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CORROSION PROTECTION OF ALUMINUM

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This invention deals with a process of treating aluminum surfaces for the purpose of making them corrosion-resistant. The invention applies equally well to articles of pure aluminum, articles of an aluminum-base alloy in which the aluminum is the predominant ingredient and articles coated with such "aluminum-base metals," as they will be referred to generically hereafter.

Aluminum-base metals have a great many uses in the industry. For instance, they are being used for equipment in the chemical industry and there get in contact with hot water; the water at the elevated temperatures has a corrosive effect on the aluminum or aluminum alloys which is a most undesirable reaction. In the first place, the service life of the aluminum is impaired by this corrosion and, in the second place, the water or solution is contaminated by the corrosion products.

Another instance where aluminum has to withstand the corrosive influence of hot water is in neutronic reactors, such as the material testing reactor. The fissionable material of such reactors is often jacketed with aluminum or an aluminum-base alloy and the cooling water contacts the jackets of these fuel elements. The cooling water of neutronic reactors was found to have an especially high corrosive effect due to the heat developed by the radiation. It is of prime importance that the aluminum jacket is not corroded to a point where the water can leak into the fuel elements, because a most hazardous situation is created thereby.

It has been considered to apply a protective film to the aluminum jackets. Such a protective film or cladding would allow thinner aluminum jackets and consequently larger cores, or else longer exposures to radiation, higher temperatures, and it would bring about fewer failures.

It was suggested to expose, in an autoclave, surfaces of aluminum-base metals, at about 100° C. and superatmospheric pressure, to an aqueous solution which contains chromic acid in a concentration of from 5 to 100 parts per million and has a pH value of between 3 and 8. This process previously investigated resulted in films that did not adhere too well to the aluminum article; consequently the protection obtained by that method was not satisfactory.

It has now been found that the corrosion resistance of aluminum-base metal surfaces can be radically improved by also treating them in an autoclave with an aqueous chromic acid solution, however of a concentration of from 0.5 to 3% by weight and having a pH value of below 2. The chromic acid can be present in the form of free chromic acid, a chromate or a dichromate, but the solution has to have a pH value of below 2. The preferred conditions are a chromic acid concentration of between 1 and 2% and a pH value of about 1. (A 1% chromic acid solution normally has a pH value of about 1.2 and a 0.1% chromic acid solution a pH value of 2.2.) The autoclave temperature satisfactory for the process is between 160 and 180° C., and the treatment time ranged from 20 to 50 hours.

The film formed by the process of this invention is thin; it always adhered extremely well to the surface. Spectrographic analyses showed that it consisted of aluminum oxide with some chromium absorbed therein and that it had no crystalline structure; it was of a greenish brass color. The film has excellent corrosion resistance to hot water and even to hot water that contains sodium dichromate in a concentration of about 2 p.p.m.

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It is advisable to subject the aluminum article to a pretreatment prior to the coating step proper; this is done, for instance, by immersion in a solution containing about 1% sodium carbonate and 0.3% sodium dichromate dihydrate at approximately 65° C. for 20 minutes; by this, localized corrosion that sometimes takes place during autoclaving is reduced to a minimum.

In the following, two examples are given to illustrate the process of this invention.

Example I

Six groups of uranium fuel elements, 8 inches long, having a diameter of 1.4 inches and canned in 1245 aluminum (an alloy containing at least 99.45% by weight of aluminum; iron; silicon in a maximum content of 50% of that of iron; up to 0.04% Cu; 0.03% Mn; 0.01% Mg; 0.03% Cr; 0.01% Ni; 0.03% Zn; 0.03% Ti; Bi, Pb, Sn up to 0.01% each; Li up to 0.008%; Cd up to 0.003%; B and Co up to 0.001% each), were autoclaved each in a different aqueous liquid, namely:

(1) Tap water
(2) Deionized water
(3) Steam condensate
(4) Steam condensate plus 1% $Na_2Cr_2O_7$
(5) Steam condensate plus 0.1% CrO_3
(6) Steam condensate plus 1% CrO_3

The treatment in the autoclave was at 160° to 180° C. for forty hours. The pH value of the 1% chromic acid solution ranged from 1.1 to 1.4. After removal from the autoclave, the slugs were air-dried.

The slugs were then charged into tubes in reactors and irradiated for 700–950 megawatt days per ton under constant flow of hot water containing from 0.5 to 2 p.p.m. sodium dichromate. The specially treated slugs were loaded alternately with standard (steam-autoclaved) slugs.

At the end of the exposure, the slugs treated with 1% chromic acid (run No. 6) showed significantly less corrosion than those subject to any of the other five treatments. All other treatments gave equivalent results, thus showing a marked benefit from the use of a 1% chromic acid.

The next example demonstrates the criticality of the chromic acid concentration.

Example II

Slugs were used that were 8 inches long, had a diameter of 1.4 inches and were canned with "1100 aluminum" (an alloy containing at least 99.00% by weight of Al; up to 1.0% of Si+Fe; up to 0.20% Cu; up to 0.05% Mn; up to 0.10% Zn; and up to 0.15% of other metals not exceeding 0.05% of each), a commercial aluminum of a purity of above 99%.

These slugs were subjected to a preparatory treatment comprising immersion in an alkaline cleaning solution followed by rinsing with running water for 10 to 15 minutes and air-drying for between 1 and 2 days; this was for the purpose of removing grease and dirt. Then the slugs were autoclaved according to the invention, namely at a temperature of 170°±10° C. for 40 hours; different liquid media, steam condensate, 0.1% chromic acid (pH=2.2) an 1% chromic acid (pH=1.2) were used for different slugs for this autoclaving treatment. After this, the slugs were air-dried, inspected for visible flaws and weighed.

The slugs thus treated were then inserted, as will be described, in tubes for exposure in a nuclear reactor. Thirty-two fuel slugs each were inserted into two tubes.

In each tube, slugs autoclaved with the chromic acid were alternated with slugs autoclaved with a steam condensate only. While one tube contained the slugs treated with the 0.1% chromic acid, the other tube contained the slugs treated with the 1% chromic acid. These two tubes were placed into a nuclear reactor and exposed there to neutron bombardment.

Cooling water was flowed through the tubes containing the slugs, while in the reactor; consequently the aluminum cans surrounding the fuel material were in contact with water of elevated temperature. The amount of radiation was about the same in both tubes.

After removal of the tubes from the reactor, 16 slugs of each tube, namely those subjected to the most severe corrosion conditions, were again inspected and weighed. The loss of weight was taken as an indication of corrosion, the lesser weight decrease indicating the lower degree of corrosion. The results of these tests are summarized in the table below.

It is obvious from the above experiments that the chromic acid of the lower concentration did not yield as satisfactory results as did the chromic acid having a concentration of 1% and a pH of 1.2. An unexpected and quite striking feature is that the steam condensate provided a film of higher protective power than did the 0.1% chromic acid, which proves criticality of restricting the pH value to below 2.

It will be understood that this invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A process of protecting an article having a surface of aluminum-base metal against corrosion, comprising immersing said article in an aqueous chromic acid solution of a concentration of between 0.5 and 3% by weight and a pH value of below 2, and heating said solution and said article in a hermetically sealed system at from 160 to 180° C. for from 20 to 50 hours whereby a corrosion-resistant, well-adhering film is formed on said surface.

2. The process of claim 1 wherein the chromic acid solution has a concentration of between 1 and 2% and a pH value of about 1.

Solution Used in Autoclave	Weight Loss After Exposure in Reactor, Grams Per Slug							
	position of slug in reactor tube							
	1	3	5	7	9	11	13	15
0.1% CrO_3 (pH=2.2)	6.25	10.40	12.31	16.28	12.60	12.38	10.85	11.98
1% CrO_3 (pH=1.2)	1.57	2.02	1.56	2.92	3.94	3.52	3.70	5.18
	position of slug in reactor tube							
	2	4	6	8	10	12	14	16
Steam Condensate	5.66	7.06	10.12	10.46	11.06	10.71	6.13	4.78

References Cited in the file of this patent

UNITED STATES PATENTS

2,227,469 Thompson et al. ---------- Jan. 7, 1941
2,315,564 Thompson et al. ---------- Apr. 6, 1943
2,768,104 Schuster et al. ---------- Oct. 23, 1956
2,784,122 Cox et al. ---------- Mar. 5, 1957
2,858,244 Long et al. ---------- Oct. 28, 1958

FOREIGN PATENTS

860,306 Germany ---------- Dec. 18, 1952

OTHER REFERENCES

Goldowski: Abstract of application Ser. No. 619,264, published April 29, 1952, 657 O.G. 1582, 1 page. Copy in 148/6.27.