Chemical polishing of samples obtained by selective laser melting from titanium alloy Ti6Al4V

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Abstract. The paper discusses a method of chemical polishing of Ti6Al4V samples and presents the results of our study. The samples were produced by selective laser melting, which is an increasingly popular method of producing thin-walled, geometrically complex products. The document analyzes how polishing with solutions featuring a varying content of hydrofluoric and nitric acids affects the etching rate and alters the superficial roughness of the samples in both the longitudinal and the transverse directions. We have thus formulated the recommendations on the optimum composition and concentration of such acidic solutions for polishing Ti6Al4V products made by selective laser melting.

High operating properties of titanium-alloy parts, including their good corrosion resistance and biocompatibility, make these alloys popular in various industries [1, 2]. Today, titanium alloys are widely used in aerospace, mechanical engineering, medicine, and other industries. They are used for making high-precision thin-walled and geometrically complex parts sometimes containing inner channels and cavities [3, 4].

The rapidly developing additive technologies can produce any product layer-by-layer if there is a digital 3D model for this product [5, 6]. Such processes are sometimes referred to as "growth" due to their gradual nature. Depending on the technology, it's either a down-top or top-down production process, which affects the properties of the object produced.

Selective laser melting, or SLM, is an additive manufacturing technology which forms a three-dimensional product by pre-programmed laser consequential melting of powder layers. SLM features high material utilization ratio and minimizes post-machining stock removal, which makes SLM a preferred technology for geometrically complex parts, especially when made of titanium alloys. SLM-produced parts are currently too rough, having an Ra of up to 4.5 µm and an Rz of up to 32 µm, which is too much for parts used in aerospace, mechanical engineering, or medicine.

Post-machining of geometrically complex thin-walled parts produced by SLM is a very relevant question, as it comes to machining the inner surfaces and removing non-smelted powder particles from the surface. Mechanical machining is not always efficient enough due to the geometric complexity, thin walls, and low removable-stock reserves. Besides, as titanium allows have low thermal conductivity, the mechanical machining of thin parts

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might result in structural and phase changes inn the material, which generate tensile residual stresses and result in the warpage of parts [7, 8].

This paper discusses chemical polishing of Ti6Al4V parts. The main reagent used for the chemical polishing of titanium and titanium alloys is hydrofluoric acid (HF) [9]. When polishing this titanium alloy, the reaction is as follows:

$$Ti + 3HF \rightarrow TiF_3 + \frac{3}{2}H_2 \uparrow \qquad (1)$$
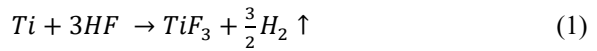
When polishing titanium or its alloys using HF, it produces titanium trifluoride and hydrogen gas. Despite the fact that HF erodes titanium as such, it has some negative effects. First of all, hydrogen gas produced by the reaction is a flammable and explosive product, presenting a fire hazard. Second, HF quickly reduces its concentration in a solution, which requires regular replenishment to keep the acid content sufficiently high. Third, the polishing rate is quite low. Finally, the polished surface might still be non-satisfactory [10, 11]. To eliminate some of these drawbacks, nitric acid is added to the HF solution. The etching reaction is then written as:

$$Ti + 6HF + 4HNO_3 \rightarrow H_2TiF_6 + 4NO_2 \uparrow + 4H_2O \qquad (2)$$
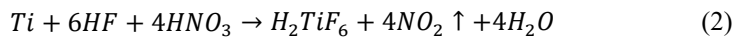
As can be seen from the reaction equation, titanium etching produces hexafluorotitanic acid, nitrogen dioxide, and water. Using this solution stabilizes HF, prevents the production of hydrogen, and even accelerates the etching at specific nitric acid concentrations.

We've run a series of field experiments to study how using varying-content HF- and nitric-acid solutions would affect the chemical polishing of titanium alloys, namely the etching rate and the surface quality [12].

Ti6Al4V was the titanium alloy of our choice. This is a titanium-aluminum-vanadium alloy that has a dual-phase structure (α+β) and is hardened by heat treatment, including quenching and aging that makes it stronger though somewhat less ductile [13, 14].

Table 1. Chemical composition of Ti6Al4V, %

Ti	Al	V	C	Fe	Si	Zr	O₂	N₂	H₂	Other impurities total
			not exceeding						
Base	5.3–6.8	3.5–5.3	0.10	0.60	0.10	0.30	0.20	0.05	0.015	0.30

Samples were produced by selective laser melting on an SLM 280 machine [15] and had the following dimensions: 35 mm in length, 10 mm in width, and 2 mm thick. These were the production parameters: laser radiation power P = 275W, scanning rate S = 805 mm/s. Before polishing, all the samples were checked for weight and surface roughness in longitudinal and transverse directions. The etching conditions were the same for each sample under analysis. We used 50 ml of solution at 25°C. All the solutions had been produced by weight percentage. For etching, we used polypropylene containers.

Tables 2 to 4 present the initial parameters and the chemical polishing results for 3%, 5% and 10% HF solutions; the tables also show how these solutions affected the polishing rate.

Tables 5 and 6 present the longitudinal and transverse surface roughness data for these specific solutions presented in tables 2 to 4.

Table 2. Initial parameters and chemical polishing results for various 3% HF solutions

Chemical polishing solution	Sample thickness before etching, mm	Sample thickness after etching, mm	Average loss of thickness, mm	Rate of etching, mm/min	Sample weight before etching, g	Sample weight after etching, g	Etching time, min
3%HF	2.14	2.06	0.08	0.005	2.9399	2.8561	15
3%HF+3% HNO$_3$	2.12	2.08	0.04	0.003	2.5321	2.4679	15
3%HF+6% HNO$_3$	2.15	2.06	0.09	0.006	2.6495	2.5834	15
3%HF+10% HNO$_3$	2.13	2.08	0.05	0.003	2.8357	2.7695	15
3%HF+15% HNO$_3$	2.15	2.09	0.06	0.004	2.5432	2.4848	15
3%HF+20% HNO$_3$	2.15	2.07	0.08	0.005	2.6423	2.5602	15

Table 3. Initial parameters and chemical polishing results for various 5% HF solutions

Chemical polishing solution	Sample thickness before etching, mm	Sample thickness after etching, mm	Average loss of thickness, mm	Rate of etching, mm/min	Sample weight before etching, g	Sample weight after etching, g	Etching time, min
5%HF	2.19	2.07	0.12	0.008	2.9141	2.7726	15
5%HF+3% HNO$_3$	2.18	2.10	0.08	0.005	2.9990	2.9061	15
5%HF+6% HNO$_3$	2.15	2.07	0.08	0.005	2.9509	2.8176	15
5%HF+10% HNO$_3$	2.07	2.02	0.05	0.003	2.2521	2.1037	15
5%HF+15% HNO$_3$	2.05	2.02	0.03	0.002	2.0485	1.9074	15
5%HF+20% HNO$_3$	2.06	2.02	0.04	0.006	2.3538	2.1896	7

Table 4. Initial parameters and chemical polishing results for various 5% HF solutions

Chemical polishing solution	Sample thickness before etching, mm	Sample thickness after etching, mm	Average loss of thickness, mm	Rate of etching, mm/min	Sample weight before etching, g	Sample weight after etching, g	Etching time, min
10%HF	2.15	2.00	0.15	0.021	3.0660	2.8681	7
10%HF+3% HNO$_3$	2.15	2.00	0.15	0.021	2.9074	2.7084	7
10%HF+6% HNO$_3$	2.10	1.95	0.15	0.021	3.2482	2.8574	7
10%HF+10% HNO$_3$	2.12	2.00	0.12	0.024	3.5643	3.333	5
10%HF+15% HNO$_3$	2.14	2.01	0.13	0.026	3.6154	3.4718	5
10%HF+20% HNO$_3$	2.10	1.95	0.15	0.030	3.3727	2.9954	5

Table 5. Surface roughness before and after chemical polishing with various 3% HF solutions

Chemical polishing solution	Sample surface roughness, µm		Surface alteration ratio
	Before polishing	After polishing	
3%HF	Ra = 4.36	Ra = 3.97	1.10
3%HF+3% HNO$_3$	Ra = 4.36	Ra = 3.35	1.30
3%HF+6% HNO$_3$	Ra = 4.24	Ra = 3.06	1.38
3%HF+10% HNO$_3$	Ra = 4.26	Ra = 3.96	1.07
3%HF+15% HNO$_3$	Ra =3.93	Ra = 4.21	0.93
3%HF+20% HNO$_3$	Ra = 4.18	Ra = 3.42	1.22

Table 6. Surface roughness before and after chemical polishing with various 5% HF solutions

Chemical polishing solution	Sample surface roughness, µm		Surface alteration ratio
	Before polishing	After polishing	
5%HF	Ra = 3.78	Ra = 2.86	1.32
5%HF+3% HNO$_3$	Ra = 3.78	Ra = 2.05	1.84
5%HF+6% HNO$_3$	Ra =3.63	Ra = 2.41	1.50
5%HF+10% HNO$_3$	Ra = 6.70	Ra = 4.30	1.56
5%HF+15% HNO$_3$	Ra = 6.70	Ra =4.19	1.60
5%HF+20% HNO$_3$	Ra =6.70	Ra = 4.98	1.34

**Table 7**. Surface roughness before and after chemical polishing with various 10% HF solutions

Chemical polishing solution	Sample surface roughness, µm		Surface alteration ratio
	Before polishing	After polishing	
10%HF	Ra = 4.27	Ra = 2.39	1.79
10%HF+3% HNO$_3$	Ra = 4.27	Ra = 2.23	1.91
10%HF+6% HNO$_3$	Ra = 4.22	Ra = 4.44	0.95
10%HF+10% HNO$_3$	Ra = 3.99	Ra = 1.69	2.36
10%HF+15% HNO$_3$	Ra = 3.99	Ra = 2.15	1.85
10%HF+20% HNO$_3$	Ra = 4.22	Ra = 2.64	1.60

SLM-produced parts have superficial convexities and concavities, the location of which depends on the laser scanning strategy. Chemical polishing solutions affect the surface

evenly, which is why measuring the surface roughness perpendicularly to the track direction yields different results compared to measuring along the track.

As shown by this study, chemical polishing with a hydrofluoric acid solution is a rather slow process that generates a by-product. The by-product is hydrogen gas. Adding nitric acid to the solution accelerates etching, eliminates hydrogen gas production, and produces a smoother surface. Increasing nitric acid content above ten percent has no significant effect on the etching rate. Besides, higher HF concentrations result in the generation of titanium oxide on the surface; the oxide is white-colored and extremely difficult to remove.

Initial surface roughness and the presence or absence of non-smelted sections do affect the etching rate and the surface roughness of SLM-produced samples polished by a HF-HNO_3 solution, see Figure 1.
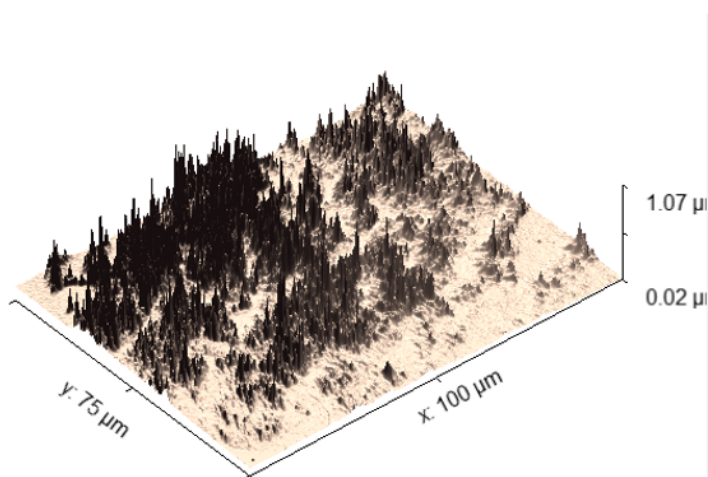
Fig. 1. Surface image after polishing.

The effect of the above factors on the quality of polishing manifests itself in the accumulation of H_2TiF_6 и NO_2 in the superficial depressions, the size and location of which depends on the laser scanning strategy; this, in its turn, prevents the solution from polishing the surface and worsens its final roughness.

Based on our experiments to study the effect of varying concentrations on the etching rate and the surface quality of Ti6Al4V samples polished with a HF- and nitric-acid solution, we have found that the most optimal solutions are 10%HF+10%HNO_3 and 5%HF+6%HNO_3. The longitudinal and transverse surface roughness was 2.36 and 1.24 times lower, respectively, when polished with the former solution, or 1.50 and 11.34 times lower when polished with the latter solution.

The presented method for polishing Ti6Al4V parts by a hydrofluoric acid solution with added nitric acid can be used for the post-machining of SLM-produced thin-walled geometrically complex parts. The authors recommend using a 10% HF- and nitric-acid solution as the basic chemical-polishing solution for titanium alloys.

Polishing titanium alloys with HF+HNO_3 solutions can be intensified by circulating the solution or shaking the sample. This removes the accumulated hexafluorotitanic acid, nitrogen dioxide, and water from the surface.

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