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## Effect of the chemical milling process on the surface of titanium aluminide castings

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### Abstract

Most of titanium aluminide (TiAl) castings used in the automotive and aeronautical industries, such as turbines, are high added-value parts with complex geometries. Due to high reactivity of TiAl cast into ceramic moulds, most of the castings require post-processing in order to remove a brittle surface layer named alpha case. Furthermore, the complex geometry and thin walls of this type of components makes difficult to cast net shape parts; so, near-net shape components with machining allowance are often produced to improve mould filling (better fluidity). To solve this technological limitation, the chemical milling process is used to eliminate this layer and the machining allowance. In bibliography there are only a few systematic studies about the influence of chemical milling in TiAl surface castings. So, this experimental work seeks to contribute to understand the influence of this finishing process on the TiAl castings surface quality (dimensional accuracy, roughness and microhardness) and intends to establish which of the two chemical solutions tested is better for chemical milling of TiAl castings.

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### 1. Introduction

Chemical milling (CM) is a surface finishing process that has been used since the 50s and is characterized by the use of a strong acidic or basic solution for the surface dissolution of metals such as titanium, aluminum or steel. Due to the capability of removing metal, this process is used to remove a brittle and hard surface layer named alpha case, formed on the surface of titanium and its alloys by dissolution in the liquid alloy of carbon, nitrogen and especially oxygen from the ceramic material of the shell, during the investment casting process. Some of the problems associated with the existence of alpha case are: initiation of cracks and their propagation, embrittlement of the alloy due to the change of

microstructure on the surface of the melt [1-3], reduction of fatigue resistance, lower ductility and difficulty to be machined [4]. So, it is mandatory to remove it. In Fig. 1 is presented a microstructure of a Ti alloy with alpha case layer on the left.



Fig. 1. Ti10V2Fe3Al alloy microstructure, alpha case on sample's surface (left layer), etched with Kroll's reagent [5].

During the project the parts were dimensioned with a machining allowance corresponding to the alpha case

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layer which will be removed by chemical milling [6,7]. The metal removal, based on chemical reactions, is achieved by submerging the castings into a solution that reacts with their surface and removes the allowance. In order to promote a homogeneous metal removal, the bath should be permanently stirred [8]. In comparison with conventional machining, the process of chemical milling is capable of removing metal from castings with complex geometry, with thin thickness without causing deformations and maintaining tight tolerances [6,9]. However, this process is relatively inefficient, expensive, dangerous, due to the type of chemical solutions, and also harmful to the environment [8].

To reach this type of finishing it is necessary that the chemical solution promotes a good and homogeneous metal removal rate and eliminates or avoids the formation of the hydrogen embrittlement on the surface of the parts. At the end of chemical milling the castings should detain a bright and smooth finishing. Some additional aspects, such as process efficiency, air quality in the surroundings, capability to recycle the solution or neutralize it and not being harmful to the environment, must also be considered in process implementation [8,9].

In chemical milling of titanium alloys the most used solution, according with ASM [4], is a combination between hydrofluoric acid (HF) and nitric acid ( $\text{HNO}_3$ ), as shown in Table 1, because of the high acidity which improves the metal removal rate [8]. The HF is used due to its high acidity. However, there is the possibility of a hydrogen layer formation on the casting surface, due to the high affinity of the titanium for hydrogen, which can promote the embrittlement of the components surface. Thus,  $\text{HNO}_3$  is employed because it helps to reduce the danger of contamination by hydrogen. The proportion of HF in the chemical milling bath varies in a range between 1 and 10% and the proportion of  $\text{HNO}_3$  between 1 and 40%. These solutions are used at a temperature of 40 to 60°C [8,10,11].

Table 1. Solution commonly used on chemical milling of titanium alloys [9].

Alloy	Type of product	Chemical solution	Surface finishing Ra ( $\mu\text{m}$ )
Titanium alloys	Sheet, plate, forging	HF, $\text{HNO}_3$	0.25-1.0
	Casting	HF, $\text{HNO}_3$	0.75-1.5

However, for TiAl castings, a different mixture is proposed by Chen [12], which replaces  $\text{HNO}_3$  by

sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and adds some sodium chloride (NaCl).  $\text{H}_2\text{SO}_4$  is used to promote a good surface finishing and NaCl prevents hydrogen embrittlement. This solution should be used at a temperature between 38°C and 52°C [12].

## 2. Experimental Procedure

In order to perform the experimental tests, turbine investment castings in Ti-33.7Al-4.77Nb-1.05Cr were used. The ceramic shells used to obtain these castings have an yttria face-coat and details of its preparation are presented in previous works [13,14].

These specimens were immersed in two different acid solutions. The composition of these solutions is presented in Table 2 [15].

Table 2. Composition of the chemical solutions [13,15].

Solution (vol.%)	HF	$\text{HNO}_3$	$\text{H}_2\text{SO}_4$	Erkantol	NaCl	$\text{H}_2\text{O}$
1	4.5	7.5	-	5	-	83
2	2	-	4	-	3.5	90.5

The use of a wetting agent “Erkantol” on solution 1 is due to the fact that it allows a greater wettability of the specimens to be chemically milled.

Both solutions were placed on a 550 L volume tub. However, only 250 L of the two solutions were used for the chemical millings tests. The temperature of both solutions was 35°C, measured with a thermometer  $\pm 0.1^\circ\text{C}$ , in order to make an accurate comparison and it was also the maximum temperature possible to reach by the bath heating system available. Fig. 2 a) shows the apparatus. This tub contains an agitation system and small plastic floating balls on the surface to prevent the solution vaporization during the heating cycle. A thermoplastic tray (Fig. 2 b)) was also made to support the TiAl standard test castings and to promote bath circulation in the bottom area of the parts.

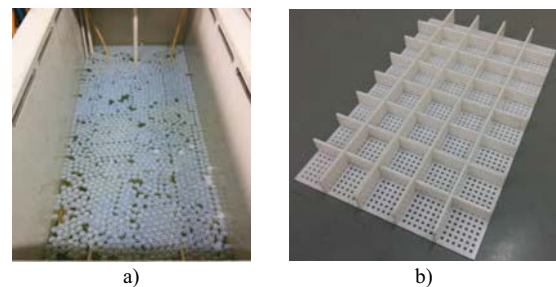


Fig. 2. a) Tub used on experimental tests and b) tray to support the TiAl test castings.

Based on previous tests [13], 3 turbines were immersed during 40 min on both solutions and posteriorly washed with fresh water to remove any traces of the acid solution. After that, the dimensional control of 3 specimens treated by each solution was realized by 3D Scanning, using a GOM equipment ATOS III Triple Scan, to verify the homogeneity of the chemical milling and to determine if the designed dimensional values were reached. Roughness tests were also conducted to evaluate the surface finish (Ra), using a Hommelwerke roughness meter. Three measurements were made in each sample with a 4.8 mm measurement length. The specimens were also weighted in a precision balance with a resolution of 0.0001 g, and measured using a caliper, to determine the metal removal rate (MRR) in mm/min and g/min. Microhardness (50 gf), using a Shimadzu equipment, in a cross section of metallographic prepared samples, was also measured to prove if the alpha case layer was removed. SEM/EDS analysis was performed to identify the composition of the surface and determine contaminations derived from the chemical milling with solution 1 (because in this case a white deposit was detected).

### 3. Results

#### 3.1. Metal removal rate (MRR)

Figs. 3 and 4 present the values of MRR in g/min and mm/min, respectively, obtained after the chemical milling with both solutions. As one can see, TiAl specimens chemical milled with solution 1 show a greater weight reduction and fast removal rate. This is a result of the higher amounts of acids in solution 1. These results were already expected due to previous tests made with both solutions but in a smaller tub with only 5 L of volume [13].

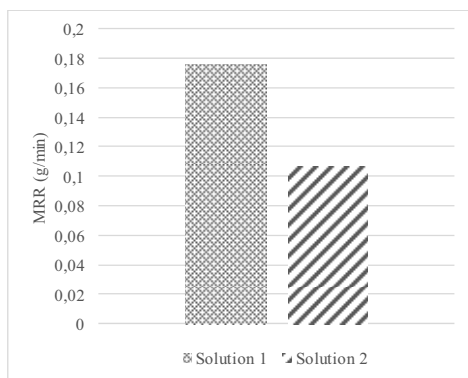


Fig. 3. MRR values in g/min.

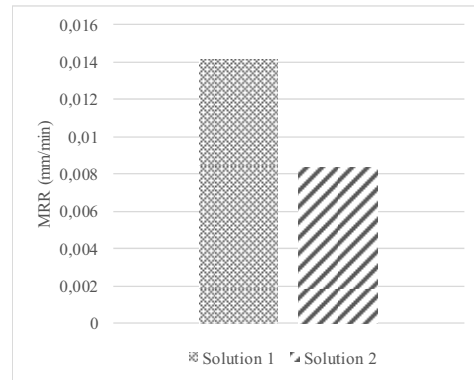


Fig. 4. MRR values in mm/min.

#### 3.2. Reactivity analysis

In order to verify the existence of the alpha case surface layer, microhardness tests were performed in some of the TiAl specimens before and after chemical milling. Fig. 5 presents the microhardness profile of a TiAl turbine before the chemical milling operation. As shown, a hardened layer with 470 HV and around 0.1 mm was identified (hardness variation from 470 to 280 HV). However, this layer is not the traditional alpha case as it is evident in microstructure of Fig. 6 in comparison with alpha case appearance shown previously in Fig. 1. This hardened layer is a consequence of a faster cooling in the interface metal/ceramic shell, called thermic alpha case, due to the difference between pouring temperature of about 1640°C and pre-heating temperature of about 900°C and cooling inside the mould for only 2 min [13]. After chemical milling, it was observed that the surface hardness was reduced to values around 300-350 HV, using both solutions (Fig. 7), which proves that the chemical milling is capable to eliminate this hardened layer.

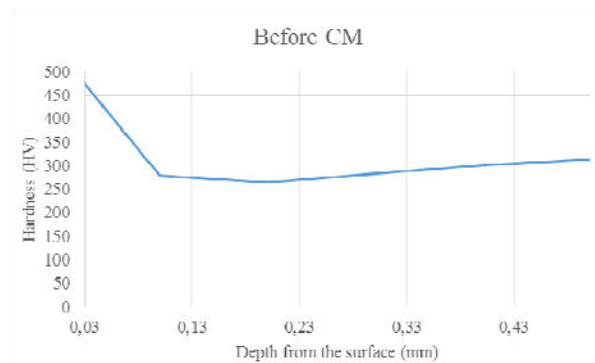


Fig. 5. Microhardness profile of a TiAl casting before chemical milling.



Fig. 6. Surface of the TiAl casting before chemical milling, without traditional alpha case.

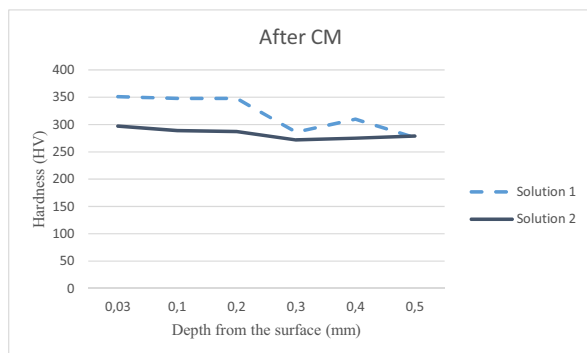


Fig. 7. Microhardness profiles of the TiAl casting after chemical milling with solution 1 and with solution 2.

### 3.3. Roughness tests

Table 3 shows the results of the Ra parameter determined in the roughness test. It is possible to infer that solution 1 contributes to a major increase on the roughness of the TiAl specimens. This can be explained due to the deposition of a white deposit (visible to the human eye) on the surface of the turbines. This problem did not occur with solution 2.

Table 3. Ra roughness values for the turbines milled with both solutions.

Solution	Before CM ( $\mu\text{m}$ )	After CM ( $\mu\text{m}$ )	Increase (%)
1	2.05	4.17	103.46
2	3.23	3.74	15.85

### 3.4. 3D scanning

3D scanning of all the samples was performed to evaluate the degree of uniformity of material removal. The goal of this work was eliminating approximately 0.2 mm of material (predicted machining allowance) uniformly across the surface due to the constant agitation of the solution around the castings during chemical milling. It was verified that the values

obtained were around this value for both solutions. Fig. 8 is an example of the dimension control using the 3D Scanning GOM equipment ATOS III Triple Scan.

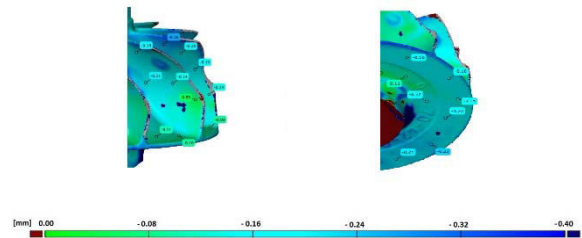


Fig. 8. Geometry of the test castings chemical milled during 40 min.

### 3.5. Surface analysis

TiAl parts milled with solution 1 exhibit a whitish surface (Fig. 9 b)), which probably means that an oxide layer was formed as a reaction product. However, this defect was not identified on the parts chemically milled with solution 2, as can be seen in Fig. 9 c) (absence of white deposit).

In order to identify the composition of such layer, the specimens milled by the solution 1 were analysed by SEM/EDS (Fig. 10). As shown in Fig. 10 b), the presence of a great amount of oxygen was detected on the surface of the TiAl part; so, it is possible to assume that the oxide layer deposited on the surface is formed by  $\text{TiO}_2$ . Fig. 11 shows the microstructure of the surface where it is possible to observe the difference between the oxide area and a clean region (Z1 and Z2, respectively). The presence of such layer could be responsible for the discrepancy between the roughness values (Table 3) of the specimens chemically milled with both solutions.

## 4. Conclusions

The metal removal rate was higher for the solution 1 and lower for the solution 2. There is no traditional alpha case layer on the surface of the TiAl test castings. The existing hardened layer is due to a faster cooling on the interface metal/ceramic shell. This layer was removed in the chemical milling tests using both solutions.

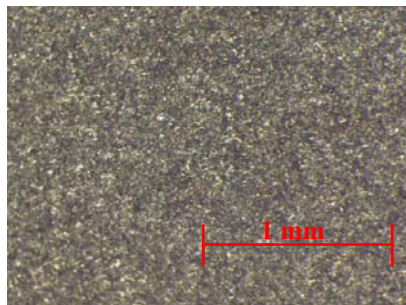
TiAl specimens chemical milled by solution 1 were rougher due to a chemical reaction with the bath that promotes the deposition of a whitish layer of  $\text{TiO}_2$  on the turbines surface.

After 3D Scanning, it was found that the metal removal rate was mostly uniform, which revealed an

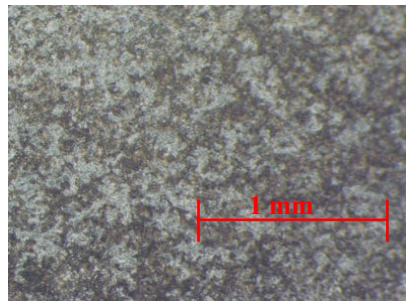
improvement relatively to other tests made previously without stirring, enhancing the relevance of the stirring system.

SEM/EDS analysis showed that the whitish layer deposited on the surface of the parts is composed by  $\text{TiO}_2$ . This oxide layer became visible when the specimens were exposed to the atmosphere and it was common to all the test castings chemically milled with solution 1.

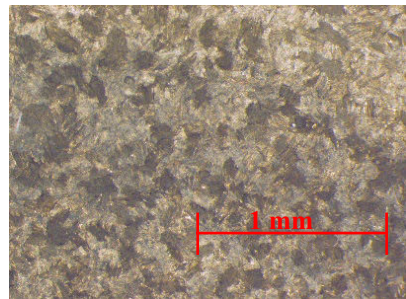
The best solution to perform the chemical milling process of a TiAl alloy is the solution 2 because it provides lower roughness and, consequently, better surface's castings. However, this solution reveals a lower metal removal rate than solution 1. In order to counter this disadvantage, the duration of exposure to this solution should be increased and/or temperature also increased, with a new system.



a)

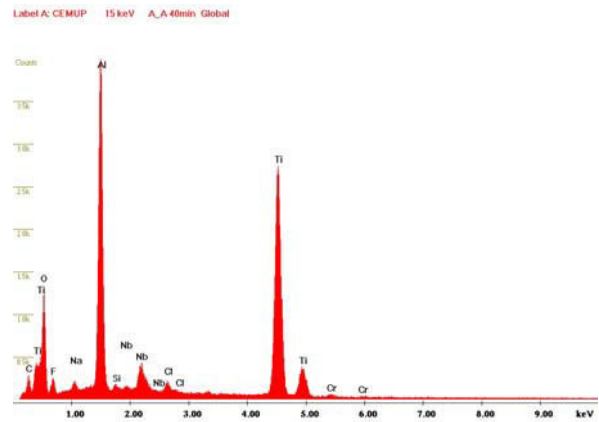


b)

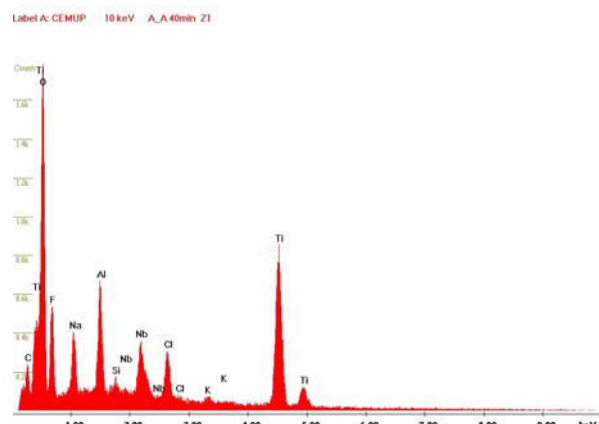


c)

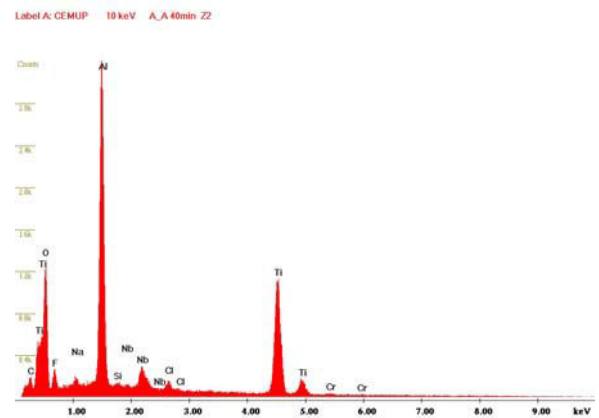
Fig. 9. Microstructure of the surfaces of TiAl turbines obtained in a stereoscopic microscope: before chemical milling (a), after chemical milling with solution 1 (b), revealing a whitish deposit, and after chemical milling with solution 2 (c).



a)



b)



c)

Fig. 10. Spectra of the elements present on the surface of TiAl sample treated with solution 1: global analysis (a), Z1 of Fig. 11 whitish deposit rich in oxygen (b) and Z2 of Fig. 11 (c), similar to global analysis.

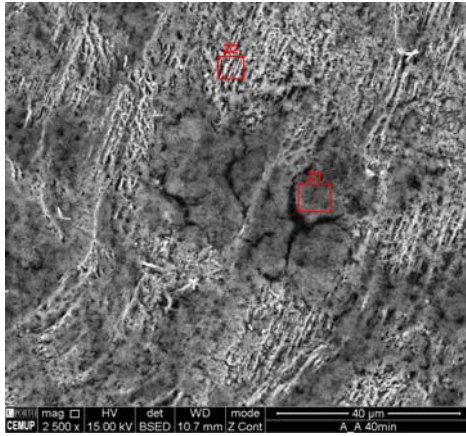


Fig. 11. Microstructure of the surface of TiAl sample obtained by SEM.

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