289	47,2	99,8
Ti6Al4V	0,219	33,6	50,5	0,316	32,4	95,8

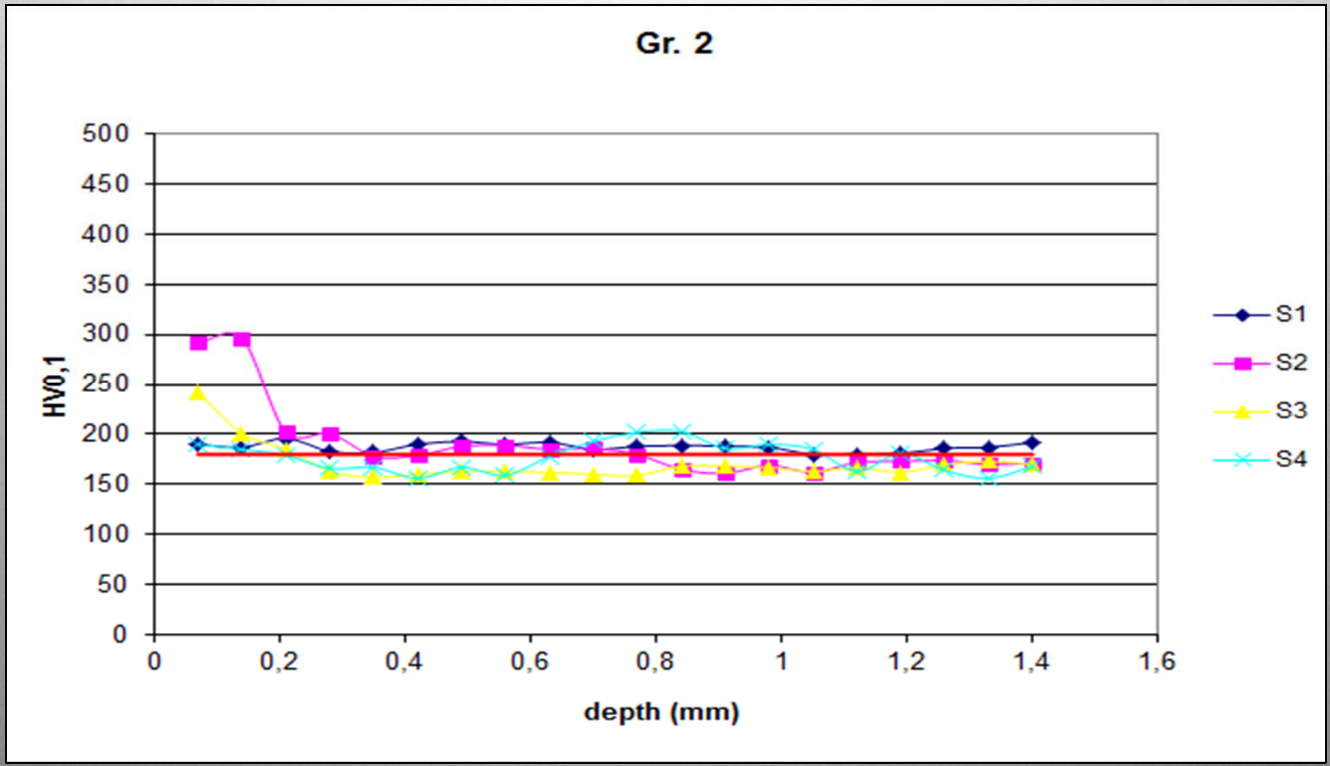
Measurements obtained according to standard ASTM 1447

UPPER LIMIT FOR H_2 = 150 ppm

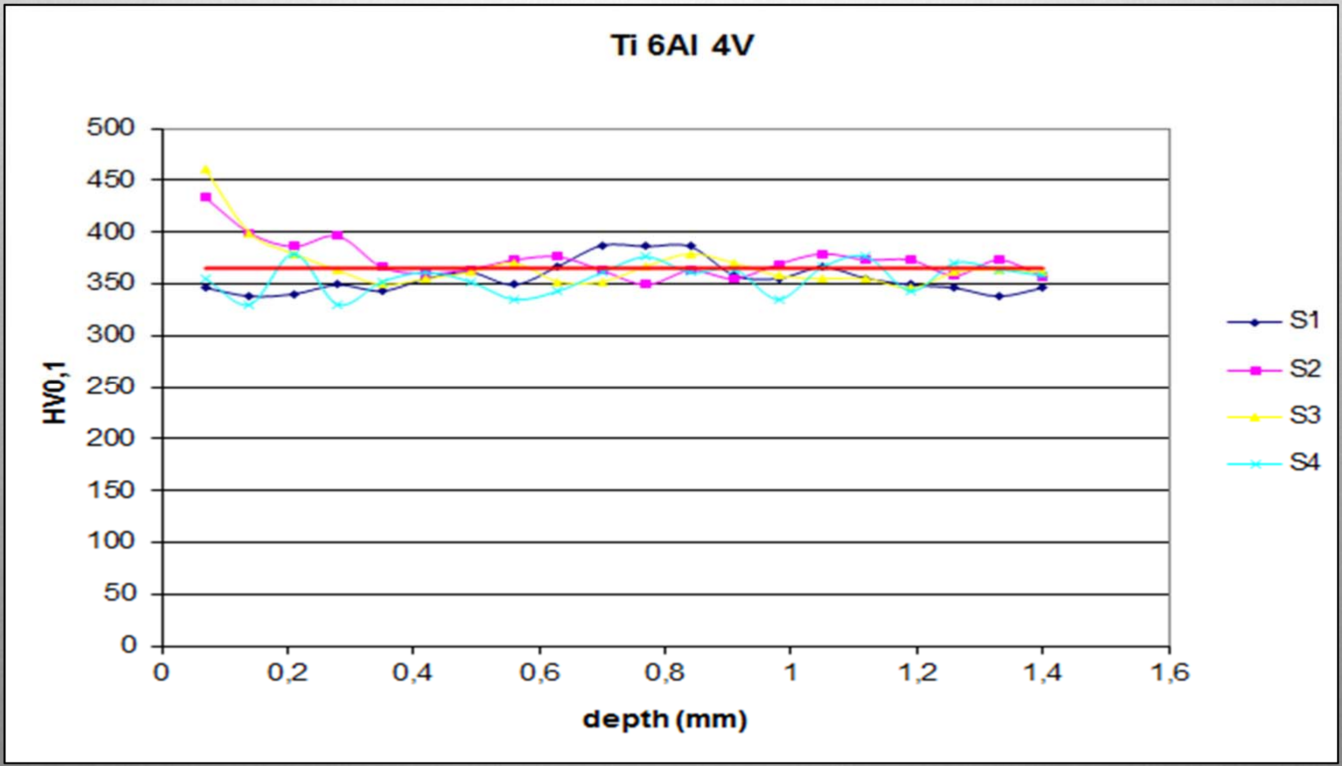
The hydrogen absorption by titanium alloys is one of the main drawbacks of their pickling process.
It may result in the degradation of mechanical properties, and can cause embrittlement and reduction of fatigue life of the components.

	Gr. 2 - surface			Ti 6Al 4V - surface		
	O (%)	N (ppm)	H (ppm)	O (%)	N (ppm)	H (ppm)
S1	0,1425	37,5	88,6	0,2064	51,6	140,8
S2	0,1481	34,8	35,7	0,2154	33,6	50,5
S3	0,1546	48,5	105,4	0,2185	55,4	359,1
S4	0,1570	58,2	95,7	0,2309	57,1	139,6

HARDNESS PROFILE AFTER CHEMICAL MILLING – 30 min

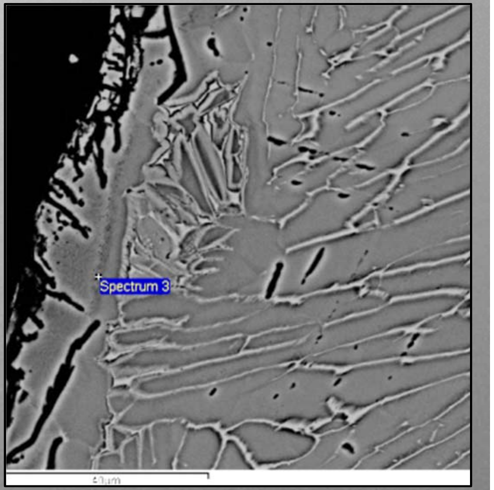


HARDNESS PROFILE AFTER CHEMICAL MILLING – 30 min



COMMENTS & CONCLUSIONS

1) The α-case layer which is formed during casting of titanium and its alloys using ZrO_2 mold (thickness 0,3 – 0,4 mm) can be efficiently removed using commercial products as solutions S1 or S4. Using correct baths service conditions (in terms of concentration, temperature and dissolved Ti into the solution), the cycle time for removing the hardened layer is equal to 30 – 40 minutes.
2) The removal rate of Gr.2, or generally pure Ti with alpha based structure is approximately 10-15% faster that Ti 6Al 4V alloy. Moreover, pure Ti shows a bigger tendency to be etched and revealing the grain boundaries and its microstructures.
3) Generally, all the tested solutions show a tendency to remove a bigger quantity of material where the wall thickness is higher

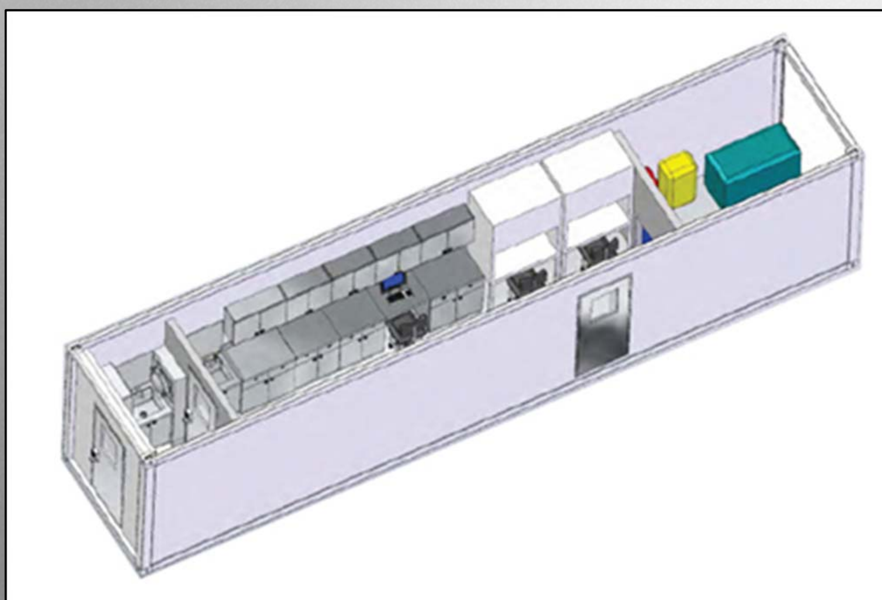
4) Controlling the correct service conditions of the bath on industrial scale, is a crucial aspect for keeping the amount of metallic Ti dissolved into the solution below the limit of 6-7 gr./liter. Because of this, is important knowing the exposed surface of the components under treatment, and consequentially the weight reduction required for the α-case removal

5) The H_2 adsorption caused by chemical milling needs to be controlled because, already with short cycle time, getting near the upper limit of 150 ppm is simple. Solutions containing H_2SO_4 (or the ion SO_4^{--}) the amount of absorbed hydrogen tends to increase

6) The solution S4, which contains HNO_3, allows obtaining a very high level of surface finishing on treated specimens with reduced roughness

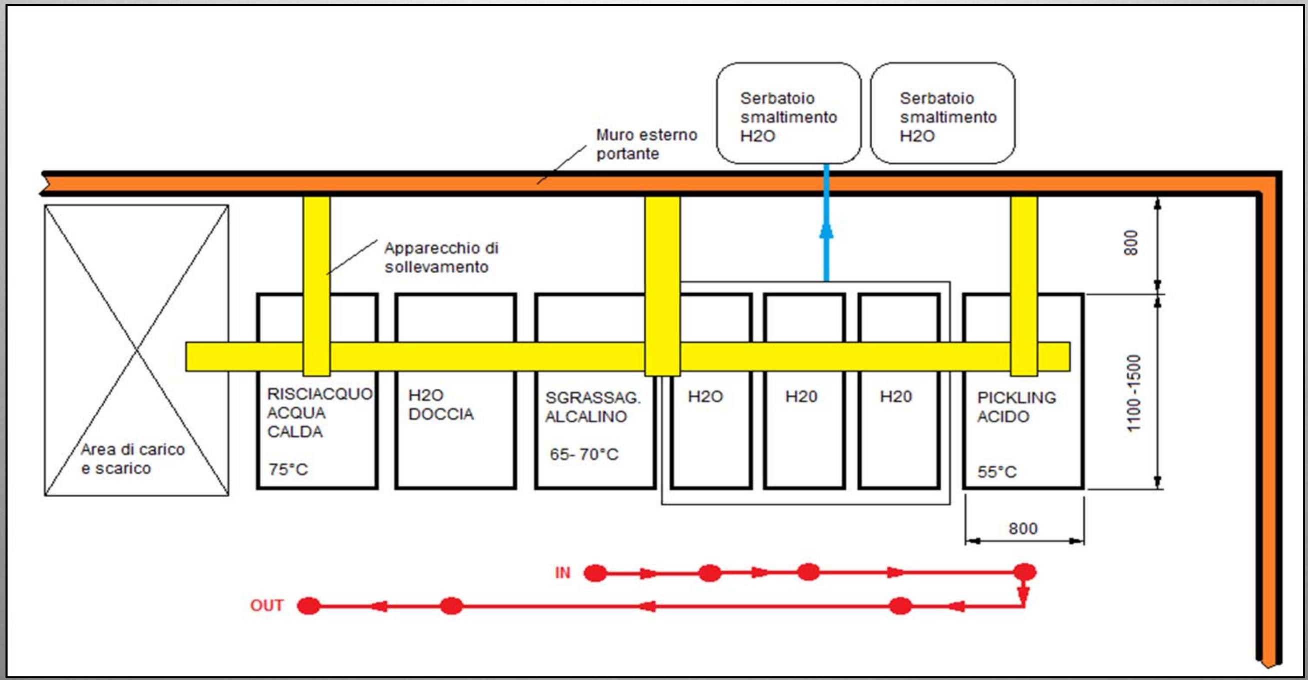
FUTURE DEVELOPMENTS

Short term target (end 2012): construction of chemical milling line on laboratory scale



FUTURE DEVELOPMENTS

Middle term target (2013/2014): construction of chemical milling line on industrial scale



Thanks for your attention!