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Anthony et al.

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[54] **CORROSION RESISTANT ALUMINUM ALLOYS**

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[73] Assignee: **Swiss Aluminum Limited,** Chippis, Switzerland

[22] Filed: **Mar. 14, 1974**

[21] Appl. No.: **451,074**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 414,862, Nov. 12, 1973, Pat. No. 3,878,871.

[52] **U.S. Cl.** **148/32;** 75/141; 74/146; 75/148

[51] **Int. Cl.²** **C22C 21/02**

[58] **Field of Search** 75/141, 142, 143, 138, 75/147, 148, 146; 148/32, 32.5

[56] **References Cited**

UNITED STATES PATENTS

3,219,492 11/1965 Anderson et al. 75/138

3,639,107 2/1972 Thompson 75/138

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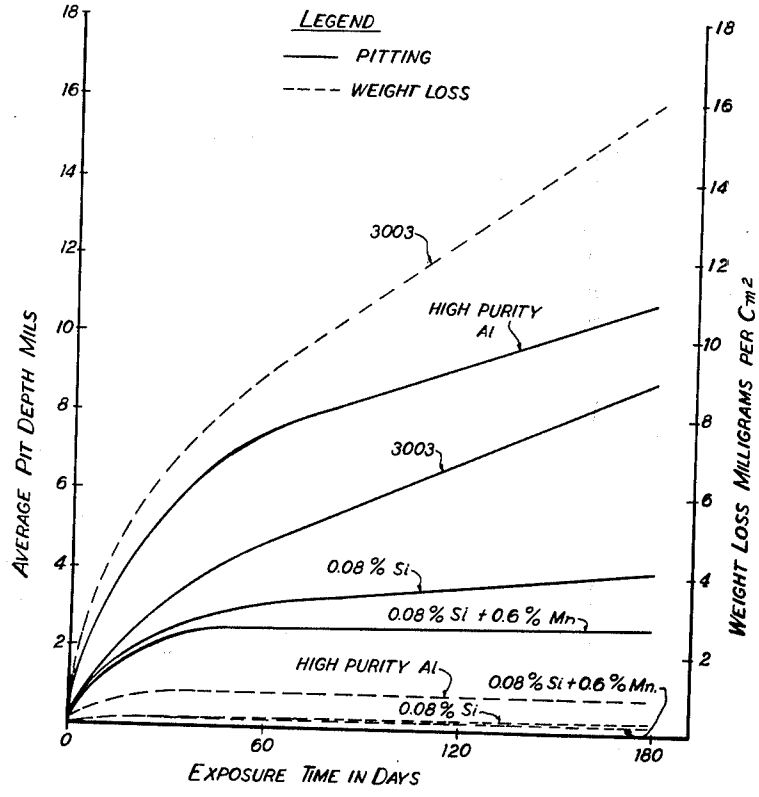
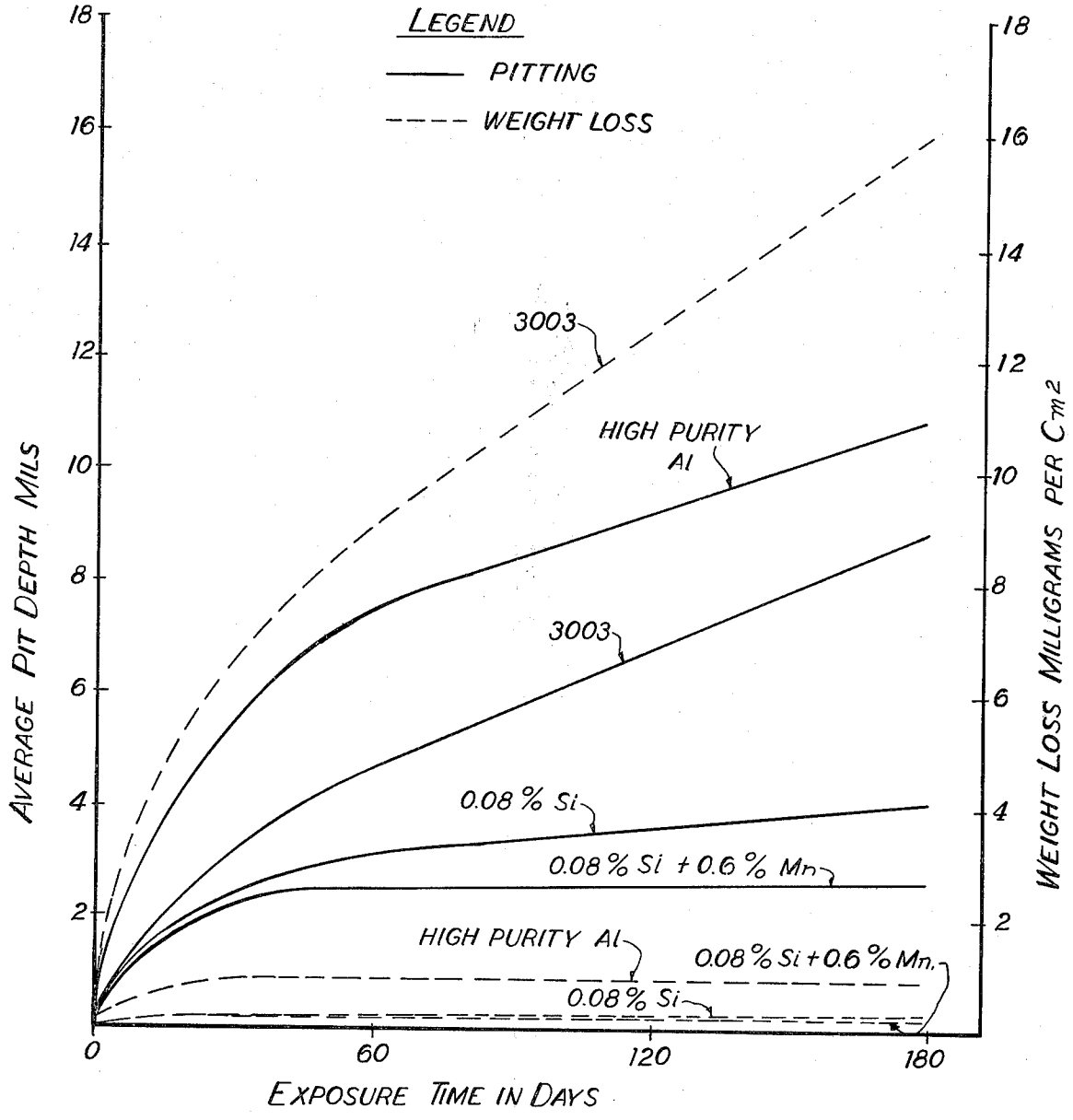
Attorney, Agent, or Firm—Robert H. Bachman; David A. Jackson

[57] **ABSTRACT**

A corrosion resistant aluminum alloy based on commercial purity aluminum with deliberate additions of silicon and manganese and with a restricted iron content. The silicon and manganese ranges are controlled to provide an aluminum-silicon solid solution and to restrict or eliminate cathodic particles which have been found to cause pits. The alloy is highly resistant to corrosion, especially in environments where the alloy comes into contact with impure water.

7 Claims, 1 Drawing Figure




LEGEND
PITTING
WEIGHT LOSS
3003
HIGH PURITY Al
3003
0.08 % Si
0.08 % Si + 0.6 % Mn
HIGH PURITY Al
0.08 % Si + 0.6 % Mn.
0.08 % Si
AVERAGE PIT DEPTH MILS
WEIGHT LOSS MILLIGRAMS PER Cm2
EXPOSURE TIME IN DAYS
0
60
120
180
2
4
6
8
10
12
14
16
18

CORROSION RESISTANT ALUMINUM ALLOYS

CROSS REFERENCE TO RELATED APPLICATION

This case is a continuation-in-part of copending application Ser. No. 414,862, by William H. Anthony and James M. Popplewell for "A Corrosion Resistant Aluminum Composite", filed Nov. 12, 1973 now U.S. Pat. No. 3,878,871.

BACKGROUND OF THE INVENTION

Many industrial processes result in the formation of a large amount of waste steam. Economic considerations require that the heat content of this steam should be recovered by condensing the steam. This condensation process is performed by passing the steam over metal tubes through which cooling water is passed. The cooling water is commonly impure, and contains impurities which cause severe corrosion problems and thereby add to the expense of the industrial process. Such condensors contain large quantities of tubing and represent a large potential market for any alloy which can withstand the corrosion effects of the cooling water. The preferred materials at present are stainless steel, and admiralty brass. Unfortunately, materials used heretofore in condensor applications have not been entirely satisfactory when considered from a price-performance viewpoint. Aluminum has not received much consideration because previously considered alloys have not had an adequate combination of resistance to pitting and general corrosion.

Many other industrial processes are also candidates for the application of a more corrosion resistant tubing of moderate cost. Examples include oil refinery and general chemical industry piping and tanks, irrigation equipment for agriculture, and automotive radiator applications.

SUMMARY OF THE INVENTION

The aluminum alloy of the present invention contains from 0.05 to 0.5% silicon, from 0.2 to 0.8% manganese and a maximum of 0.2% iron. Additionally, titanium may be present as a grain refining agent up to 0.1% titanium. The balance of the alloy consists of commercial purity aluminum. The alloy of the present invention possesses a unique resistance to pitting corrosion and has a low general corrosion rate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The composition of the alloy of the present invention in the following description of the preferred embodiments is given in weight percentages unless otherwise specified.

The broad and preferred composition limits for the alloy of the present invention are given in Table I below:

TABLE I

	Broad			Preferred		
Silicon	0.05	–	0.5	0.15	–	0.25
Manganese	0.2	–	0.8	0.3	–	0.6
Iron	0.0	–	0.2	0.0	–	0.08
Chromium	0.0	–	0.1	0.0	–	0.05
Magnesium	0.0	–	0.3	0.0	–	0.1
Copper	0.0	–	0.1	0.0	–	0.05
Titanium	0.0	–	0.05	0.005	–	0.015

TABLE I-continued

	Broad			Preferred		
Zinc	0.0	–	0.1	0.0	–	0.05

The essential components of the alloy are manganese and silicon. The remaining elements may be present as impurities up to the level shown in Table I. Titanium may be present as a purposeful addition for grain refinement of the alloy. The zinc has not been found to have any detrimental effects on the corrosion behavior of the alloy and its level has been chosen to permit the use of zinc bearing scrap in the production of the alloy. Naturally, any of the foregoing impurities may be present in levels as low as 0.001%.

A major cause of pitting corrosion in aluminum alloys is the presence of particles in the alloys which are cathodic or anodic to the matrix of the alloy. Such particles act to set up galvanic cells when the alloy is in a conducting medium. Such cells act as initiation sites for the formation of pits. Particles which are likely to cause pitting include; silicon, $FeAl_3$, $CuAl_2$, $MnAl_6$ and α(AlFeSi). In the course of the present research it was found that the presence of a cathodic particle of $FeAl_3$ in a 6061 Alloy could lead to the formation of a pit in as little as one hour when the alloy was exposed to flowing tap water at a temperature of 30°C.

The alloy composition of the present invention has been selected on the basis of the constitutional relationship which has been derived for the aluminum-manganese-silicon-iron quaternary system by H. W. L. Phillips, Journal of the Institute of Metals, Vol. LXIX, 1943. From this phase diagram it appears that the presence of about 0.4% manganese will surpress the formation of the $FeAl_3$ particles. However, particles of α(AlFeSi) remain. For this reason the iron concentration in the present invention has been limited, since α(AlFeSi) particles are also detrimental to the corrosion behavior of aluminum alloys, although to a much lesser degree than $FeAl_3$ particles.

Other research has indicated that the pitting resistance of aluminum can be greatly improved by the introduction of silicon, provided that the silicon is in solid solution. The concentration range over which the silicon will remain in solid solution is largely dependent upon the iron and manganese concentrations, and the presence of magnesium. The silicon levels of the alloy of the present invention have been chosen in light of these considerations.

The preceeding discussion of the present invention will be better understood through consideration of the following illustrative examples:

EXAMPLE I

A series of castings were made using high purity aluminum as a base. The high purity aluminum contained the following impurities; 0.001% iron and 0.001% silicon. To this base the following deliberate additions were made:

A. 0.08% silicon

B. 0.6% manganese + 0.08% silicon

c. No addition

The castings were homogenized at 1100°F for 16 hours and were air cooled. The ingots were then scalped and hot rolled from 1.5 inches to 0.25 inch at a starting hot rolling temperature of 825°F. The ingots

were then cold rolled to 0.040 inch gage and flash annealed at 1100°F for 10 minutes. After the flash annealing the samples were cold rolled 25% to 0.030 inch gage.

Samples from these three alloys were cleaned and then exposed to flowing New Haven tap water at a temperature of 30°C which was replenished once a week. A sample of Alloy 3003 was used as a control. After 60, 120 and 180 days, samples were removed and analyzed for weight loss and pit depth. The data is displayed in FIG. 1. These results demonstrate the definite superiority of the alloy of the present invention over high purity aluminum and the commercial alloy, 3003 control sample. It is evident that a combination of manganese and silicon results in an alloy superior in both overall corrosion rate and pit depth. Table II shows the approximate analysis of the water used in the examples.

TABLE II

WATER ANALYSIS (ppp)
Al CONDENSER TUBING PROJECT

	New Haven Tap Water	Test with Continuous Refreshment with New Haven Tap Water	Test with Intermittent Refreshment Once a Week
Cl	17.9	12.8	1.1
	.24	.13	0.06
Fe			
Cu	.02	.05	0.01
pH	7.2	6.8	7.8
O_2	7.5	12.0	8.4
CO_2	5.0	3.0	2.0
Solids	90.0	109.0	120.0
Hardness ($CaCO_3$)	55.8	37.8	68.2
Alkalinity ($CaCO_3$)	40.5	19.3	58.5
Calcium	35.7	14.2	32.2
Sodium	5.0	4.0	7.0
Sulfate	60.0	65.0	47.0

Example I employed a test in which the water was changed only once a week and it is evident that over a period of one week the chloride concentration decreases significantly. Because of the corrosive effect of chloride ions, subsequent tests were performed using continuous replenishment of the tap water in order to increase the severity of the test.

EXAMPLE II

A series of experimental ingots were cast using a high purity aluminum base but containing from 0.05 to 0.063% iron. The composition of these alloys is given in Table III along with 60 day corrosion data.

TABLE III

CORROSION TEST RESULTS AND SPECTROSCOPIC ANALYSES ON EXAMPLE II ALLOYS AFTER 60 DAYS EXPOSURE TO NEW HAVEN TAP WATER

Fe	Percentage Composition Si	Mn	Cr	Mg	Pit Depth (mils) Mean	Max	Weight Loss mlgms/cm²
.056	.11	.43	—	—	15.0	22.5	12.8
.051	.23	.31	—	—	8.4	17.8	15.1
.055	.23	.45	—	—	8.8	15.3	15.4
.053	.10	.64	—	—	10.2	19.7	14.2
.050	.03	1.0	—	—	13.3	20.2	17.6
.061	.10	.63	.20	—	13.2	18.0	13.1
.061	.098	.61	.21	1.04	16.7	22.4	10.3
3003 Control					—*	27.1*	17.7

*27.1 mill thick coupon was perforated

The castings were homogenized at 1100°F for 16 hours and water quenched. They were subsequently scalped and hot rolled from 1.5 inches to 0.175 inch using a starting hot rolling temperature of 825°F. The alloys were then cold rolled to 0.072 inch and given a 2 hour anneal at 650°F with a controlled cooling rate of 50°F/hr down to 400°F, and then cold rolled to 0.05 inch. The alloys were tested according to the procedure described in Example I except that the water was replenished every 12 hours. An approximate analysis of the water used is given in Table II.

Examination of the corrosion data which is presented in Table III indicates that there is a type of synergistic effect on the pitting resistance over certain ranges of silicon and manganese. The optimum manganese level apparently lies between 0.4 and 1.0% and preferably near 0.4% while the optimum silicon level is at least 0.2%. The presence of 0.2% chromium has an adverse effect on the pitting resistance as does the presence of 1.0% magnesium, while manganese has a beneficial effect up to 0.6% but detrimental at the 1% level. Therefore 0.8% seems to be the cut off point in usefulness. The detrimental effect of magnesium is due to the depletion of the solid solution concentration of silicon by the formation of magnesium silicide. Because the thickness of the 3003 control sample was less than the thickness of the other samples, and complete perforation occurred, it is not possible to accurately compare the pitting resistance of the 3003 control sample with the experimental alloys, however, examination of the samples indicated that the pitting of the 3003 sample was approximately twice as severe as the pitting of the best sample of the present invention.

EXAMPLE III

Three alloys having a base composition of 0.1% silicon and 0.6% manganese were cast and processed to 0.050 inch sheet according to the procedure described in Example II. The purpose was to determine whether or not pitting was effected by varying the iron content of the alloy. An additional purpose was to investigate the effect of the addition of titanium diboride as a grain refiner on the pitting performance. The alloys were exposed to New Haven tap water as described in Example

II. The results are shown in Table IV and indicate that the alloy consisting of deliberate additions of 0.1% silicon and 0.6% manganese perform approximately as well from a pitting standpoint after exposure of 60 and 180 days, regardless of whether the iron content is 0.01% or 0.063%.

In view of the well known highly detrimental effect of iron on pitting resistance of aluminum alloys, the efficacy of the manganese addition is clearly demonstrated. The addition of the titanium diboride in an amount sufficient to be effective as a grain refiner had no detectable effect on the pitting resistance of the alloy.

countered, whether in power plants or petroleum refineries.

TABLE V

Si	Mn	Fe	Cr	Mg	Cu	.2% Y.S.	U.T.S.	Elong.
.23	.31	.051	<.01	<.01	.0145	19.4	19.65	4.5
.23	.45	.035	<.01	<.01	.014	20.7	21.1	4.7

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims and all changes which come within the meaning and range of equivalency are intended to be placed therein.

What is claimed is:

1. A corrosion resistant aluminum base alloy resistant to pitting and corrosion in an aqueous environment consisting essentially of from 0.05 to 0.5% silicon, wherein the silicon is present in solid solution, from 0.2 to 0.8% manganese, from 0.001 to 0.2% iron, from 0.001 to 0.1% chromium, from 0.001 to 0.1% magnesium, from 0.001 to 0.1% copper, from 0.001 to 0.05% titanium, from 0.001 to 0.1% zinc, balance aluminum.

2. An alloy according to claim **1** wherein the silicon is from 0.15 to 0.25%.

3. An alloy according to claim **1** containing less than 0.4% manganese.

4. An alloy according to claim **1** wherein the iron content is from 0.001 to 0.08%.

5. An alloy according to claim **1** containing from 0.001 to 0.05% chromium, from 0.001 to 0.05% copper, from 0.005 to 0.015% titanium, and from 0.001 to 0.05% zinc.

6. An alloy according to claim **1** wherein the magnesium content is less than 0.01%.

7. An aluminum base alloy article highly resistant to pitting and corrosion in an aqueous environment wherein the alloy consists essentially of from 0.05 to 0.5% silicon, wherein the silicon is present in solid solution, from 0.2 to 0.8% manganese, from 0.001 to 0.2% iron, from 0.001 to 0.1% chromium, from 0.001 to 0.1% magnesium, from 0.001 to 0.1% copper, from 0.001 to 0.05% titanium, from 0.001 to 0.1% zinc, balance aluminum.

* * * * *

TABLE IV

CORROSION TEST RESULTS AND SPECTROSCOPIC ANALYSES OF EXAMPLE III ALLOYS EXPOSED FOR VARIOUS TIMES UP TO 180 DAYS IN NEW HAVEN TAP WATER

Percentage Composition					Pit Depth (mils) 60 Days		120 Days		180 Days		Weight Loss mlgms/cm² 60	120	180
Fe	Si	Mn	Ti	B	Mean	Max	Mean	Max	Mean	Max	Days	Days	Days
.016	.107	.62	—	—	9.2	20.9	9.9	15.8	15.0	23.6	9.0	18.7	29.2
.014	.093	.61	.014	.004	9.7	15.9	8.8	12.6	17.0	30.0	10.0	17.3	28.7
.063	.10	.64	—	—	10.2	17.8	14.9	25.3	15.7	20.4	10.4	17.4	28.6

EXAMPLE IV

The alloys of the present invention have moderate mechanical properties. Alloys having compositions as listed in Table V were cast and processed according to the process described in Example II. The final cold reduction was 30% and the resultant mechanical properties are listed in Table V.

The alloys of the present invention have a wide potential area of usefulness, encompassing almost any application in which a metallic article must come into contact with relatively impure water or other aqueous media. Typical of such applications are tubing or piping for the flow of aqueous media and heat exchangers for the transfer of heat to or from an aqueous medium. The alloy of the present invention is particularly suitable for the fabrication of thin wall tubing, as for example welded tubing formed from metal strips. Such tubing would normally have a wall thickness of from 0.02 to 0.375 inch depending upon the tube diameter, and a diameter of from ⅛ inch to 16 inches. Of course, thick wall tubing and piping may be fabricated having a wall thickness of as much as 1.0 inch. The alloy of the present invention may also be used in the fabrication of items such as tube sheets, and tube spacers and supports. In general, the alloy of the present invention is useful whenever aqueous corrosion problems are en-

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,923,557

DATED : December 2, 1975

INVENTOR(S) : William H. Anthony and James M. Popplewell

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading, before "Popplewell" insert ---James M.---;

In the heading, "Swiss Aluminum Limited" should read ---Swiss Aluminium Limited---.

Page 1, Issue Date of Patent "Aug. 27, 1975" should read ---Dec. 2, 1975---.

Signed and Sealed this

thirtieth Day of *March 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks