Etching Titanium with HF and Nitric Acid Solutions
Part 2

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Chemcut

For etching titanium, hydrofluoric acid (HF) is the primary chemical used. The etching reaction is shown as:

$$Ti + 3HF \rightarrow TiF_3 + 3/2H_2\uparrow$$ [1]

The etching of titanium, with HF, produces titanium tri-fluoride and hydrogen gas. Although HF, by itself, will etch titanium, there are some disadvantages to using HF alone. First, there is the formation of hydrogen gas that is flammable and explosive. This can create a potential fire hazard. Secondly, the HF tends to dissipate quickly, requiring regular chemistry additions. Thirdly, the etch rate is relatively slow. To offset some of these disadvantages, nitric acid is added to the HF solution. This reaction is shown as:

$$Ti + 6HF + 4HNO_3 \rightarrow H_2TiF_6 + 4NO_2\uparrow + 4H_20$$ [1]

Here the etching of titanium produces hexafluorotitanic acid, nitrogen dioxide, and water. With this solution, the HF tends to be more stable, the hydrogen gas is eliminated, and the etch rate increases.

The purpose of this testing was to document the etch rates and undercut of titanium when etching with a HF and HNO_3 solutions at various concentrations and selected spray pressures on imaged panels. Previous testing had shown that as the acid concentration increased, so did the etching rate. However, those tests were done using blank sheets of titanium, rather than imaged panels. For this series of tests, the titanium panels were imaged, etched, cross-sectioned, measured, and evaluated for etch rate and undercut.

The machine used for the etching was a Chemcut model 2315. The useable conveyor width is fifteen inches and the effective chamber length is twenty-two inches. It is equipped with four spray tubes, top and bottom. The spray tubes oscillate perpendicular to the direction of material travel. Each spray tube has four, solid cone, nozzles rated at 0.75gpm @ 40psi. The oscillation rate used for the testing was 30 sweeps per minute. The etching temperature used was 110°F (43.3°C). The spray pressures selected for the evaluation were 15psi (1.03bar), 20psi (1.38 bar), 25psi (1.72 bar), and 30psi (2.07 bar). The conveyor speed was set at 7.3 inches per minute, for an etch time of three minutes. The etching solutions were comprised of 5% HF, by weight, and 5%, 10%, and 15% HNO_3, by weight. Chemical additions were made, during the testing, to maintain the concentrations and compensate for the increased etching solution volume.

The panels were imaged with a line pattern (fig.1) consisting of lines 10-mil (254µ), 12.5-mil (317.5µ), 15-mil (381µ), 17.5-mil (444.5µ), and 20-mil (508µ). Each group of lines was rotated 90° from the adjacent group. The panels were also conveyed at a 45° angle to try and minimize any directional bias.

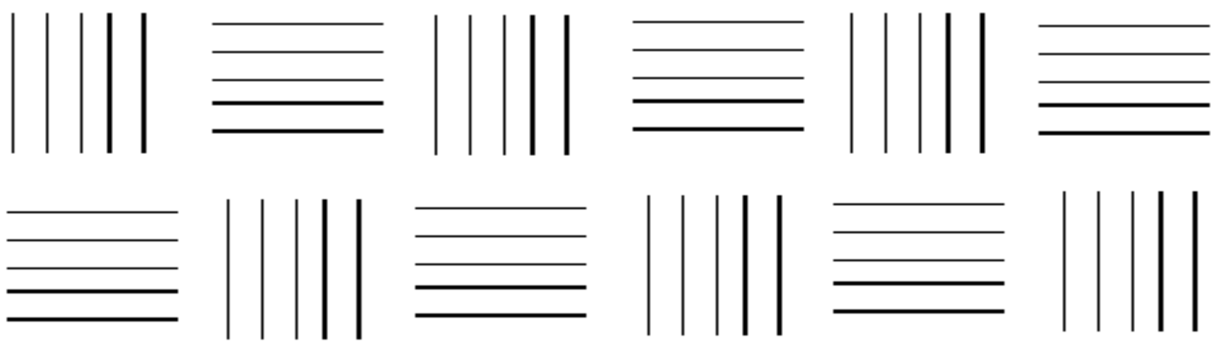
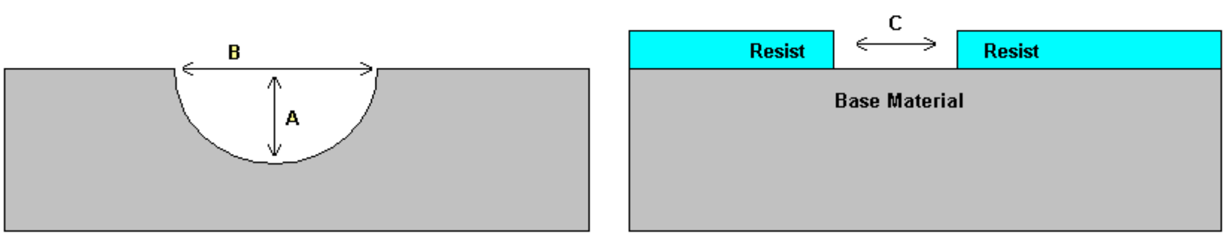


Fig.1

The etch resist, that Chemcut had on hand, was not suitable for HF etching. Therefore, the panels were imaged by an outside vendor and returned to Chemcut, ready to be etched. They were etched, two at a time, under each set of chemical and spray pressure conditions. For example, 2 each using 5%HF+5% nitric @ 15psi, 2each using 5%HF+5% nitric @ 20psi, and so forth. Two coupons were removed, at random, from each of the panels to provide four cross-sectional samples from each set of processing conditions. The etch depths and line widths were measured and averaged to provide a composite result for each etching condition and line width. The etch rates and undercut percentages were then calculated using the following formulas (fig. 2).

Etch Rate = A/3



Undercut Ratio = A/(B-C/2)

100/UR = % Undercut

Fig. 2

The following chart shows the average etch rates, in microns per minute, at each spray pressure under each chemical concentration (fig. 3).

Solution	Spray Pressure (psi) – Etch Rates (microns per minute)			
	15 (1.03Bar)	20 (1.38Bar)	25 (1.72Bar)	30 (2.07Bar)
5%HF+5%HNO_3	20.58	21.28	21.36	21.12
5%HF+10%HNO_3	29.36	29.26	29.00	29.84
5%HF+15%HNO_3	32.82	33.60	34.06	34.10

Fig. 3

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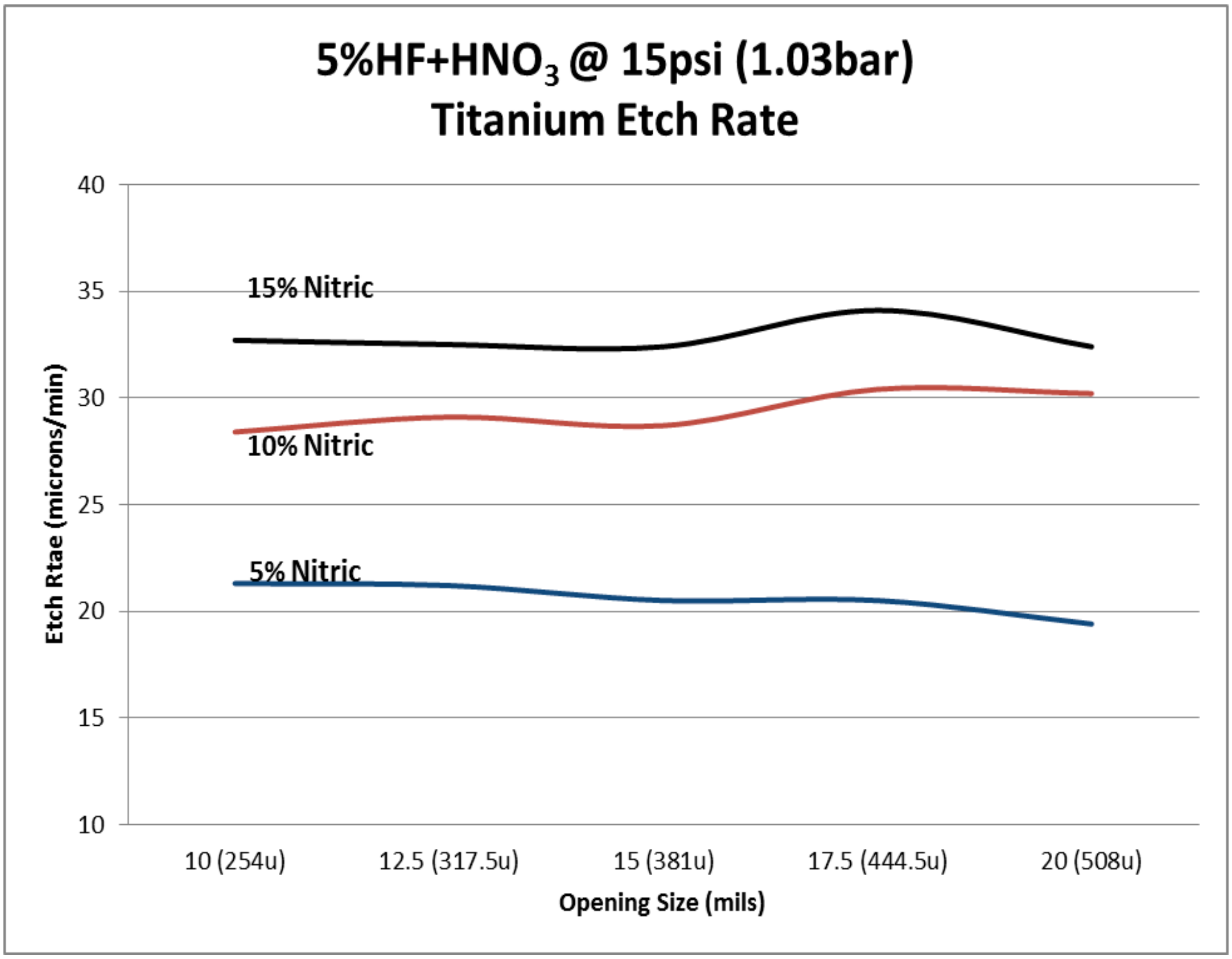
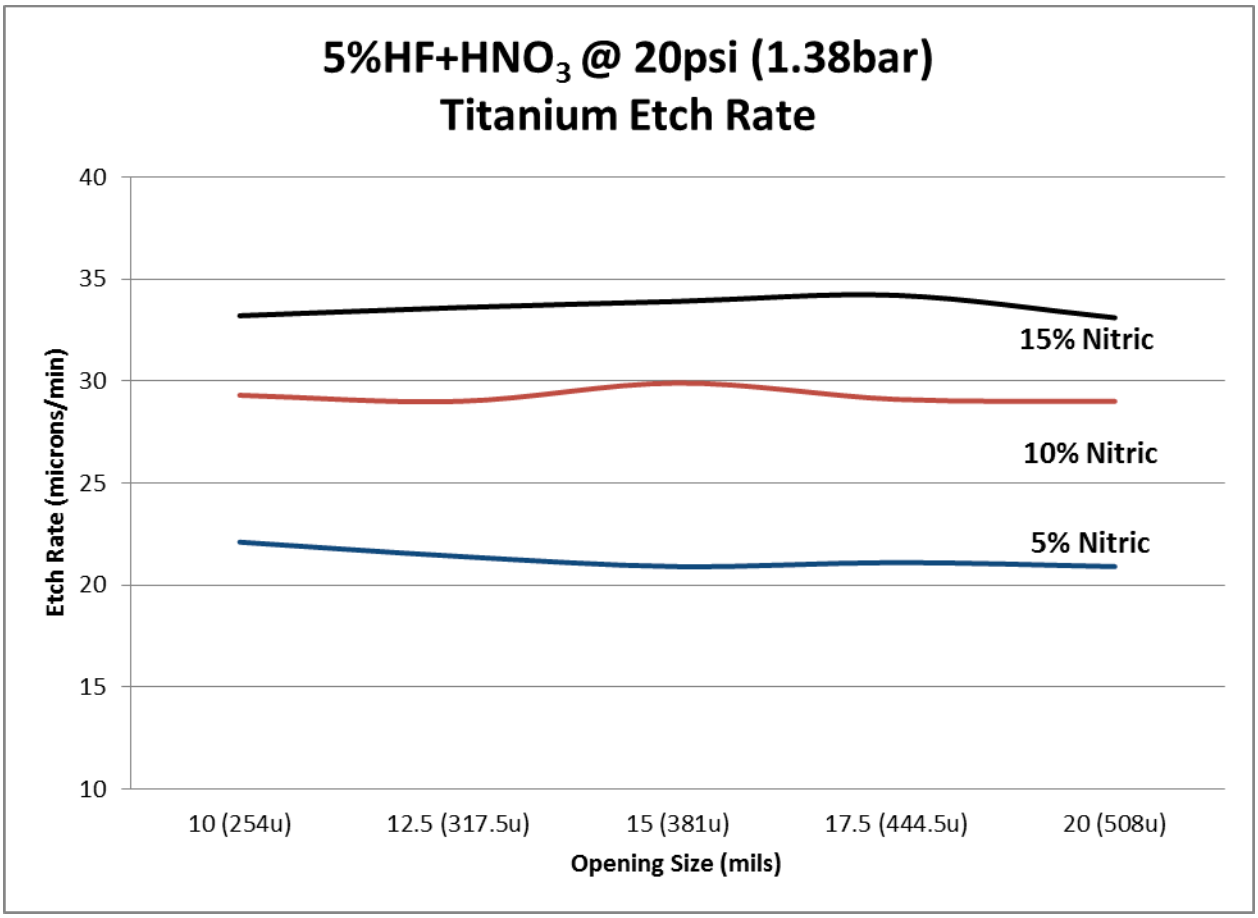
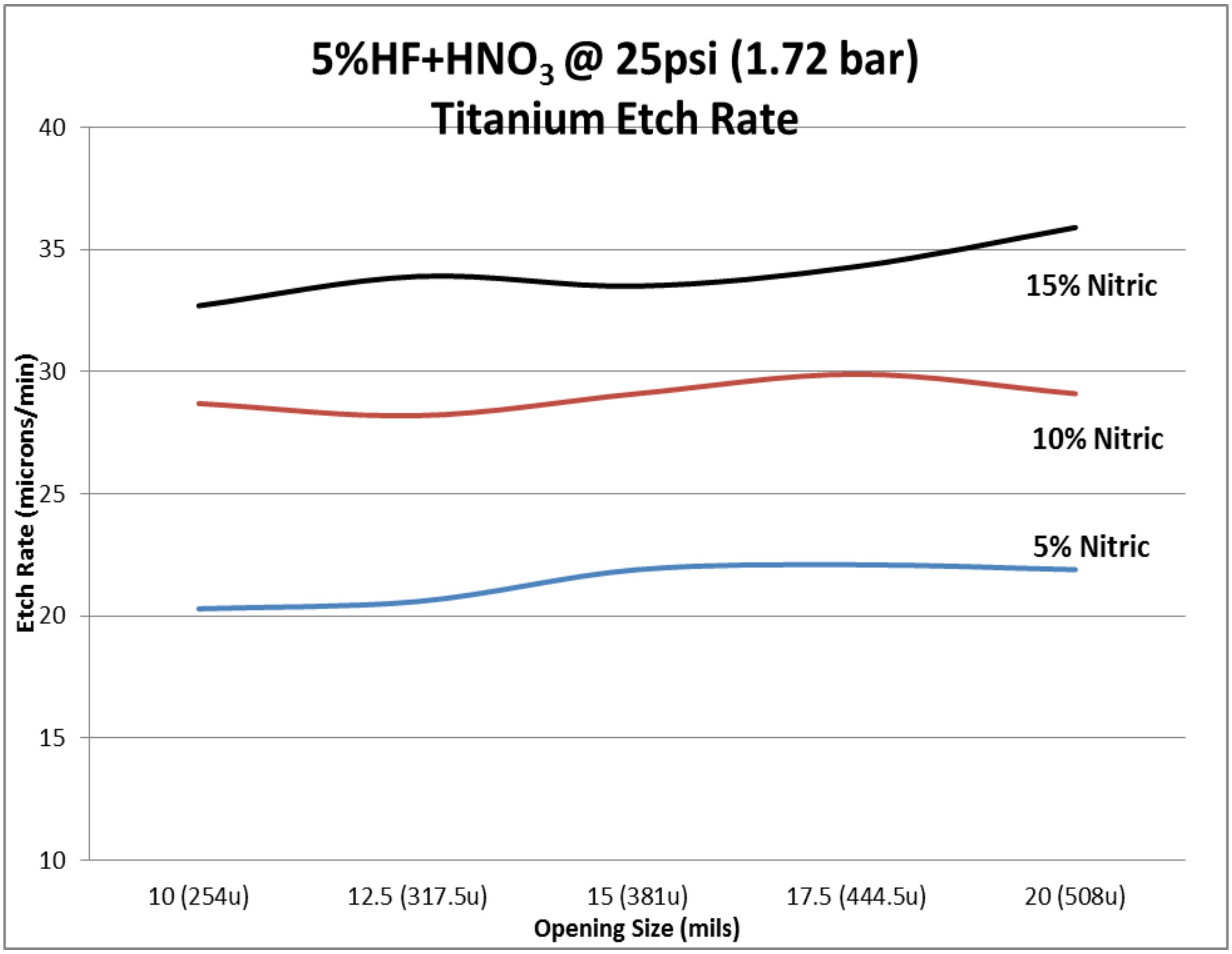
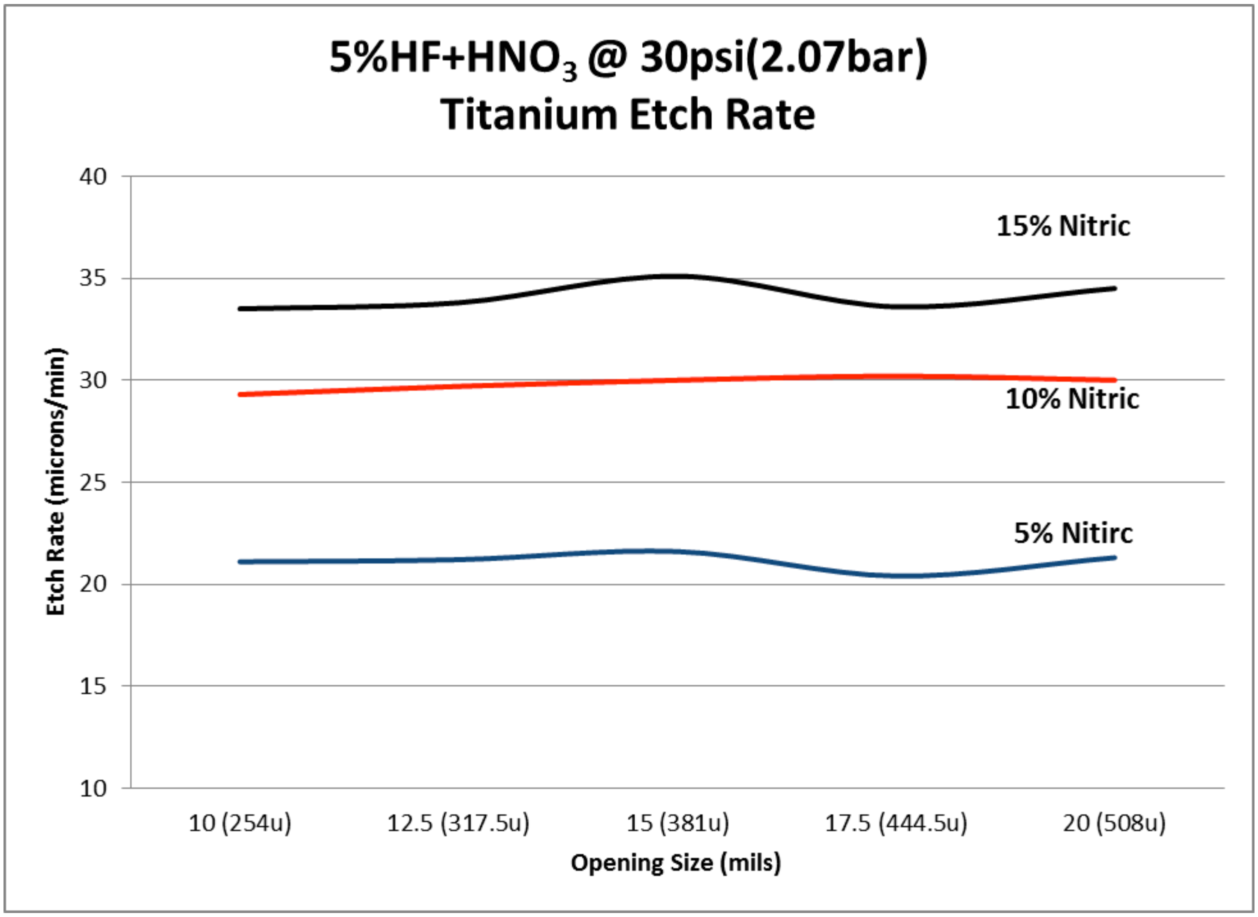
The etch rate increases very slightly as the spray pressure increases. The chart indicates that spray pressure plays a very minimal role in the etch rate. As a general rule, the larger the area exposed for etching, the faster the etch rate. The following graphs show the etch rates for the various line widths under each of the spray pressures and chemical concentrations.





5%HF+HNO3 @ 20psi (1.38bar)
Titanium Etch Rate
40
35
30
25
20
15
10
Etch Rate (microns/min)
15% Nitric
10% Nitric
5% Nitric
10 (254u)
12.5 (317.5u)
15 (381u)
17.5 (444.5u)
20 (508u)
Opening Size (mils)


5%HF+HNO3 @ 25psi (1.72 bar)
Titanium Etch Rate
Etch Rate (microns/min)
40
35
30
25
20
15
10
15% Nitric
10% Nitric
5% Nitric
10 (254u)
12.5 (317.5u)
15 (381u)
17.5 (444.5u)
20 (508u)
Opening Size (mils)



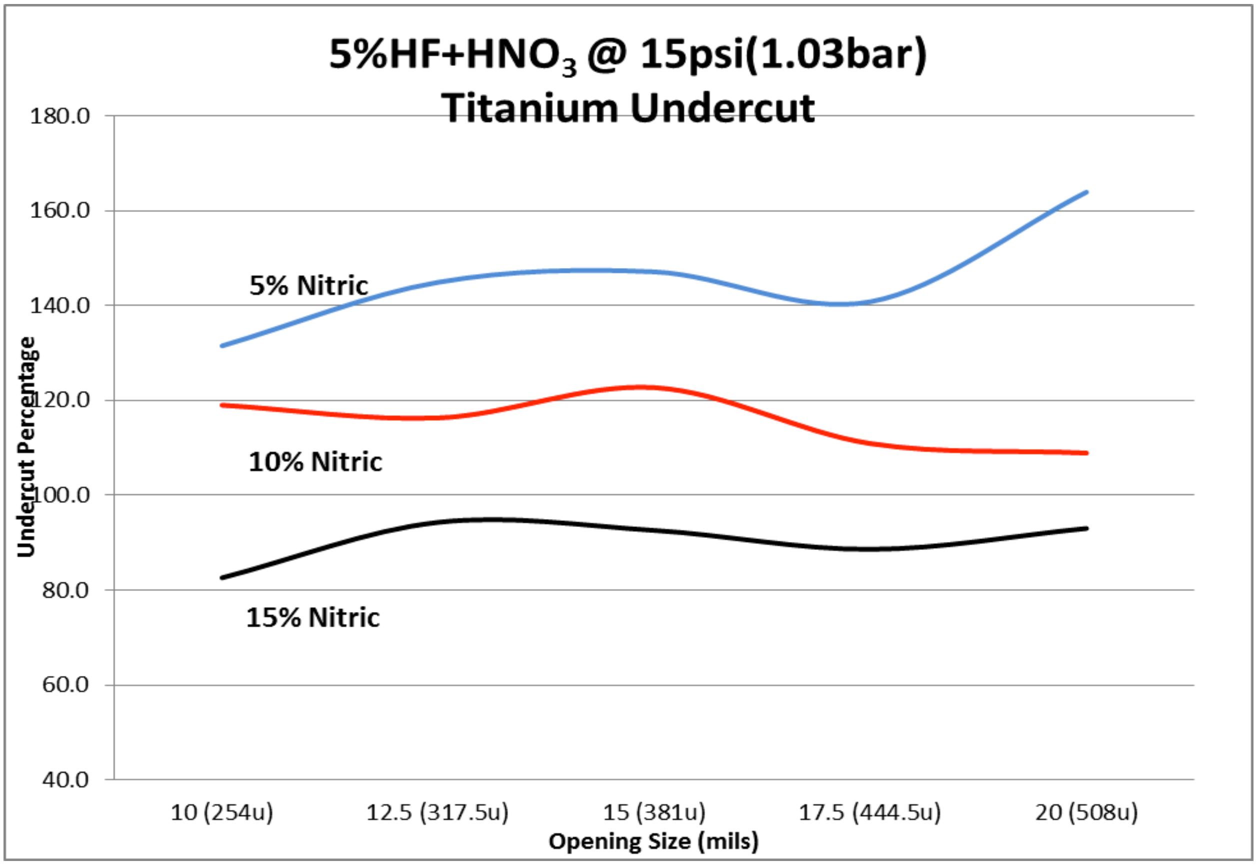
As seen by the graphs, the size of the opening, to be etched, has very little influence on the etch rate, regardless of the acid concentration or spray pressure.

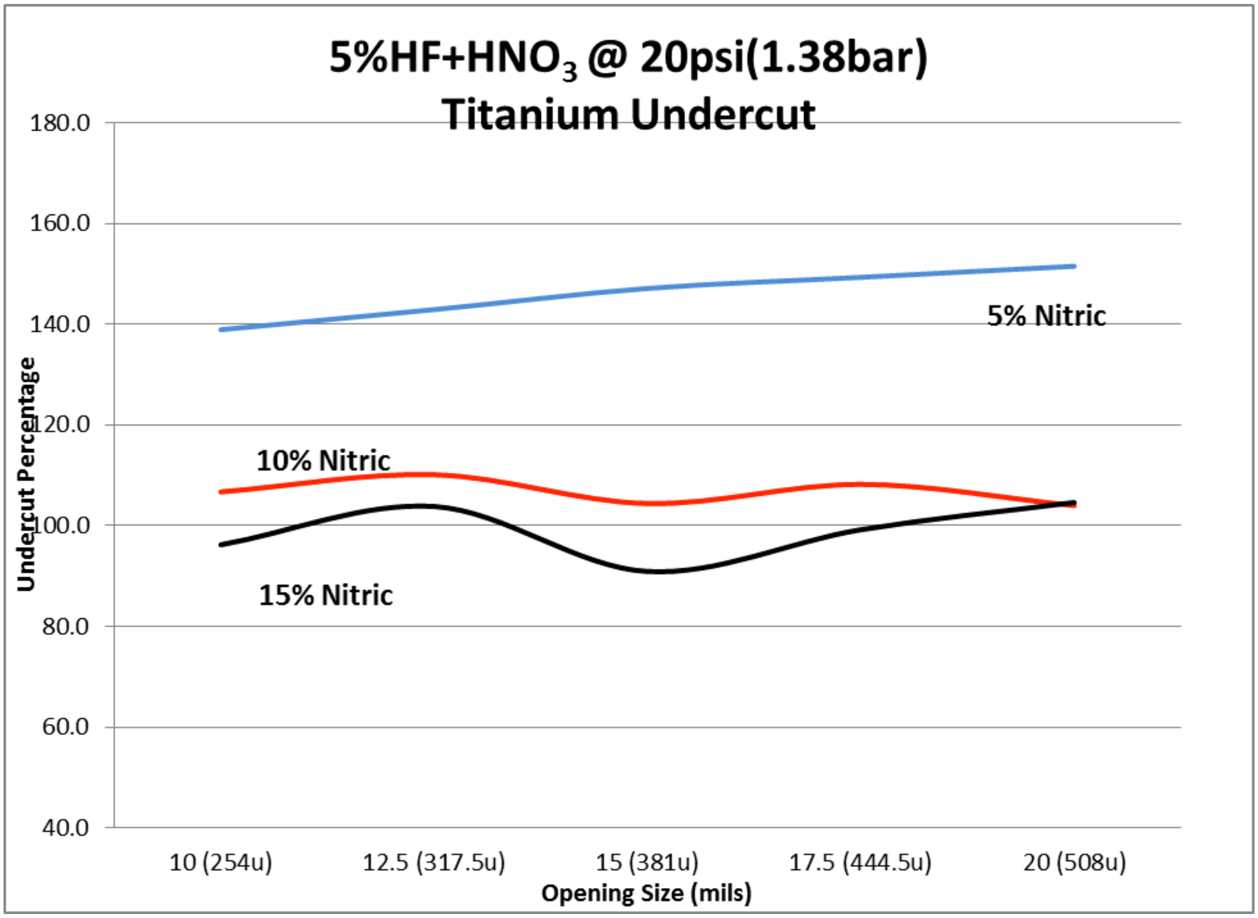
The undercut of the titanium was rather severe. In most cases, the lateral etch was more than the vertical etch. The best undercut percentage was 82.6% on the 10-mil line using 5%HF+15% nitirc @ 15psi. The worse undercut percentage was 163.9% on the 20-mil line using 5%HF+5% nitric @ 15psi.

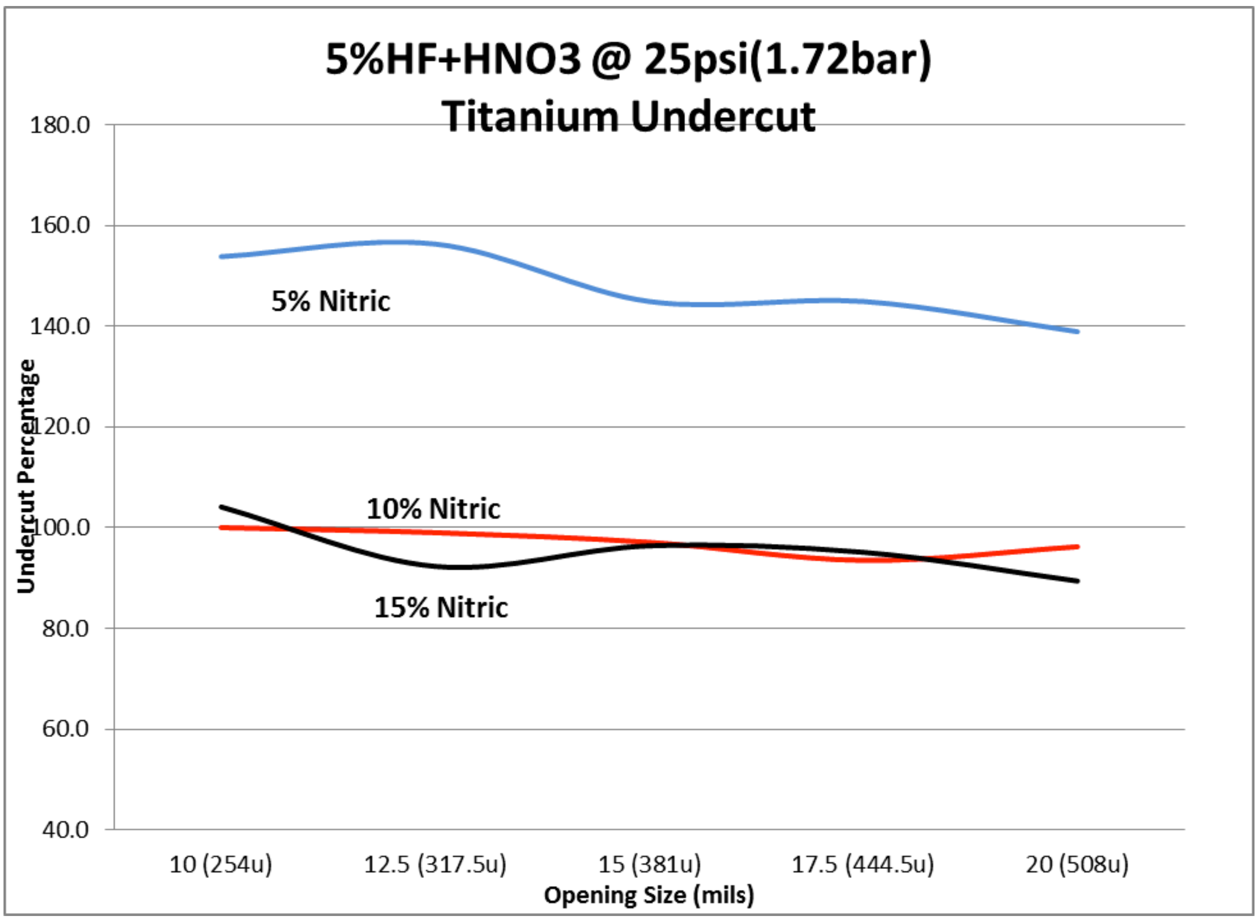
The following chart (fig.4) show the average undercut percentages at the various spray pressures and chemical concentrations.

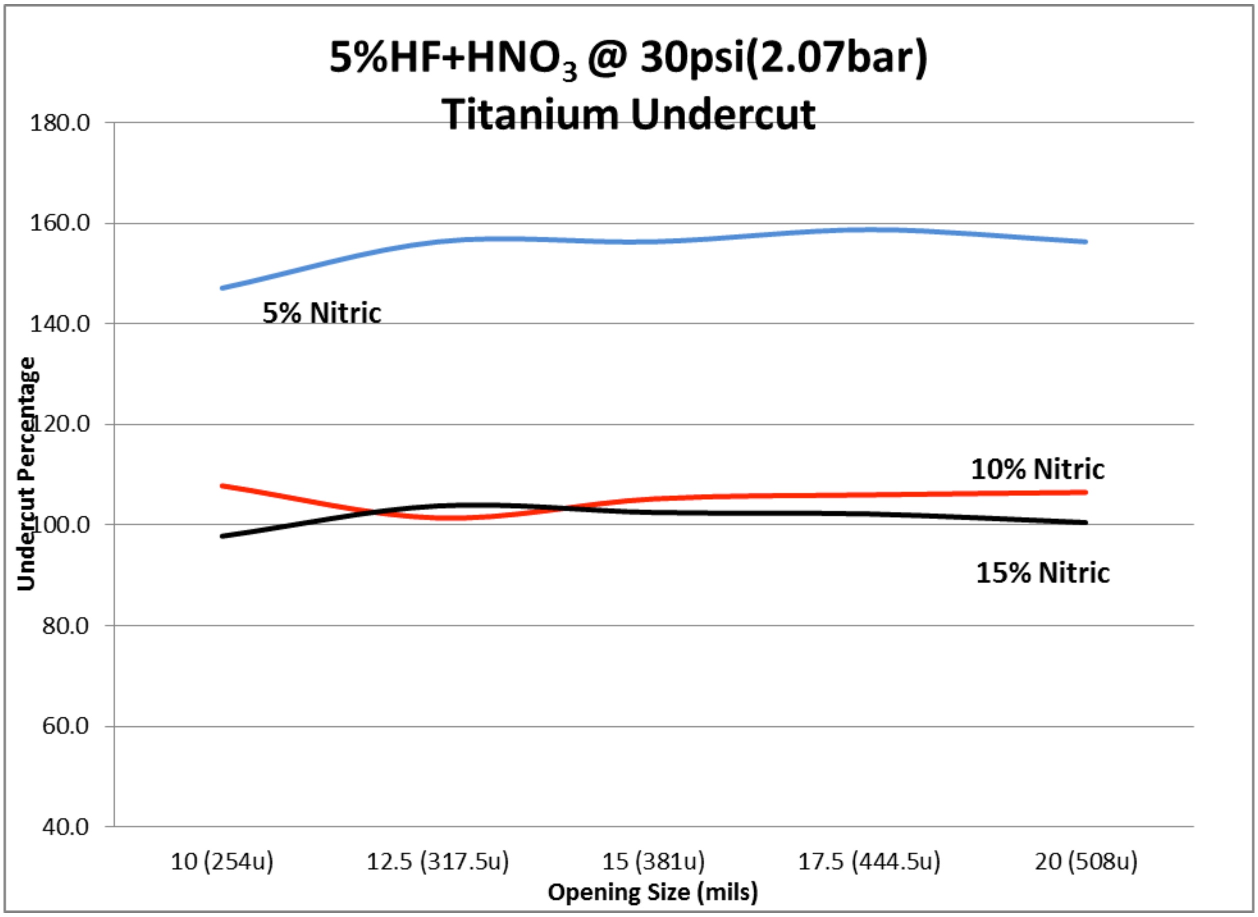
	Spray Pressure (psi) – Undercut Percentages			
Solution	15 (1.03Bar)	20 (1.38Bar)	25 (1.72Bar)	30 (2.07Bar)
5%HF+5%HNO_3	145.6%	145.9%	147.8%	154.9%
5%HF+10%HNO_3	115.6%	106.7%	97.2%	105.4%
5%HF+15%HNO_3	90.2%	98.9%	95.5%	101.4%

The next four graphs show the undercut percentages at the different chemical concentrations and spray pressures.




5%HF+HNO3 @ 20psi(1.38bar)
Titanium Undercut
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
Undercut Percentage
5% Nitric
10% Nitric
15% Nitric
10 (254u)
12.5 (317.5u)
15 (381u)
17.5 (444.5u)
20 (508u)
Opening Size (mils)


5%HF+HNO3 @ 25psi(1.72bar)
Titanium Undercut
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
Undercut Percentage
5% Nitric
10% Nitric
15% Nitric
10 (254u)
12.5 (317.5u)
15 (381u)
17.5 (444.5u)
20 (508u)
Opening Size (mils)



Summary

The spray pressure has very little effect on the etch rate when etching titanium with HF and Nitric acid solutions. In fact, excessive pressure could be damaging to the etch resist. The chemical concentrations and the dwell time are the more dominant factors. The undercut of titanium is rether severe. Undercut of 100% (1:1), or more, can be expected.

[1] Allen D M, 1986, The Principles and Practice of Photochemical Machining and Photoetching, Pg. 97