252/101 CROSS REFERENCE EXAMINER 150

United States Patent Office 3,264,219 Patented August 2, 1966

3,264,219

METHOD OF PICKLING AND CHEMICALLY MILLING ZIRCONIUM AND ZIRCONIUM ALLOYS

John W. McGrew, Westminster, and Kurt Jakobson, Annapolis, Md., assignors to Martin Marietta Corporation, New York, N.Y., a corporation of Maryland

No Drawing. Filed Feb. 14, 1963, Ser. No. 258,638
4 Claims. (Cl. 252—79.3)

This invention relates to the surface treatment of zirconium and zirconium alloys to remove metal and scale therefrom. More particularly, the invention concerns a novel method for controlled etching, chemical milling, or pickling of zirconium and its alloys with an aqueous solution of an alkali metal fluoride.

The processing of zirconium and its alloys is of importance in connection with the operation of nuclear reactors in which they serve as containers for the nuclear fuel. An alloy of zirconium which is extensively used for this purpose is Zircaloy-2, which has the composition Sn 1.5%, Fe 0.12%, Cr 0.10%, Ni 0.05%, balance Zr, all by weight.

It is known in the prior art to employ as etchants for zirconium alloys, hydrofluoric acid, or aqueous solutions of ammonium bifluoride, or combinations of hydrofluoric acid and nitric acid.

These prior art etchants and milling agents have several disadvantages. Hydrofluoric acid baths are highly toxic and corrosive and create safety problems for workers. The hydrofluoric acid-nitric acid solution is highly corrosive and requires costly resistant equipment in the plant. Moreover, in typical hydrofluoric acid-nitric acid combinations, such as 39% HNO_3–3.8% HF, the acidity is so high that the bath is too fast-acting to serve successfully as an agent for chemical milling and polishing. In order to reduce the etching rate and to obtain better control, it has been proposed to employ aqueous solutions of ammonium bifluoride, $NH_4F.HF$, either in combination with nitric acid, or followed by a nitric acid rinse. Such baths can contain a nonionic surfactant such as an alkyl polyoxyethylene glycol amide. However, bifluoride salt baths of themselves are not entirely satisfactory for chemical milling or etching of zirconium and its alloys because it is well known that solutions of fluoride salts attack zirconium. Hence where fluoride salts per se are employed, the operation must be confined to a comparatively narrow range of process temperature and fluoride concentration. There has therefore existed a need for an aqeous bath which would provide the advantages of low toxicity and freedom from corrosion characteristic of fluoride salt baths while at the same time providing a wider latitude of processing temperatures, fluoride concentrations, absence of free nitric acid and/or hydrofluoric acid, and a readily controllable rate of attack on the metal.

In accordance with the invention, it has been found that aforementioned disadvantages are eliminated and the desirable characteristics of safety, noncorrosiveness, controllable rate of attack on metal, and wider range of concentrations and temperatures are attained by employing an aqueous solution of an alkali metal fluoride which contains in addition, sulfamic acid NH_2SO_2OH, or an alkali metal salt of sulfamic acid. The alkali metal salts of sulfamic acid which are suitable include potassium,

sodium, and ammonium sulfamates. The alkali metal fluorides which may be employed include water soluble fluorides of potassium, sodium, and ammonium. Furthermore, double fluoride salts of alkali metals, such as potassium, sodium, and ammonium bifluoride may also be employed together with sulfamic acid and its alkali metal salts, in concentrations equivalent to those employed for the normal fluoride salts.

The precise role of the sulfamic acid is not known, but it appears to exert a regulating as well as a potentiating action upon the fluoride salt which permits a relatively slow rate of attack upon the zirconium metal or zirconium alloy, thus making it easier to maintain close tolerances, while at the same time the concentration range of the fluoride salt may be varied over a wider range according to the objective desired, whether etching, chemical milling or pickling, than was possible with hitherto employed preparations.

The proportion by weight of sulfamic acid or its salt to fluoride salt is not critical, but in general the baths of the invention contain a greater proportion of the sulfamic acid compound.

Thus, the amount of sulfamic acid present in the bath will advantageously range from about 5% to about 25% by weight, or an amount of alkali metal sulfamate sufficient to furnish the equivalent range of sulfamic acid.

The amount of alkali metal fluoride employed will advantageously range between about 1% and about 6% by weight, preferably between about 2% and about 5%.

A preferred bath of the invention comprises an aqueous solution of about 10% sulfamic acid and about 4% potassium fluoride, by weight.

The optimum acidity of such milling and polishing baths is related to the fluoride salt used and is about 2.75 for NaF and about 3.75 for KF and NH_4F. At higher acidities, below pH 2.75 or even pH 2.5, the activity of the bath increases so that it becomes more suitable for etching and pickling applications. At pH values above about 4, the bath may exhibit a tendency to produce pitting. The milling baths in the range of about 2.75 to 3.75 exhibit favorable rates of metal removal, producing a relatively slow rate of attack upon the metal and making it easier to maintain close tolerances. At the same time the surface material is removed evenly, but at sufficiently rapid rates to provide practical and effective milling.

As indicated previously the weight ratio of sulfamic acid to fluoride salt is not critical, but it will advantageously be maintained between about 4:1 and about 2:1.

The general method of treatment of the zirconium or zirconium alloy comprises the steps of first subjecting the metal to a degreasing treatment in accordance with conventional procedures, as for example, vapor degreasing in stabilized perchlorethylene at elevated temperature. The metal is then further cleaned with an alkaline solution, such for example an aqueous solution of trisodium phosphate, also at elevated temperature. The metal is then thoroughly rinsed, preferably first with tap water, and then with demineralized water.

The etching, pickling or milling step is carried out by immersing the metal in a suitable solution of sulfamic acid or an alkali metal sulfamate, and an alkali metal fluoride, the concentrations of the ingredient being determined by the type of treatment. The time of immersion will depend upon the amount of metal to be removed,

but may range up to about 5 minutes. Thus, the milling rate of a bath at pH 2.75 is approximately 0.3 mil per minute exposure. The temperature of the bath may range between about 18° C. and about 50° C., but 35° C. is preferred.

The treatment step is accompanied by the formation of a grayish-black smut, which builds with increasing rapidity after about 3 or 4 minutes immersion in the bath, decreasing the bath's reactivity. This smut may be removed by rinsing the metal thoroughly in tap water, followed by brief immersion in a solution of nitric acid of concentration 50% HNO_3 by weight until the smut is dissolved. At times mere dipping in nitric acid solution is sufficient.

If the removal of a considerable amount of surface metal is required, it may be necessary to expose the work to alternate milling treatment and smut removal until the desired condition is achieved. The treatment is carried out at room temperature.

Following the smut removal step, the metal is rinsed thoroughly, first with tap water, then with demineralized water, and is finally dried, for example, by means of a hot air blast.

The following examples illustrate preferred procedures of the invention, but are not to be regarded as limiting:

Example I

An aqueous chemical milling bath was prepared by dissolving in water 10.6% by weight of sulfamic acid, and 4.2% by weight of potassium fluoride. The bath temperature was adjusted to 35° C. A rod of Zircaloy-2 was subjected to vapor degreasing in stabilized perchlorethylene at 249° F. for 15 minutes. The metal was further cleaned by immersion into a solution of trisodium phosphate at 180° F. for 5 minutes, rinsed thoroughly, first with tap water and then with demineralized water. The metal alloy was immersed in the aforementioned bath for 3 minutes, removed, rinsed thoroughly in tap water, and then subjected to smut removal by immersion in a 50% HNO_3 solution for 2 minutes at room temperature. The article was then rinsed thoroughly, first with tap water, then with demineralized water, and finally dried by means of a hot air blast to give an evenly milled, smooth surface.

In this way, an average of 0.80 mil of the Zircaloy-2 was milled away as a result of treating six work pieces.

Also, six like treatments were performed when the Zircaloy-2 was immersed in the milling bath for 1 minute and 5 minutes. In the first instance 0.32 mil of the alloy and, in the second instance, 1.07 mils of the alloy were milled away.

A number of other baths were formulated with sodium, potassium or ammonium sulfamate ($NaOSO_2NH_2$, $KOSO_2NH_2$, $NH_4OSO_2NH_2$) in various combinations with the acid salts of sodium, potassium or ammonium fluoride (NaF—HF, KF—HF, NH_4F—HF) in concentrations which were approximately equivalent to the most effective sulfamic acid-potassium fluoride concentration set out in the example above. Additionally, baths were formulated with sulfamic acid and fluorides other than potassium fluoride, i.e., sodium fluoride, NaF, and ammonium fluoride, NH_4F, on an equivalent fluoride basis.

Representative additional baths and milling rates on Zircaloy-2 are set out below. The methods of treatment and evaluation were those set out in Example I. The average milling rates were determined by measuring the amount milled away after one minute, three minutes and five minutes.

Example II

Bath:	Percent
Ammonium sulfamate	12
Ammonium bifluoride	8
Sulfamic acid	3.5

Milling rate: About 0.3 mil/minute.

Example III

Bath:	Percent
Potassium sulfamate	9.5
Ammonium bifluoride	4
Sulfamic acid	3.5

Milling rate: About 0.4 mil/minute.

Example IV

Bath:	Percent
Sulfamic acid	10
Sodium fluoride	3

Milling rate: About 0.3 mil/minute.

Example V

Bath:	Percent
Sulfamic acid	10
Ammonium fluoride	3

Milling rate: About 0.2 mil/minute.

The test result with these baths, using Zircaloy-2, were well defined. It appears that any combination of these ingredients which produces a solution whose pH is 4 or less, with no insolubles present, shows some activity as a milling solution. The optimum acidity for chemical milling and polishing in these baths is in the pH 2.75 to 3.75 range. The reactivity of the bath increases steadily to an exclusively etching solution as the pH decreases below 2.5. Above pH 4, there is a tendency to pit. The baths in the range pH 2.75 to 3.75 are sufficiently slow to remove surface material evenly and sufficiently fast to be practical. The formation of a grayish-black smut, which can be removed in a nitric acid bath, is a milling rate control mechanism. If the removal of a considerable amount of surface material is required, it is necessary to expose the work alternatively to the milling formulation and smut removals as in the nitric acid bath. As pointed out above the milling rate of a bath at pH 2.75 in Example I and certain of the other baths is approximately 0.3 mil per minute exposure but the aforementioned smut builds up rapidly after about 4 or 5 minutes and the reactivity decreases steadily until the smut is removed in the nitric acid solution. A quick dip in the nitric acid may be all that is required to remove the smut.

In the claims, it will be understood alkali metal fluoride is inclusive of both the normal salt and the double salt, known as the bifluoride, and that the quantities specified in the claims refer to the quantities of the normal salt, or equivalent quantities of the double salt.

The rates mentioned above may be contrasted with the rates of removal of metal from Zircaloy-2 in the nitric acid-hydrofluoric acid bath mentioned earlier, which is almost linear with time, and averages about 1.4 mils per minute.

Clearly such a rapid rate of metal removal is more aptly designated as metal etching and such an acid bath is more aptly designated as an etchant. It was found impossible to remove metal from zirconium and zirconium alloys to conform with close tolerances, such as required in certain classes of threads, when such etching baths were used. On the other hand, the desired tolerances were readily obtained in the milling baths of this invention.

It will be apparent the foregoing details are given for illustrative purposes and that many variations in these details may be made without departing from the spirit of the invention or its scope as defined in the appended claims.

What is claimed is:

1. A controlled chemical milling process for the surface treatment of zirconium and zirconium alloys to remove precise amounts of metal and scale therefrom which comprises immersing and chemically milling the metal to a desired smaller dimension in a treating bath consisting essentially of an aqueous solution containing between about 5% and about 25% by weight of a member of the group consisting of sulfamic acid and its alkali metal salts and between about 1% and about 6% by weight of an alkali metal fluoride, the amount of sulfamic acid

present being in excess of the amount of alkali metal fluoride.

2. The method of claim 1 in which the metal is further treated in a nitric acid bath to remove smut formations.

3. The controlled chemical milling process for zirconium alloys to remove precise amounts of metal and scale therefrom which comprises immersing and chemically milling the metal to a desired smaller dimension in a treating bath consisting essentially of an aqueous solution of a member of the group consisting of sulfamic acid and its alkali metal salts and an alkali metal fluoride, said bath having a pH above about 2.5 but not above a pH of 4.

4. Method for the controlled chemical milling of zirconium and zirconium alloys comprising immersing and chemically milling the metal to a desired smaller dimension in a bath consisting essentially of an aqueous solution of about 10% by weight of sulfamic acid and about 4% by weight of potassium fluoride at a temperature between about 18° C. and about 50° C.

References Cited by the Examiner

UNITED STATES PATENTS

2,220,451	11/1940	Hunt	252—142
2,879,186	3/1959	Fischer	252—142 XR
3,033,795	5/1962	Brevik	252—79.3 XR

LEON D. ROSDOL, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

W. E. SCHULZ, *Assistant Examiner.*