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PICKLING ZIRCONIUM AND ZIRCONIUM BASE ALLOYS

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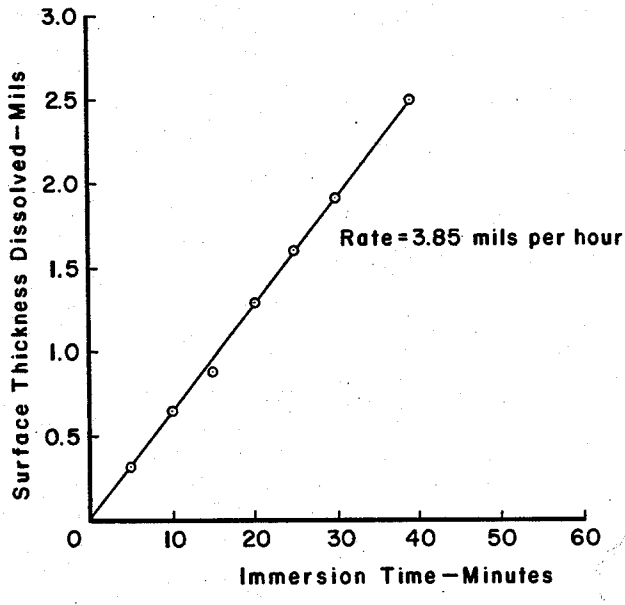


Fig. 2

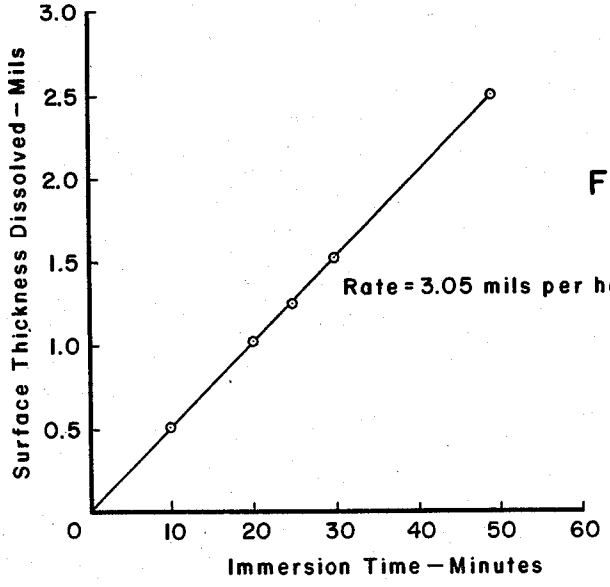


Fig. 1

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PICKLING ZIRCONIUM AND ZIRCONIUM BASE ALLOYS

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The present invention relates to improved etching and pickling solutions and a process for pickling zirconium and zirconium base alloys.

In the presently accepted procedure for the fabrication of zirconium and zirconium base structural members especially for applications such as reactor components, mechanical operations, such as machining the alloy gives rise to a layer of disturbed metal at the surface which extends for an appreciable depth. As this disturbed layer exhibits a more rapid corrosion rate than does the bulk metal, it is removed by chemical dissolution.

A known method of surface pickling consists of the removal of from 1 to 2 mils from the surfaces of zirconium alloy members by bright etching in an aqueous solution containing predetermined proportions by volume of nitric acid and hydrofluoric acid. This admittedly hazardous reagent is capable of producing severe burns upon even momentary skin contact, and is contained in brick tanks with polyvinyl chloride liners as it even attacks stainless steel at a rapid rate. In the majority of processes involving zirconium and zirconium base alloys in which the alloy is to be pickled, a large ratio of etchant volume to component surface area is desired as the zirconium-acid reaction is exothermic, and the etchant temperature should be maintained below 120° F. Items pickled at temperatures in excess of the upper limit result in tapered and irregular surfaces and are more prone to be contaminated.

Contamination occurs when the etchant is not thoroughly rinsed from the surfaces or when the etchant is permitted to dry on the member. In the latter event, the residue is insoluble in water. Inadequate rinsing, which allows some of the etchant to dry on the surface, leaves the alloy with poor corrosion resistance and subsequently it leads to the formation of undesirable white corrosion products when exposed to high temperature water.

The difficulties which could result from this condition, namely the occurrence of white corrosion products, are several. First, the white corrosion product could be evidence of a sufficiently accelerated fluoride attack to significantly reduce the thickness of the zirconium and its alloys. Second, a bulky corrosion product would reduce the heat transfer coefficient. Third, a non-adherent zirconium oxide product, especially in nuclear reactors, could be carried away by a coolant and thus increase the contamination and accessibility problem.

Summing up, the present state of the art of zirconium and zirconium base alloy surface preparation involves the use of the hazardous hydrofluoric-nitric acid etchant procedure with its stringent rinse requirements, difficult contaminant problems, and critical temperature control for maintenance of dimensional tolerances and questionable over-all efficiency.

In pickling zirconium and zirconium base alloys, using modifications of the standard hydrofluoric nitric acid procedure, it has been observed that the higher the percentage of nitric acid in the reagent, the slower the rate of reaction. Hydrofluoric acid alone produces a violent exothermic reaction with zirconium and its alloys, whereas nitric acid alone does not attack the alloy. Apparently the nitric acid acts as an inhibitor and serves to control the reaction rate.

Some work has been done on the substitution of ammonium fluoride for the hydrofluoric acid in dissolving formulations recommended for application in decladding zirconium and zirconium base reactor fuel elements. These formulations are ineffectual in the controlled pickling of zirconium base alloys containing tin as they are incapable of dissolving certain components of the alloy which are believed to be tin and zirconium hydride. These appear as a black deposit on the metal surface during the dissolving process and result in poor surface finish quality.

Therefore, it is an object of the present invention to provide an aqueous etching and pickling solution comprising predetermined proportions of ammonium persulfate, hydrofluoric acid and/or ammonium bifluoride, with or without acetic acid and/or ammonium nitrate.

It is another object of the present invention to provide an aqueous etching and pickling solution for zirconium and zirconium base alloys comprising predetermined proportions of ammonium persulfate, hydrogen fluoride and/or ammonium bifluoride, with or without acetic acid and/or ammonium nitrate.

It is still another object of the invention to provide a process for etching and pickling zirconium and zirconium base alloys in aqueous solutions comprising predetermined proportions of ammonium persulfate, hydrofluoric acid or ammonium bifluoride, with or without acetic acid and/or ammonium nitrate.

Other objects will, in part, be obvious and will, in part, appear hereinafter.

Reference should be made to the following detailed description and drawing, in which the two figures are graphs plotting time against surface thickness dissolved.

In accordance with the present invention, there is provided an improved etching and pickling solution for zirconium and zirconium base alloys. The solution comprises predetermined proportions of ammonium persulfate, hydrofluoric acid and/or ammonium bifluoride, with or without acetic acid and/or ammonium nitrate. The solution is characterized by a slow, linear pickling rate with better control of surface dissolution and reduced stringent rinse requirements to avoid staining. Members treated with the solution have high surface finish quality. Furthermore, the solutions will result in lower pickling tank cost by substitution of an alloy such as stainless steel for the container or tank material in place of the brick, polyvinyl chloride lined tanks now required for pickling of zirconium and its alloys.

The pickling solution of this invention may comprise an aqueous solution of (1) either .5% to 5% by weight hydrofluoric acid or from .5% to 8% by weight ammonium bifluoride, or both, the amount of hydrogen fluoride supplied by mixtures of ammonium bifluoride and hydrofluoric acid totaling at least 0.3% and not in excess of 3% and (2) from 3% to 30% by weight ammonium persulfate. In addition, there may be present either acetic acid or ammonium nitrate. Acetic acid is highly desirable in amounts of from 3% to 20% by weight and ammonium nitrate in amounts of from 2% to 6%.

The etching and pickling solution may be prepared in a resistant container and mixed by any suitable means. It is preferred to mix the solution in a tank of stainless steel, or of another inert material, taking care that the ammonium persulfate is dissolved first in the water to protect the stainless steel tank from fluoride attack when the fluoride component is added. The ammonium persulfate functions as an inhibitor of fluoride attack on metallic zirconium in the pickling process. The acetic acid and/or ammonium nitrate, while they are not necessary constituents in the pickling solution, are highly desirable since the acetic acid inhibits hydrogen embrittlement of zirconium while the ammonium nitrate, in con-

junction with ammonium persulfate, insures a complete solution of any tin and zirconium hydride remaining on the surface of the zirconium base alloys containing tin.

Zirconium and zirconium base alloy members may be etched or pickled by suspending the members on a fixture laterally disposed across the opening of the pickling tank containing the pickling solution. The fixture and the tank may be composed of an alloy such as stainless steel or other inert metals, the dimensions of the same being determined by the dimensions of the members being pickled. The pickling solution also may be applied to members of the alloy by any suitable means, such as hosing or spraying. The solution is preferably maintained at a temperature of from 70° F. to 120° F. The time in solution is regulated by the desired depth of surface dissolved with which it has a linear relationship.

It may be desirable in some cases to modify the action of the pickling solution on the zirconium and zirconium base alloy members by inducing an electrical current in the members. The members may be made the anode, and the cathode may be composed of any suitable material, such as graphite or platinum. The surface dissolution of the members is facilitated by electrolysis. However, it should be understood that it is not necessary to induce an electrical current in the members to achieve the results as described in the present invention.

The surfaces produced by the solution of these processes appear bright and of a quality equal to the surfaces produced by means of the standard nitric-hydrofluoric acid pickling procedure. In addition, the attack produced by the pickling solutions of the present invention is easily controllable and appears to be linear with time, as is illustrated by FIGS. 1 and 2.

In the following examples, six sample coupons (.7" x .7" x. .08") each weighing approximately 4 grams were sectioned from an alloy member and each was pickled in a pickling solution, five of which differed in composition, each solution being initially at room temperature. The alloy comprised approximately 1.5% by weight of tin, 0.1% by weight of chromium, 0.05% by weight of nickel, 0.1% by weight of iron and the balance being zirconium. All solution percentages used are by weight.

Example I

A sample couplon was immersed in an aqueous pickling solution comprising 2.5% ammonium biflouride, 4% ammonium nitrate, and 20% ammonium persulfate for a period of 20 minutes. The coupon surfaces were shiny and uniform in dimensions.

Referring to FIG. 1, there is a graph plotting surface thickness dissolved over a period of time. The sample was measured at frequent intervals and shows a straight line relationship.

Example II

A sample coupon was immersed in an aqueous pickling solution comprising 1.7% by weight hydrogen fluoride (added as 50% HF solution), 7% glacial acetic acid and 20% ammonium persulfate for a period of 30 minutes. The surfaces also appeared shiny and uniform in dimensions.

Referring to FIG. 2, there is a graph plotting surface thickness dissolved over a period of time. The sample was measured at frequent intervals and shows a straight line relationship.

Example III (Prior Art)

A sample coupon was immersed in an aqueous pickling solution comprising by volume, 39% nitric acid (sp. gr. 1.42) and 3% hydrofluoric acid (52% by weight aqueous solution) for a period of 5 minutes. The coupon appeared dull and rough surfaced.

Another sample coupon was immersed in aqueous solution of the same composition of this Example III, for a period of 5 minutes while the solution was being vigorously agitated. The pickling reaction was very rapid and uncontrollable. The resulting coupon appeared bright and shiny but the surfaces became very irregular due to the rapid fluoride attack. Both coupons evidenced a substantial weight loss.

In order to illustrate the criticality of the presence of appreciable amounts of ammonium persulfate in the compositions of this invention, the following solutions were prepared without ammonium persulfate.

Example IV

A sample coupon was immersed in an aqueous pickling solution comprising 3% ammonium fluoride for a period of 5 minutes with constant agitation. The surfaces of the coupon were covered with a black coating, believed to be tin and/or zirconium hydride.

Example V

A sample coupon was immersed in an aqueous pickling solution comprising 2.5% ammonium fluoride and 4% ammonium nitrate for a period of 5 minutes with constant agitation. The surface of the treated coupon appeared coarse, stained and somewhat pitted.

The above described pickling solutions of the invention can be employed to pickle, with equally good results to those set forth in examples 1 and 2, zirconium metal and members of an alloy consisting essentially of from 0.1% to 2.5% by weight of tin, a total of from 0.1% to 2% by weight of at least one metal from period 3 of the periodic table selected from the group consisting of iron, nickel and chromium, with or without from 0.03% to 1% by weight of beryllium, and the balance zirconium.

It is to be understood that the above description should be interpreted as being illustrative and not limiting.

We claim as our invention:

1. An aqueous etching and pickling solution suitable for zirconium and zirconium base alloys consisting essentially of from 3% to 30% by weight ammonium persulfate to inhibit fluoride attack on zirconium, at least one of the group acetic acid and ammonium nitrate in the solution, there being up to 20% by weight acetic acid, and up to 6% by weight ammonium nitrate, the acetic acid being employed to inhibit hydrogen embrittlement of zirconium and the ammonium nitrate being employed to insure a complete solution of any tin or zirconium hydride remaining on the surface of a zirconium base alloy containing tin, and at least one hydrogen fluoride containing compound selected from the group consisting of hydrofluoric acid and ammonium bifluoride in an amount to provide at least 0.3% and not more than 3% by weight of hydrogen fluoride.

2. An aqueous etching and pickling solution suitable for etching zirconium and zirconium base alloys consisting essentially of, by weight, from 0.3 to 3% hydrogen fluoride, not exceeding 20% of acetic acid and 3% to 30% ammonium persultfate.

3. An aqueous etching and pickling solution suitable for etching zirconium and zirconium base alloys consisting essentially of, by weight, from 0.5% to 8% ammonium bifluoride, not exceeding 6% of ammonium nitrate and 3% to 30% ammonium persulfate.

4. An aqueous etching and pickling solution suitable for etching zirconium and zirconium base alloys consisting essentially of, by weight, 1.7% hydrogen fluoride, 7% acetic acid and 20% ammonium persulfate.

5. An aqueous etching and pickling solution suitable for etching zirconium and zirconium base alloys consisting essentially of, by weight, 2.5% ammonium hydrogen fluoride, 4% ammonium nitrate and 15% ammonium persulfate.

6. The process of pickling zirconium and zirconium base alloys, comprising, applying to members of the alloy an aqueous pickling solution consisting essentially of from 3% to 30% by weight ammonium persulfate at least one hydrogen fluoride containing compound selected

from the group consisting of hydrofluoric acid and ammonium bifluoride in an amount to provide at least 0.3% and not more than 3% by weight hydrogen fluoride for a period of time at a temperature of from 70° F. to 120° F.

7. The process of pickling zirconium and zirconium base alloys, comprising, applying to members of the alloy an aqueous pickling solution consisting essentially of, by weight, from 0.3% to 3% hydrogen fluoride, not exceeding 20% of acetic acid, and 3% to 30% ammonium persultfate for a period of time at a temperature of from 70° F. to 120° F.

8. The process of pickling zirconium and zirconium base alloys, comprising, applying to the members of the alloy an aqueous pickling solution consisting essentially of, by weight, from 0.3% to 3% ammonium bifluoride, not exceeding 6% of ammonium nitrate, and 3% to 30% ammonium persulfate for a period of time at a temperature of from 70° F. to 120° F.

9. The process of pickling an alloy consisting essentially of from 0.1% to 2.5% by weight of tin, a total of from 0.1% to 2% by weight of at least one metal from the group consisting of iron, nickel, and chromium, from 0.03% to 1% by weight of beryllium, and the balance zirconium, comprising applying to the members of the alloy an aqueous pickling solution consisting essentially of, by weight, from 0.3% to 3% hydrogen fluoride, not exceeding 20% of acetic acid up to 6% ammonium nitrate and 3% to 30% ammonium persulfate for a period of time at a temperature of from 70° F. to 120° F.

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