



Standard Practice for Descaling and Cleaning Zirconium and Zirconium Alloy Surfaces¹

This standard is issued under the fixed designation B614; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers a cleaning and descaling procedure useful to producers, users, and fabricators of zirconium and zirconium alloys for the removal of ordinary shop soils, oxides, and scales resulting from heat treatment operations and foreign substances present as surface contaminants.

1.2 It is not intended that these procedures become mandatory for removal of any of the indicated soils but rather serve as a guide when zirconium and zirconium alloys are being processed in the wrought, cast, or fabricated form.

1.3 It is the intent that these soils be removed prior to chemical milling, joining, plating, welding, fabrication, and in any situation where foreign substances interfere with the corrosion resistance, stability, and quality of the finished product.

1.4 Unless a single unit is used, for example, solution concentrations in g/l, the values stated in either inch-pound or SI units are to be regarded separately as standard. The values stated in each system are not exact equivalents; therefore, each system must be used independently of the other. SI values cannot be mixed with inch-pound values.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see Sections 2 and 6.

2. Processing Soil Removal

2.1 Grease, oil, and lubricants employed in machining, forming, and fabricating operations on zirconium and zirconium alloys should be removed by employing one of the methods or a combination of methods as listed: (1) alkaline or emulsion soak-type cleaners, (2) ultrasonic cleaning, (3)

acetone, citrus based cleaners, or safety solvent immersion washing or vapor degreasing, or (4) electrolytic alkaline cleaning system. In the electrolytic system, the work can be either anodic or cathodic polarity provided voltage and current density are controlled to avoid anodizing. Removal of these soils is recommended prior to heat treatment or application of acid treatment designated in Section 4. When electrolytic systems are employed, the voltage should be controlled to prevent the occurrence of spark discharge and subsequent pitting. The use of trichloroethylene is not prohibited and can be used; however its use is hazardous enough to preclude it as a recommended solvent in this standard. Care must be exercised when using chemical solvents. There are hazards associated with their use, such as flammability, carcinogenicity, and ozone depletion (see 6.1.)

3. Blast Cleaning

3.1 Mechanical descaling methods such as sandblasting, shot blasting, and vapor blasting may be used to remove hot work scales and lubricants from zirconium surfaces if followed by thorough conditioning and cleaning as described in Section 4.

3.2 Aluminum oxide, silicon carbide, silica sand, zircon sand, and steel grit are acceptable media for mechanical descaling. Periodic replacement of used media may be required to avoid excessive working of the metal surface by dull particulate.

3.3 Roughening of exposed surface areas may occur from grit or shot if cleaning of the entire surface is accomplished by blasting. Partial cleaning for preserving the surface finish is to be preferred in conjunction with proper pickling procedures.

3.4 Any abrasive or shot blast cleaning may induce residual compressive stresses in the surface of the material or zirconium structure. Warpage may occur in sections that are subsequently chemical milled or contour machined.

3.5 In most cases, blast cleaning is not intended to eliminate pickling procedures completely. However, there are cases where blast cleaning does not need to be followed by a pickling operation. Abrasives may not remove surface layers contaminated with interstitial elements such as carbon, oxygen, hydrogen, and nitrogen. When these elements are present in

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excessive amounts, they are preferably removed by controlled acid pickling in accordance with 4.3.

4. Pickling and Descaling

4.1 Recommended post treatment of shot or abrasive blasted zirconium surfaces may include acid pickling as described in 4.3 to ensure complete removal of metallic iron, oxide, scale, and other surface contaminants. Note that pickling does not need to be the final surface conditioning. Mechanical methods may be acceptable as final conditioning steps.

4.2 Scale and lubricant residues developed on mill, foundry, forged, or fabricated zirconium products usually require conditioning by one of the following commercial methods prior to final pickling as described in 4.3 to produce a completely scale-free surface.

4.2.1 Proprietary solutions of caustic- or organic-based compounds in tap water in accordance with the manufacturer's recommendation.

4.2.2 Molten alkaline-based salt baths operating at 1200 to 1300°F (650 to 700°C) in accordance with prescribed procedures.

4.2.3 Oxides and heat tints developed below 1000°F (540°C) can frequently be removed by pickling in a nitric acid – hydrofluoric acid solution. Common input acid strengths used are 70 % by weight for HNO₃ acid and 48 % by weight for HF acid. HF acid at 60 % strength has been used in the past but there are additional transportation restrictions on this higher strength acid.

4.2.4 The pickling acid solution is composed of 25 to 50 % by volume of 70 % strength HNO₃ acid and 3.8 to 8.8 % by volume of 48 % strength HF acid. The balance is clean filtered water. This yields a solution having 350 to 700 mg/L of nitric acid and 36 to 84 mg/L of hydrofluoric acid. Pickling should be done in a solution with a temperature less than 120°F (50°C) and preferably nearer to 90°F (30°C).

4.2.5 Abrasive methods such as wheel or belt grinding, high-speed tool steel or carbide grinding, or both, segmented flapper wheels, and grit or shot blasting, when available, may

be used when surface configuration is such that the scaled areas are readily accessible.

NOTE 1—The pickling rate (weight loss per unit time – mg/dm² per minute) of zirconium and zirconium alloys is dependent on acid concentrations and temperature. The following table and Fig. 1 show these relationships.

Vol% HNO ₃	Vol% HF	Temp	WT Loss
80	1.0	100	1.00
80	2.0	100	2.00
80	3.0	100	3.00
80	4.0	100	4.00
80	5.0	100	5.00
30	1.0	100	1.75
30	2.0	100	2.75
30	3.0	100	3.75
30	4.0	100	4.75
30	5.0	100	6.40
39	3.5	110	5.00
39	3.5	140	8.00
39	3.5	160	11.00

4.2.5.1 For example, the use of 30 % HNO₃ with HF at 100°F increases the pickle rate compared to the use of an 80 % HNO₃ solution with the same HF concentration. Also, an increase in temperature from 110 to 160°F more than doubles the pickle rate (5.0 to 11.0 mg/dm² in 7 min.).

4.3 Following mechanical abrading or chemical conditioning, the material may be further treated to clean the surface completely using the following solution:

4.3.1 Material that has been mechanically abraded in accordance with 3.1, or chemically conditioned in accordance with 4.2.1 and 4.2.2, may be finish-cleaned by immersion in an acid solution composed of 25 to 50 volume % (350 to 700 g/L) of nitric acid (70 %) and 3 to 7 volume % (36 to 84 g/L) of hydrofluoric acid (60 %) at 120°F (50°C) maintaining a ratio of 10 parts nitric acid to 1 part hydrofluoric acid. Hydrofluoric acid at 48 % concentration can be used in place of the 60 % concentration. If this is done, the ratio of nitric to hydrofluoric should be 8 to 1.

NOTE 2—Most of the acid pickling following molten salt bath conditioning is accomplished in the sulfuric or nitric-hydrofluoric acid solution.

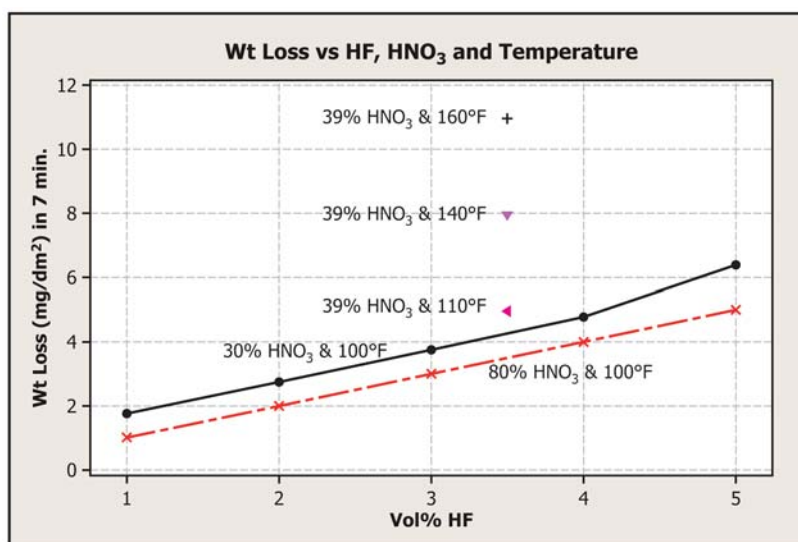


FIG. 1 WT Loss vs HF, HNO₃ and Temperature

The material is cycled through the salt bath, water rinse, and acid until all of the scale has been completely removed. Final brightening is obtained by a brief cycle in the nitric-hydrofluoric solution, in accordance with 4.3.

NOTE 3—In the nitric-hydrofluoric pickling solution, the ratio of nitric acid to hydrofluoric acid is more important than the concentration of either of these two acids. When this ratio is maintained at 10 to 1, hydrogen absorption during pickling is minimized. Hydrofluoric acid at 48 % concentration can be used in place of the 60 % concentration. If this is done, the ratio of nitric to hydrofluoric should be 8 to 1.

NOTE 4—The components should be rinsed immediately and thoroughly in cold tap water following pickling to avoid staining of the surfaces with residual fluorides or chlorides which may be detrimental in some services.

NOTE 5—In the processing of zirconium mill products and fabrications, an oxygen-rich layer is unavoidable where there is a combined exposure to high temperatures and an oxidizing atmosphere. In the removal of this oxygen-rich layer by pickling in strong solutions of nitric and hydrofluoric acids, it is extremely important that all residual oxide and scale have been removed to prevent preferential etching of the finished product.

5. Inspection

5.1 Visual inspection of material cleaned in accordance with this practice should show no evidence of paint, oil, grease, glass, graphite, lubricant, scale, abrasive, iron, or other forms of contamination.

5.2 Hydrogen absorption during the cleaning process should be minimized and well within tolerable limits if the procedures outlined are followed. Periodic monitoring of the cleaning system can be accomplished by processing samples of known hydrogen content through the complete system followed by chemical analyses. A hydrogen increase greater than 2 to 5 ppm

over the original product analyses may be cause for replacing the acids or adjusting the composition to reduce the extent of hydrogen pickup.

5.3 Additional evaluation of product cleanliness may be obtained by chemical milling of an expendable sample test piece. It is recommended that approximately 0.001 to 0.002 in. (0.025 to 0.05 mm) shall be removed from each surface. After chemical milling, the surface should be uniformly smooth and bright with the absence of peaks indicative of residual scale or contamination.

6. Hazards

6.1 Cleaning using this practice involves the use of hazardous chemicals. These chemicals are as follows: acetone, nitric acid, hydrofluoric acid, molten cleaning salts, and alkaline cleaning solutions. Before using any of these materials consult a standard reference on safe use of chemicals or the manufacturer's recommendations for safe handling.

6.2 Grinding and grit blasting of zirconium can create a fine metal dust that is flammable and dangerous if allowed to accumulate. Precautions should be taken to dispose of such dust by burning in small (approximately 1-lb (0.5-kg)) quantities.

NOTE 6—Burning of Zr fines may not be permitted in all jurisdictions.

7. Keywords

7.1 cleaning; descaling; zirconium; zirconium alloys

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