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INFLUENCE OF THE ETCHING TIME OF TI6AL4V TITANIUM ALLOY WITH SELECTED ACID SOLUTIONS ON CHANGES IN PHYSICAL PARAMETERS OF THE ELEMENT

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Abstract: *Chemical surface treatment is one of the methods of finishing metals and their alloys. Chemical etching of surfaces is increasingly used for products manufactured using additive methods, also known as 3D printing. The article presents a method of finishing the surface of titanium alloy Ti_6Al_4V ELI elements produced traditionally using a bath in HF/HNO_3 solutions. The influence of etching solutions on the surface quality and material loss was presented. As the etching time increased, the penetration of solutions into the surface increased, which resulted in an increase in the depth of the lowest profile recess (Rv parameter) relative to the height of the highest profile elevation (Rp parameter). The etching process affected the surface of the tested material, causing its hardness to decrease. The highest parameters of hardness decrease were obtained in a 3-minute etching process for B and C solutions. Extending etching to 15 minutes for individual solutions resulted in a varied effect, and in extreme cases, an increase in the surface hardness of the tested material. The obtained results showed a mass loss that was strictly dependent on time.*

Keywords: Ti_6Al_4V titanium alloy, etching process, HNO_3 acid solution, solution of HNO_3 + HF acid mixture.

1. Introduction

Producing implants that replace skeletal defects, the medical industry requires high strength, plasticity and hardness of the material. An equally important aspect is the possibility of creating a porous implant structure, which constitutes a scaffold and allows for the reconstruction of natural tissue. The most popular material in this area is the titanium alloy Ti_6Al_4V, which is used due to its biocompatibility with human tissue, as well as its low weight and corrosion resistance (Dallago et al., 2018). The efficiency of tissue penetration into the biomaterial depends on the pore size. Produced biomaterials must perform their functions properly have macropores ranging from 50 to 500 µm (Jones et al., 2003). Surface modification methods are able to improve speed and quality osseointegration processes, which results in increased bone deposition and a shorter repair period (Rieger et al., 2015, Shokuhfar et al., 2014, Torres et al., 2015, Vasconsellos et al., 2017, Yavari et al., 2016 and Zuo et al., 2013). The main purpose of the treatments is to create a passive layer on the surface of the elements, constituting a protective layer against corrosion for the material. The passive layer includes: TiO, Ti_2O_3 and TiO_2 (Baszkiewicz et al., 2006). As a result of chemical etching, porous TiO_2 is formed on the surface of the titanium alloy. The pore size and thickness of the TiO_2 layer depend on the concentration of the solutions and the duration of the process (Oishi et al., 2022). Based on the polarization curves obtained in experimental studies (Sutter et al., 1990), solutions with different surface interaction characteristics were determined. Manipulating the amount of HF makes it possible to control the polishing speed and the degree of interference in the material geometry. Experimental studies have shown a significant loss of mass of the etching material as a function of time

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for the solution proportions of 1.3 % HF and 9 % HNO_3 (Bijlmer et al., 1970). After achieving the maximum weight loss, surface passivation occurs.

The aim of this article is to present the results of preliminary research on the assessment of the influence of the etching process time and the type of etching solution on selected physical parameters of Ti_6Al_4V titanium alloy elements.

2. Methods

The tests used Ti6Al4V titanium alloy in the form of a drawn rod with a diameter of 12 mm in the annealed state, made in accordance with the AMS 4928 standard. The rod was cut and ground using intensive cooling on rollers approximately 3.5 mm high (base diameter 12 mm). Three samples were prepared for each test, and the shape of the samples is shown in Fig. 1.

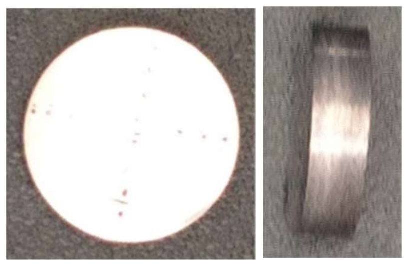

Fig. 1: Samples for the study of the influence of the etching process.

The samples were then heat treated in a vacuum oven in temperature t = 800 °C, maintained for an 1 hour.

The samples were chemically etched in acid solutions, the chemical composition of which was determined based on scientific publications (Bijlmer et al., 1970; Wysocki et al., 2016). To carry out the process, three chemical solutions with different amounts of components were prepared, as shown in Tab. 1.

Mark	Percentage of the substance in the etching solution			Total solution volume
	HF [%]	HNO_3 [%]	H_2O [%]	H_2O [ml]
A	2.0	20.0	78.0	500
B	1.3	9.0	90.0	500
C	1.0	5.0	95.0	500

Tab. 1: Percentage and volume fraction of a substance in the etching solution.

The sample etching process was carried out in three etching solutions for three adopted times, being multiples of the interval of 3 minutes: I - t = 3 minutes, II - t = 6 minutes, III - t = 15 minutes. The samples prepared in this way were tested before and after chemical polishing for: mass, surface roughness by profilometr MahrSurf XR20 and surface hardness by HV5 Vickers hardness tester.

3. Results

3.1. Mass measurement

Analysis of the test results for the mass of samples before and after the etching process indicates that the loss of material depends on the solution used and the duration of the process, as shown in Fig. 2.

The highest mass loss Dm was observed for etching solution B, while the lowest value was obtained for solution A. During the first three minutes of the etching process, the mass loss was:

- for solution A – Dm = 0.020 %,
- for solution B – Dm = 0.034 %,
- for solution C – Dm = 0.025 %.

Further mass loss (in the time interval 3 min < t ≥ 6 min) occurred:

- for solution A – Dm = 0.007 %,

- for solution B – Dm = 0.006 %,
- for solution C – Dm = 0.006 %.

Standard deviation results of 0.00043 g were obtained for the test performed. The presented results indicate that the intensity of interference of solution B was the highest compared to solutions A and C. The obtained results did not indicate the moment of stopping the mass loss in the etching process.

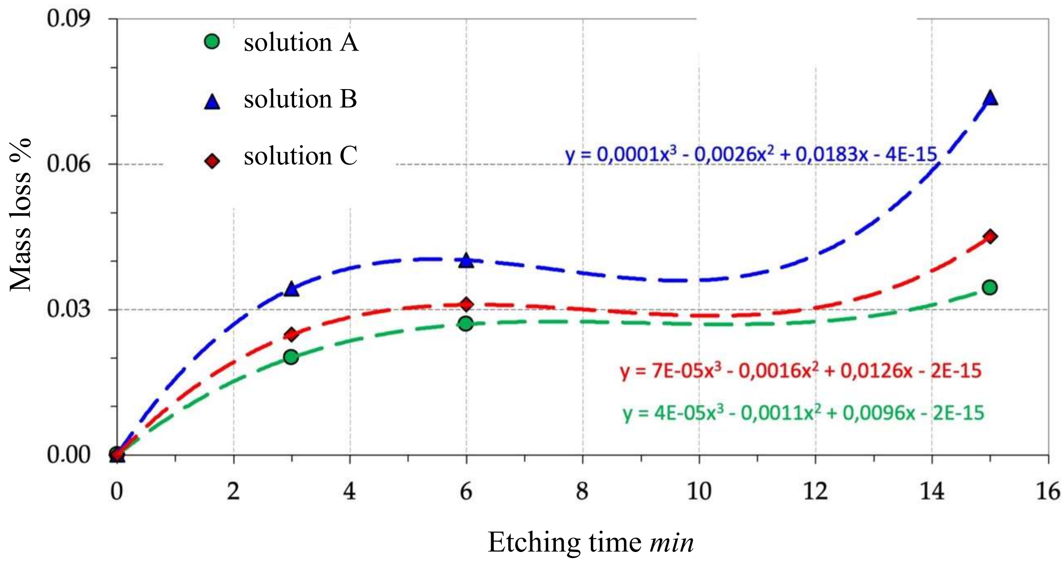

Fig. 2: Relationship Dm = f(t) for the accepted etching compounds.

3.2. Roughness measurement

The following parameters were considered when testing the surface roughness: average R_a, total R_z, smoothness R_p, recess R_v. Analysis of the results presented in Tab. 2 indicates that for most samples there was an increase in surface roughness after the chemical etching process. Only in the case of the Ra parameter for solution A and the etching time did it not give a linear change result. Therefore, the results obtained for this parameter were further examined.

Roughness parameter	Duration of the etching process t [min]	Relative difference d_R [%] Solution A	Solution B	Solution C
	3	20.2	5.4	4.2
R_a	6	-10.3	5.2	17.8
	15	8.0	36.7	32.5

Tab. 2: Relative differences in the roughness values of the sample surface before and after the etching process.

For solutions B and C, the value of the Ra parameter increased with the increase of the etching time. In the case of solution A, the value of the Ra parameter was variable, initially it increased by 20.2 % after 3 minutes of etching, then decreased by 30.5 % after 6 minutes, to increase again by approximately 20 % after 15 minutes of etching process.

Changes in the value of the relative difference d_R of sample roughness were in the range:

- R_a – -10.3 % ≤ d_R ≥ 36.7 %,
- R_z – 93.9 % ≤ d_R ≥ 228.7 %,
- R_p – 43.0 % ≤ d_R ≥ 221.9 %,
- R_v – 209.3 % ≤ d_R ≥ 1 056.8 %.

3.3. Hardness measurement

The analysis of the results presented in Tab. 3 shows that for the duration t = 15 minutes, an increase was achieved for all solutions used. The highest relative difference value was obtained for solution C.

Etching time t = 6 minutes, a decrease in the hardness of the material was observed. The highest value was obtained for solution C.

In the case of t = 3 minutes, the relative difference values for solutions B and C have similar values indicating a decrease in the material hardness value after the etching process. Etching the material with solution A resulted in an increase in hardness.

The largest changes in material hardness as a function of the process duration were observed for solution C, while the smallest changes were observed for solution A. The etching process in solution B, after an initial drop in hardness, resulted in its return to oscillating initial values after 15 minutes of etching.

Duration of the etching process t [min]	Relative difference d_H [%]		
	Solution A	Solution B	Solution C
3	0.1 ± 0.1	-6.1 ± 0.4	-6.2 ± 0.3
6	-1.4 ± 0.2	-0.9 ± 0.2	-2.3 ± 0.4
15	0.3 ± 0.2	0.5 ± 0.2	2.2 ± 0.1

Tab. 3: Relative differences in the hardness of the sample surface before and after the etching process.

4. Conclusions

Tests of Ti6Al4V titanium alloy samples before and after the etching process according to the presented experimental plan showed that:

a) the largest material loss was obtained for solution B,
b) the intensity of material loss decreases with the process implementation time for solutions A and C,
c) selection of the roughness parameter used to describe the surface geometry, influences the assessment of process implementation,
d) the etching process increases the surface roughness for each solution used,
e) in the initial phase after 3 minutes of etching, the hardness of the material decreases and increases with its duration for solutions B and C.

The obtained results are the basis for continuing material tests of the etched material, also in the form of samples produced using the 3D additive method.

References

Baszkiewicz J., Kamiński M. (2006) *Korozja materiałów.* Oficyna Wydawnicza Politech. Warszawskiej (in Polish).

Bijlmer P. F. A. (1970) Pickling titanium in hydrofluoric-nitric acid, *J. Met. Finish.*, 68 (1970), pp. 64–72.

Dallago M., Fontanari V., Torresani E., Leoni M., Pederzolli C., Potrich C. and Benedetti M., (2018) Fatigue and biological properties of Ti-6Al-4V ELI cellular structures with variously arranged cubic cells made by selective laser melting, *Journal of the Mechanical Behavior of Biomedical Materials*, 78, 381–394.

Jones J. R. and Hench L. L. (2003) Effect of surfactant concentration and composition on the structure and properties of sol-gel-derived bioactive glass foam scaffolds for tissue engineering, *Journal of Materials Science*, vol. 38.

Oishi T., Matsubara. T. and Katagiri A. (2022) Formation of porous TiO2 by anodic oxidation and chemical etching of titanium, *Electrochemistry*, vol. 68, iss. 2, pp. 106–111.

Rieger N.E., Dupret-Bories E., Salou A., Metz-Boutigue L., Layrolle M. H., Debry P., Lavalle C. and Vrana P. (2015) Controlled implant/soft tissue interaction by nanoscale surface modifications of 3D porous titanium implants, *Nanoscale*.

Shokuhfar T., Hamlekhan A., Chang J.Y., Choi C.K., Sukotjo C. and Friedrich C. (2014) Biophysical evaluation of cells on nanotubular surfaces: the effects of atomic ordering and chemistry, *Int. J. Nanomedicine*, 9.

Sutter E. M. M. and Goetz-Grandmont G. J. (1990) The behaviour of titanium in nitric-hydrofluoric acid solutions, *Corros. Sci.*, 30.

Torres D. L., Pereira M. C., Silva J. W. J., Codaro E. N. and Acciari H. A. (2015) Effect of Phosphoric Acid Concentration and Anodizing Time on the Properties of Anodic Films on Titanium, 10.

Vasconcellos L. M. R. and Villaça-Carvalho M. F. L. (2017) A Study About Cell Activity on Anodized Ti-6Al-4V by Means of Pulsed Current, 12, pp. 1–13.

Wysocki B., Idaszek J., Szlązak K., Strzelczyk K., Brynk T., Kurzydłowski K. J. and Święszkowski W. (2016) Post processing and biological evaluation of the titanium scaffolds for bone tissue engineering, *Materials (Basel)*.