

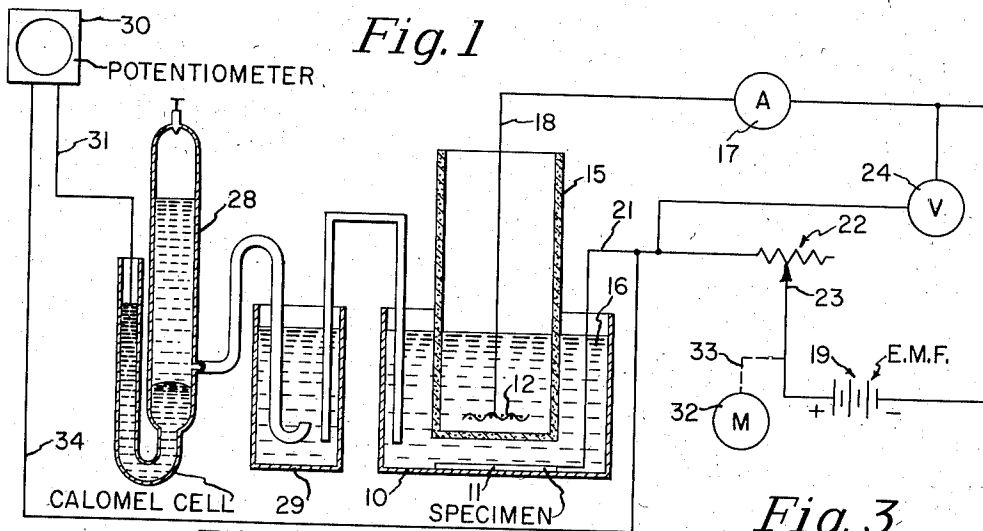
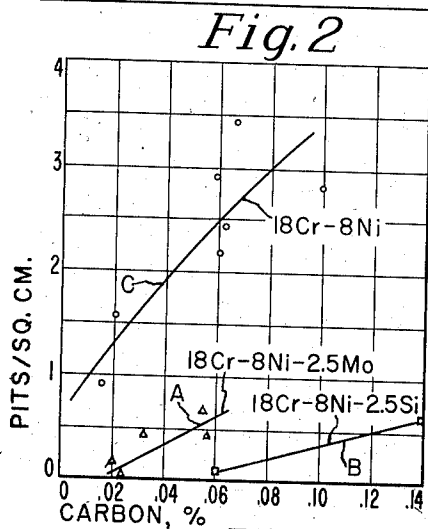
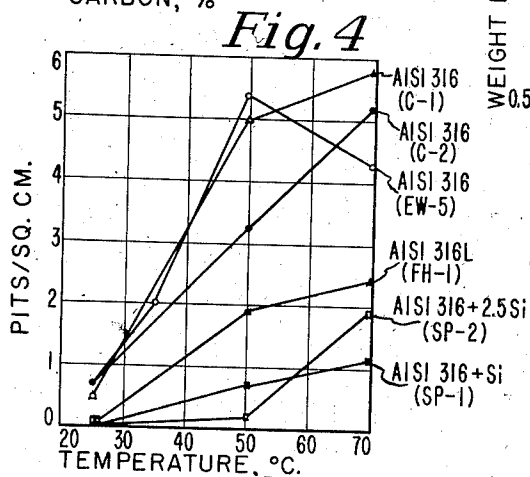
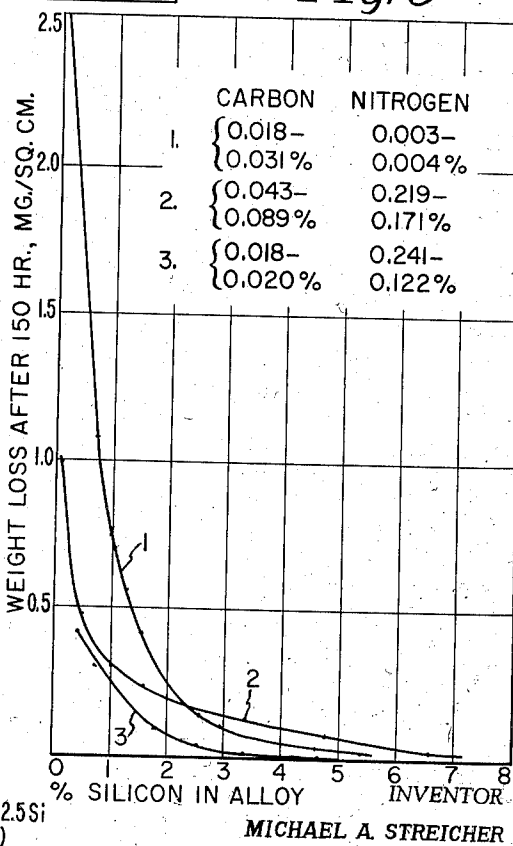
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CORROSION RESISTANT ALLOY

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CORROSION RESISTANT ALLOY

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2 Claims. (Cl. 75-128)

This invention relates to corrosion resistant alloys, and particularly to stainless steel type alloys having enhanced resistance to pitting.

The introduction into technology of stainless steels, by which is meant steels of the general type including approximately 18% chromium and 8% nickel, constituted an important advance in the control and prevention of corrosion. However, experience has shown that expensive stainless steel corrosion failures are still suffered due to pitting corrosion and, in fact, it is estimated that approximately 80% of the stainless steel corrosion failures occurring in the chemical industry is due to pitting.

Pitting corrosion, like intergranular corrosion, is characterized by highly localized deterioration, which can result in very severe damage, even though only a relatively small weight loss occurs, due to loss of mechanical properties or even perforation of the corroding metal.

The mechanism of pitting is extremely complicated and, apparently, is affected importantly by such factors as the specific nature of the medium in contact with the metal, the temperature, the pH, electrical potential considerations, and other conditions which are not, as yet, well understood and are, in most cases, not subject to control by the metal user. In general, it seems that pitting represents a breakdown in the more or less effective passivity displayed by metal alloys, which passivity results from the existence of a protective surface film on the alloy which affords more or less protection against corrosion, the protective film being developed by contact of the alloy with the corroding solution. It appears that the particular surface film developed is a result of the environment, including the specific solution involved in the system, and that pitting occurs when the protective film is disrupted locally. The breakdown of the protective films can be "healed" by the use of inhibitors, many of which are known from experience to possess beneficial properties in this regard, or the alternative approach might be adopted wherein the inherent passivity of the alloy is strengthened by alterations in composition. This invention utilizes the latter principle for the attainment of enhanced pitting corrosion resistance.

An object of this invention is to provide stainless steel compositions which have a markedly enhanced resistance to pitting corrosion. Another object of this invention is to provide stainless steel alloys which are resistant to pitting corrosion and still are austenitic in structure, with the retention of workability properties dependent on the austenitic state. Another object of this invention is the provision of stainless steels having low pitting propensities which are of relatively low cost.

The manner in which these and other objects of this invention are obtained will become apparent from the detailed description and the following drawings, in which:

Fig. 1 is a schematic representation of an electrolytic pitting apparatus which was utilized to conduct certain of the tests performed in appraising pitting corrosion resistance of alloy steels,

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Fig. 2 is a plot of percent carbon versus pits/sq. cm. for stainless steels having compositions selected in part according to this invention, a conventional 18-8 steel being included for comparison purposes,

Fig. 3 is a plot of weight loss after 150 hrs. exposure to a 10% aqueous solution of FeBr_3 in mg./sq. cm. versus percent silicon in the alloy for A. I. S. I. Type 316 stainless steels wherein the carbon and nitrogen contents were varied over the three specific ranges denoted in the legends, and

Fig. 4 is a plot of temperature versus pits/sq. cm. for conventional stainless steels and typical stainless steels modified according to this invention.

Generally, the objects of this invention are attained by modifying the compositions of conventional stainless steels by inclusion of substantial quantities of silicon and molybdenum therein while, at the same time, reducing the carbon content as low as practicable and increasing the nitrogen content to as high a level as practicable.

The concurrent regulation of the content of these four elements has resulted in a very appreciable reduction in pitting propensities, which is of a magnitude completely beyond that which can be achieved by manipulation of one or several, but not all, of the specific elements.

The functions of the three elements Si, Mo and N₂ are apparently complementary, in that each accomplishes a specific function unrelated to the functions of the others, the aggregate being the result of the ternary present. In general, an increase in the percentage content of any of the three elements recited increases the overall benefit to the alloy therefrom. At the same time, to obtain the benefits of the three individual elements it is necessary to concurrently maintain the carbon in the alloy at the lowest practicable levels. A typical composition according to this invention is an A. I. S. I. 316 stainless steel (18.79% Cr and 9.25% Ni) containing 2.4% Mo and, in addition, 2.5% Si, 0.23% N₂, and 0.039% C.

The general roles which can be ascribed to the alloying elements are believed to be as follows, it being understood that this invention is not limited in any sense by any explanation which may be postulated to explain the functions performed by any of the individual ingredients of the alloy, even if further investigations should provide additional data which would establish these explanations as erroneous.

Incorporation of Mo in the amount of 2.5% appears to increase greatly the response to passivation (by which is meant immersion for a time of the order of 30 minutes in a solution consisting of 180 ml. 65% HNO_3 and 15 g. potassium dichromate in 3000 ml. of distilled water at 70° C.), but does not appear to affect pit initiation for the alloy in the pickled condition.

Incorporation of Si in amounts of the order of 2.5% increases the pitting resistance of the alloy in the pickled condition (by which is meant immersion of the steel in a bath at 70° C. containing 360 ml. 65% HNO_3 , 60 ml. 48% HF, and 60 ml. 37% HCl in 3000 ml. distilled water), but does not alter the response to passivation.

Incorporation of increased amounts of nitrogen increases the resistance to pit initiation, in part by eliminating the ferrite phase, in favor of stabilizing austenite, but possibly, in addition, by exerting a protective action at the grain boundaries which are particularly susceptible to attack by pitting corrosion.

Maintaining the carbon content at low levels imparts enhanced resistance to pit initiation over grades of steel containing higher carbon contents. Apparently, reducing the carbon content increases both the basis pitting resistance, i. e., pitting in pickled condition, and also the response to passivation, thereby exerting a dual effect.

The amassing of the data upon which this invention is based was accomplished by the use of a special technique for determining pit initiation in stainless steel samples. According to this technique, pit corrosion propensities were evaluated by an accelerated electrolytic test wherein an apparatus of the type shown schematically in Fig. 1 was employed. Referring to Fig. 1, the apparatus comprised an electrolytic cell indicated generally at 10 which contained the test sample 11, connected as the anode, in close proximity with cathode 12, which was a platinized platinum gauze about 6 cm. in diameter disposed substantially parallel to the test sample. The gauze was mounted within a porous cup 15, which was provided to prevent diffusion of the alkaline catholyte into the solution surrounding the steel being tested. The test solution to which the sample was exposed during test is represented at 16. To facilitate control of the electrolysis carried out in the course of testing a milliammeter 17 was interposed in series with lead 18 connecting cathode 12 with the negative side of D. C. power source 19, which was a 6 volt battery. Lead 21 connecting sample 11 with the positive side of source 19 was provided with a resistance portion 22 adapted to be adjustably shunted out by sliding tap 23 completing the circuit with source 19. Voltmeter 24 was connected in shunt across leads 18 and 21. Although not necessary to the operation of the test apparatus, it was desirable to obtain readings of the electrical potential existing at the surface of the test sample, and this was accomplished by connecting a standard calomel cell 28 in communication with the test solution through conventional solution bridge 29, the potential reading being obtained by potentiometer 30, connected with the calomel cell through lead 31 and with lead 21, running to sample 11, by lead 34. As will be hereinafter described in greater detail, all tests were standardized as regards current supply by movement of tap 23 with respect to resistor 22. This was affected by providing a constant speed motor 32 for driving the tap 23 along resistor 22 through the mechanical connection indicated schematically in broken line representation at 33 from substantially non-shunted condition of the resistor to partially shunted-out condition.

The samples were cut from sheet stock 0.07" thick in squares 2" x 2". After removal of scale by grinding, stainless steel wires were spot welded to one corner for electrical contact. All of the samples were then pickled by immersion for about 20 minutes in the HNO_3 -HF-HCl solution hereinbefore described, after which the samples were rinsed and then passivated by immersion in the passivating solution hereinbefore described. After passivation, the specimens were again rinsed and dried, following which the back, sides and lead wire were covered with a transparent plastic coating, leaving an uncoated face for disposition opposite cathode 12 for conduct of the test.

The standard testing procedure, developed after extensive experimentation, consisted of exposing samples to the particular test solution 16 contained in cell 10, increasing the current from 0 to 3 ma./sq. cm. and holding for 5 minutes at this current density to develop and reveal clearly any pits which may have just been initiated upon reaching the maximum current density. Only about 15 minutes were required for the completion of each specimen test for 0.1 N NaCl test solution and the index of comparison of different samples was the measured number of pits which developed in the course of the test. These pits were visible to the eye, ranging from about 0.02" up in diameter, and thus it was possible to appraise the relative pit corrosion resistance of various stainless steels rapidly and accurately.

In order to evaluate a particular steel with the best reliability, ten specimens of the steel were tested in sequence, each in fresh test solution, with the current increasing from 0 to 3 ma./sq. cm. In each case the

pits per specimen were counted at the end of the tests and divided by the area to give the number of pits/sq. cm. Results of the ten runs were then averaged to give a value in terms of pits/sq. cm., which was the index of pitting resistance for the particular steel in the given corrosive solution at the controlled temperature. From a statistical study of typical data obtained on various types of steel at various temperatures in chloride corrosive solutions, it was found that 90% of the averages of ten such runs fell between ± 0.5 pits/sq. cm. of the "true average," i. e., the average of an infinitely large number of runs (confidence limits). Also, it was found that 95% of the time 75% of the pits/sq. cm. obtained in an individual run would be within ± 1 pit/sq. cm. of the average of 10 runs (tolerance limits).

After extensive experience with the accelerated electrolytic pitting corrosion tests, it was found that the number of pits which develop per unit of area for a specific combination of stainless steel and corrosive solution depended directly on the density of the current (ma./sq. cm. passing through the surface of the specimen) and was independent of the voltage across the cell, the specimen area, the length of time of maintaining at constant current density, the total quantity of the electrical charges passing through the cell in coulombs, or the prior appearance of pits. It must be kept in mind that pit initiation is the characteristic being measured, rather than pit growth, for example, which is more readily evaluated by gravimetric procedures, such as weight-loss measurements and the like.

The accelerated electrolytic pit corrosion tests hereinbefore described were checked against conventional corrosion tests, including classical immersion tests, seawater exposure and specific industrial plant exposure tests, and it was found that good correlation existed between all of these tests when the index under measurement was pit initiation. As a result of the extensive electrolytic testing which was completed, together with a large number of confirmatory tests of pit initiation by conventional methods, it was concluded that, as to various chlorides, for example, pitting intensity was largely an inverse function of the pH of the test solutions and that, as the pH of the solutions increased, the pitting intensity decreased. It appears that the cationic member of the chloride salt played only a minor role in pit initiation, if any at all, and that the chloride ion constituted the primary factor.

Referring to Fig. 2, three plots are given of commercial 18-8 stainless steels, in one of which (A) 2.5% Mo has been added and another of which (B) 2.5% Si has been added, pits/sq. cm. being plotted as the ordinate versus percent carbon content in the steels as the abscissa. Plot (C), for a conventional 18-8 steel, is included for comparison purposes. All specimens were tested by the accelerated electrolytic test in 0.1 N NaCl solution at 25° C. after first having been pickled and passivated. The nitrogen content of these steels was of the order of 0.02%, consequently nitrogen exerted practically no effect at all on the results obtained. From the plots, it is apparent that a low carbon content is associated with pit corrosion resistance, and that substantial benefits are obtained by the inclusion of either Mo or Si as an added alloying element in conventional stainless steels.

In addition, three sets of a minimum of five samples each of A. I. S. I. 316L stainless steel were made up to which, Series 1, various amounts of Si were added to determine the effect of this element alone, Series 2 various amounts of Si were added to a nitrogenized type 316 stainless steel (0.1-0.2% N_2), and Series 3 various amounts of Si were added to a nitrogenized type 316L steel. The range-limiting analyses of steels for each of the above series are set out in Table 1.

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Table 1

SERIES 1

Alloy	Per- cent Cr	Per- cent Ni	Per- cent Mn	Per- cent C	Per- cent N	Per- cent Si	Per- cent Mo
XA15-----	16.90	11.91	0.90	0.031	0.004	4.67	2.14
XA19-----	15.55	13.05	0.98	0.018	0.003	0.005	2.10

SERIES 2

XA25-----	15.95	12.26	0.90	0.089	0.171	6.48	2.30
XA24a-----	16.47	13.10	0.79	0.043	0.219	0.037	2.05

SERIES 3

XA20B-----	16.83	12.98	0.97	0.020	0.122	4.63	2.14
XA22B-----	16.93	13.39	0.90	0.018	0.241	0.689	2.72

All of the samples in the three series were subjected to conventional immersion corrosion tests consisting of immersion in 10% FeBr₃ solution at a temperature of 25° C., a particularly aggressive environment medium for Mo-modified stainless steels, weight loss data being determined after exposures of 25 hrs., 50 hrs., 100 hrs., and 150 hrs.

All of the samples of the three series were made up to maintain the chromium/nickel ratios such that all of the steels possessed single-phase austenitic structures independent of variations in the Ni and carbon contents with the compositions tested. The corrosion rate data obtained was in terms of over-all weight loss and, thus, incorporates the phenomena pit initiation, pit growth and general corrosion, a more complex general appraisal than is obtained with the accelerated electrolytic corrosion test hereinbefore described.

The results obtained in the FeBr₃ immersion tests are best visualized graphically, and Fig. 3 is a plot of the corrosion versus percent silicon in the alloy for the three series of Table 1, the individual plots being identified by the number of the corresponding series set out in the table. For convenience in identification the general carbon and nitrogen limits for each of the series is affixed as a legend for Fig. 3.

It will be apparent that silicon additions are most effective for the extra-low carbon steels (Series 1 and 3). Furthermore, at very low silicon levels the carbon level is not nearly as critical for the nitrogenized alloy (Series 2 and 3) as for the non-nitrogenized alloy (Series

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1). From this, it appears that nitrogen contributes to pitting corrosion resistance in a more general manner than merely by virtue of its stabilization effect for austenite. Fig. 3 also reveals that increasing the silicon content from about 2.5 to about 4% improves the corrosion resistance by a factor of 10. As a general conclusion from the data obtained, it might be stated that 18-8 stainless steels containing about 2.0-3.0% Si, about 2.5% Mo, about 0.2% N₂ and as low a carbon content as commercially practicable, e. g., not in excess of about 0.03 or .04%, possess a very superior pit corrosion resistance as compared with conventional stainless compositions.

A series of test steels was made up having the analyses set forth in Table 2, following:

Table 2

[Compositions in percent by weight]

Steel, AISI Type	Code	Cr	Ni	C	N	Mo	Si	Mn	P	S	Cu
316-----	EW-5	17.93	13.50	0.031	-----	2.47	0.31	1.77	0.023	0.006	-----
316-----	C-1	17.78	13.22	0.056	-----	2.32	0.71	1.70	0.021	0.009	-----
316-----	C-2	17.80	12.52	0.055	-----	2.28	0.58	1.53	0.017	0.005	-----
316L-----	FH-1	17.85	11.34	0.027	0.13	2.25	-----	-----	-----	-----	-----
316+Si-----	SP-1	18.05	9.92	0.072	0.062	2.21	2.39	0.61	0.012	0.010	0.08
316+Si-----	SP-2	18.79	9.25	0.039	0.23	2.40	2.50	0.77	-----	-----	0.02

A number of accelerated electrolytic corrosion tests were run on the steels having the analyses reported in Table 2 and pits/sq. cm. as a function of temperature in ° C. is plotted in Fig. 4. It is apparent that a very substantial decrease in pit corrosion propensities is obtained by utilizing substantial amounts of Si and Mo as additives to the steels, supplemented by concomitant high nitrogen and very low carbon contents.

In summary, 18-8 stainless steels generally, which comprises those steels which contain approximately 16-20% Cr and 8-14% Ni, may be improved as regards pit corrosion resistance by the incorporation of approximately 1.5-4.0% Mo, 1.5-4.0% Si and 0.1 to 0.3% N₂, while simultaneously limiting the maximum carbon content to 0.08%, and preferably to a level of 0.03% or lower.

From the foregoing it will be understood that the modified stainless steels of this invention are capable of relatively extensive modification within the essential spirit of the invention and it is intended to be limited only by the scope of the following claims.

What is claimed is:

1. A pit corrosion resistant stainless steel of the 18-8 class containing about 2.50% Si, 2.50% Mo, N₂ in the range of about 0.10% to about 0.30%, and carbon below about 0.08%.

2. A pit corrosion resistant stainless steel comprising from about 16% to about 20% of chromium; about 8% to about 14% nickel; about 1.5% to about 4.0% molybdenum; about 1.5% to about 4.0% silicon; about 0.1% to about 0.3% nitrogen; carbon below about 0.08%; the balance being substantially iron.

References Cited in the file of this patent

UNITED STATES PATENTS

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,839,392

June 17, 1958

Michael A. Streicher

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, line 1, name of inventor, for "Michael A. Stericher" read -- Michael A. Streicher --; in the printed specification, column 2, line 48, for "In corporation" read -- Incorporation --; line 70, for "basis" read -- basic --.

Signed and sealed this 19th day of August 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents