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PROCESS OF FINISHING PARTS OF ZIRCONIUM ALLOYS SUCH AS FOR USE WITH NUCLEAR REACTOR PLANTS

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ABSTRACT OF THE DISCLOSURE

Finished parts of zirconium alloys, such as envelope tubes for nuclear fuel, are surface treated by electrolytic polishing. Preferably used is a polishing bath composed of acetic acid of about 99 to 100% concentration, perchloric acid of 40% concentration and hydrochloric acid of 37% concentration in a mixing ratio of about 300:1 to 10:10 to 40 parts.

Our invention relates to a surface treating process for finishing parts made of zirconium alloys, for example the fuel envelope tubes for use in nuclear reactor plants.

Heretofore such zirconium parts have been treated for cleaning purposes with a mixed etchant of nitric acid and hydrofluoric acid. This entails the possibility that hardly soluble fluorides will form on the surface and thereafter constitute the starting spots of increased corrosion. To permit recognizing such trouble spots, the zirconium components are subjected to an oxidation treatment in an autoclave requiring, as a rule, a period of three days. Processing periods of such duration are not compatible with the normal course of fabrication, the etching process requires most exacting care, and handling the etchant acids is not free of hazard.

It is therefore an object of our invention to devise a surface treatment for such zirconium components that is not affected by the above-mentioned disadvantages.

To this end, and in accordance with our invention, the zirconium components, instead of being etched, are finished by polishing them electrolytically.

Electrolytic polishing as such has found widespread usee in various industries, but has not been applied to zirconium workpieces. Although it has become known to polish zirconium specimens for metallographic purposes with an electrolyte composed of perchloric acid and acetic acid, this method fails when employed for larger pieces because the current density becomes too high and the necessary cooling of the electrolyte can no longer be carried out to a sufficient degree. This is significant because the polishing effect decreases with increasing temperature of the electrolyte and ultimately results in producing only dull and unsightly surfaces. Confronted with this state of the art, our invention originated from the concept to also afford the electrolytical polishing of relatively large components made of zirconium or zirconium alloys; and it is therefore another object of our invention to avoid the disadvantages peculiar to the known method of applying a similar process to the preparation of metallographic specimens, and furthermore to additionally decrease the susceptibility of corrosion exhibited by zirconium alloys by securing a brilliantly metallic surface.

According to a more specific feature of the invention, these objects are achieved by electrolytically polishing the zirconium alloy parts in an electrolyte composed of acetic acid, perchloric acid and hydrochloric acid, in which the acetic acid is of higher concentration than the other two constituents and constitutes the major share of the mixture.

We have found that the mentioned problems are best solved by electrolytically polishing the zirconium workpieces in an electrolyte mixture of acetic acid of about 99 to 100% concentration, perchloric acid of about 40% concentration and hydrochloric acid of about 37% concentration, the mixing ratio being about 300:(1–10):(10–40) parts by weight.

With such an electrolyte, operating at electrolyte temperatures of up to 25° C., the applicable current densities are about 20 to about 150 A. per dm.^{2}. It has further been found that an addition of about 10 g. chloroacetic acid per 300 ml. acetic acid, preferably with a concurrent reduction in the share of the perchloric acid, also yields favorable results.

The following table indicates the composition of several electrolyte mixtures which have been found to be particularly favorable.

Parts				
CH_3COOH, 99–100%	$HClO_4$, 40%	HCl, 37%	Other additions	Current density, A./dm.^{2}
300	10	10	----------	30–40
300	10	20	----------	20–30
300	5	20	----------	30–35
300	6	40	10 g. chloroacetic acid per 300 cc. CH_3COOH.	30–50

Depending upon the amount of soiling of the zirconium surface, a treatment of 1 to 2 minutes duration suffices to attain a shiny, high-gloss surface. This is the most immediately conspicuous advantage of the treatment and is indicative of the fact that the process achieves the above-mentioned improvement in corrosion resistance by virtue of a completely smooth metal surface. The process is also less costly than those heretofore employed, and the electrolyte employed, due to its slight perchloric acid concentration, completely avoids any hazard when being handled by personnel. Contrary to chemical etching, the acid mixture employed for electrolytic polishing does not attack the metal being treated. Only when a direct voltage is applied, does metal become electrolytically dissolved at the anode.

As is generally known from electrolytic polishing, the workpiece to be polished is connected as the anode to a direct voltage. The cathode may consist, for example, of a sheet of stainless steel (such as available under the trade name V2A steel). It is important and well known as such, that the field-line densities at all points of the metal surface to be polished should be as uniform as feasible for uniform removal of material from the metal surface. The above-mentioned cooling of the electrolyte may be effected by circulating or recycling it through a separate cooling device, or by cooling the cathode sheets. In each case the application of motion to the cathode sheets or to the electrolyte will improve the uniformity of the polishing action.

Reclaiming the spent electrolyte is a relatively simple matter. The electrolyte, after having been used for polishing, is permitted to stand for some time. A major portion of the zirconium dissolved in the electrolyte then precipitates in the form of hard to dissolve salts. After removing the precipitate and replenishing the electrolyte quantity consumed, the polishing bath is again fully applicable. Such regeneration can be repeated.

The zirconium parts cleaned with the aid of the surface treatment according to the invention do not require further processing prior to being used in a nuclear reactor plant because there are no residues as will occur with the known etching method.

To those skilled in the art it will be obvious upon a

study of this disclosure that modifications and substitutions with respect to the composition of the electrolytic polishing bath may be made to some extent within the scope of our invention and without departure from the subject matter and its equivalents set forth in the claims annexed hereto.

We claim:

1. A surface treating process for finished parts of zirconium-based alloys, which comprises subjecting the otherwise finished part of zirconium alloy to electrolytic polishing in a mixture of perchloric acid, and hydrochloric acid, in a substantially nonaqueous vehicle consisting essentially of acetic acid forming the major share of the mixture.

2. The process of finishing parts of zirconium alloys according to claim 1, which comprises subjecting the parts to electrolytic polishing in an electrolyte composed of acetic acid of about 99 to 100% concentration, perchloric acid of about 40% concentration and hydrochloric acid of about 37% concentration in a mixing ratio of about 300 parts acetic acid to 1 to 10 parts perchloric acid to 10 to 40 parts hydrochloric acid, at a current density of about 20 to 150 A./dm.^{2} and an electrolyte temperature up to about 25° C.

3. The process according to claim 2, wherein the ratio of acetic acid to perchloric acid to hydrochloric acid is about 300:5 to 10:10 to 20.

4. The process according to claim 3, wherein the current density is about 30 to 50 A./dm.^{2}.

5. The process according to claim 2 wherein the electrolyte contains an addition of up to about 10 g. chloroacetic acid per 300 ml. acetic acid.

References Cited

UNITED STATES PATENTS

2,752,304	6/1956	Darmois et al.	204—140.5
2,851,406	9/1958	Bowerman et al.	204—140.5
2,871,175	1/1959	Zaremski	204—140.5
2,904,479	9/1959	McCord et al.	204—140.5
3,485,731	12/1969	Yokozawa et al.	204—141

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