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OXIDATION AND CORROSION BEHAVIOR OF MODIFIED-COMPOSITION, LOW-CHROMIUM 304 STAINLESS STEEL ALLOYS

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16. Abstract

The effects of substituting less strategic elements than Cr on the oxidation and corrosion resistance of AISI 304 stainless steel were investigated. Cyclic oxidation resistance was evalutated at 870° C. Corrosion resistance was determined by exposure of specimens to a boiling copper-rich solution of copper sulfate and sulfuric acid. Alloy substitutes for Cr included Al, Mn, Mo, Si, Ti, V, Y, and misch metal. A level of about 12% Cr was the minimum amount of Cr required for adequate oxidation and corrosion resistance in the modified composition 304 stainless steels. This represents a Cr saving of at least 33 percent. Two alloys containing 12% Cr and 2% Al plus 2% Mo and 12% Cr plus 2.65% Si were identified as most promising for more detailed evaluation.

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OXIDATION AND CORROSION BEHAVIOR OF MODIFIED-COMPOSITION, LOW-CHROMIUM 304 STAINLESS STEEL ALLOYS

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SUMMARY

An experimental screening program was conducted to determine the effects on oxidation and corrosion resistance of substituting less strategic elements for chromium in AISI 304 stainless steel. Fifty-nine experimental modified 304 stainless-steel alloys were investigated. Oxidation resistance was evaluated by 200-hour cyclic tests at 870° C. Corrosion resistance was determined by exposing specimens to a boiling copper-rich solution of copper sulfate and sulfuric acid for 48 hours. Alloy substitutions for chromium included aluminum, manganese, misch metal, molybdenum, silicon, titanium, vanadium, and yttrium plus selected combinations of aluminum with molybdenum or manganese. Substitute contents ranged from 0.1 weight percent for misch metal and yttrium to 10 weight percent for elements such as manganese, molybdenum, and vanadium.

The substitution of less strategic elements for chromium indicated that, to maintain oxidation and corrosion resistance similar to that of 304 stainless steel, the minimum amount of chromium required was about 12 percent. At lower Cr levels, very rapid oxidation and corrosion attack was noted. This level represents a chromium saving of at least 33 percent compared with 304 stainless steel. The most effective substitutes for chromium (allowing reduction of Cr content to 12%) for oxidation resistance included aluminum, silicon, titanium and combinations of aluminum and molybdenum and aluminum and manganese. Similarly, the evaluation of the corrosion resistance of the modified 304 stainless-steel alloys indicated that effective substitutes for chromium included silicon, vanadium, manganese, and combinations of aluminum and molybdenum. Modified 304 stainless-steel alloys that exhibited the most promising oxidation resistance along with promising corrosion resistance at the 12-percent chromium level included an alloy with 2.65 percent silicon and an alloy with 2 percent aluminum and 2 percent molybdenum. These alloys behaved much like 304 stainless steel, having low weight changes during oxidation testing at 870° C and an absence of grain boundary attack during corrosion testing.

INTRODUCTION

The recent energy crisis, cartel formations by aluminum producing countries, and widespread materials shortages have focused attention on the need to be aware of those materials that are essential to the nation's economy and may be considered to be in short supply here in the United States. Several conferences, such as the First National Conference on Materials Availability/Utilization sponsored by the American Society for Metals in January 1975 and the Materials Shortage Workshops sponsored by the Department of Defense in January 1975 (ref. 1) and again in February 1976 have identified those materials that should be considered to be in the shortage category.

One metal that has been placed in the shortage category as a result of these conferences and of surveys made by various government and independent agencies is chromium. This metal is of particular interest to the aerospace industry because of its important contributions in stainless steels and superalloys. With the exception of a small amount of chromium reclaimed from scrap, the United States imports all of its chromium. To assess the consequences of a potential chromium shortage and to determine actions that might be taken to prepare for such an event, the U. S. Air Force sponsored a Chromium Workshop in May 1975 (ref. 2). More recently, an ad hoc committee on Contingency Plans for Chromium Utilization has been formed under the direction of the National Research Council's National Materials Advisory Board. These and other activities have established that the bulk of chromium is consumed in the making of stainless steels and specifically 304 stainless steel. In fact, the chromium used in 304 stainless steel represented about 35 percent of the total U. S. consumption in 1974 (refs. 2 and 3). One method of conserving chromium to offset a possible chromium shortage might be to reduce the chromium content of stainless steels. Therefore, we have been investigating several means of reducing the amount of chromium in stainless steels, with primary emphasis on AISI 304 stainless steel.

The purpose of the investigation reported herein was to determine the effects of substituting more available elements for chromium on the oxidation and corrosion resistance of modified 304 stainless steel alloys. A screening study was conducted to identify alloying elements that can be used to minimize the chromium content in this alloy and still maintain the excellent oxidation and corrosion resistance of 304 stainless steel. Fifty-nine experimental alloys were produced: these included the basic 304 stainless steel composition with reduced chromium (Cr) content (as low as 8% Cr). Alloying additions included aluminum (Al), manganese (Mn), misch metal (primarily cerium (Ce)), molybdenum (Mo), silicon (Si), titanium (Ti), vanadium (V), and yttrium (Y). Cyclic oxidation tests at 870° C and corrosion tests in a boiling solution of copper rich copper sulfate ($CuSO_4$) and sulfuric acid (H_2SO_4) were used as the primary means of evaluating the experimental alloys since 304 stainless steel is commonly selected for use because of its excellent resistance to high-temperature oxidation and to lower temperature corrosion.

EXPERIMENTAL PROCEDURE

Materials

Because the purpose of this investigation was to minimize the use of Cr in 304 stainless steel (304 SS) as much as possible, alloys having the basic composition of 304 SS, but with reduced Cr contents of 16, 14, 12, 10, or 8 percent were prepared. Even though 12 percent is normally accepted as the minimum amount of Cr possible in stainless steels to provide some corrosion protection (ref. 4), lower amounts were explored to provide a comparison with alloys having less strategic elements substituted for part of the Cr and to determine the effects of removing Cr from 304 SS on oxidation and corrosion resistance.

Some alloying elements which were substituted for Cr in 304 SS were selected on the basis of their potential for protective oxide formation during high-temperature oxidation. These included Al, misch metal, Si, Ti, and Y. Other alloying elements were selected because of their potential for imparting corrosion resistance (based in part on their proximity to Cr in the periodic table (Mn, Mo, and V) and on the known ability of Mo to improve the corrosion resistance of 18% Cr - 8% Ni stainless steels (ref. 5)). Concentrations of the alloying elements substituted for part of the Cr in 304 SS were governed by the low solubility of Y and the rare earth metals (misch metal) in Fe where only 0.1 and 0.2 percent additions were made, by anticipated requirements for enhanced oxidation resistance without deleteriously affecting corrosion resistance where 1 and 2 percent Si or Ti and 2, 4, and 6 percent Al were added, and by the amount of Cr removed for those elements added to improve corrosion resistance where a one-for-one weight percent Mn, Mo, and V were substituted for Cr. Since this screening investigation was aimed primarily at oxidation and corrosion resistance, the effects of alloying additions on mechanical properties or phase stability were not considered.

Table I presents the analyzed compositions of the modified 304 SS alloys. Starting materials for this investigation included vacuum processed iron (Fe) and Ti; electrolytic Cr, nickel (Ni), and Mn; electron-beam melted Mo and V; and commercial purity Al, Si, Y, and misch metal.

Master alloys similar in composition to 304 SS, but containing less Cr were melted as 1-kilogram ingots from which the modified 304 stainless alloys were prepared. Alloy ingots were prepared by a nonconsumable, triple-arc-melting of 70-gram charges in a water-cooled copper mold, followed by drop casting into a square-cross-section mold to facilitate rolling to sheet. Commercial 304 SS, melted and fabricated under conditions similar to the experimental alloys, was used as the baseline for the oxidation and corrosion evaluations. Ingots were rolled at 925° C to 0.25-centimeter-thick sheet from which 1.2- by 2.2-centimeter specimens, each with a 0.05-centimeter hanger hole, were cut for testing. To remove the oxide scale resulting from hot rolling and to give a uniform surface in preparation for testing, samples were alumina-grit blasted, ultrasonically cleaned in trichlorethylene, rinsed in tap water, and dried.

Evaluation

Oxidation testing. - Alloy specimens were cyclic oxidation tested for 200 hours at 870° C. Although 870° C exceeds the normal use temperature of 304 SS, it was chosen to characterize the oxidation resistance of the various alloys in a reasonable length of time since oxidation of 304 SS occurs quite rapidly near this temperature. The cyclic oxidation apparatus (fig. 1) is described in detail in reference 6. Test specimens were weighed before loading into the hot zone of the static-air furnace for 1 hour and, then were automatically lifted out of the furnace to cool for a minimum of 20 minutes. This cycle was repeated until the total exposure time at 870° C reached 200 hours. Specimens were removed for weighing after the first hour of exposure and, subsequently, after 15, 30, 45, 60, 75, 90, 100, 115, 130, 145, 160, 175, 190, and 200 hours. Six alloy specimens including one 304 SS standard were loaded into the furnace.

To prevent contamination from neighboring alloys, each specimens was heated in individual ceramic tubes and was shielded during cooling. During the cooling cycle, individual spall cups were automatically positioned under the specimen to catch the oxide spall. After the 200-hour test, the accumulated spall was removed and weighed. The specimens and spall were then analyzed by X-ray diffraction to determine the nature of the oxide scale.

The specimen weight data were used to calculate specific specimen weight change data as a function of time for each alloy. The procedure used to analyze the specific specimen weight change data involved the method of multiple linear regression. The change in specific specimen weight $\Delta W/A$ with time t was fitted by least squares (ref. 7) to equation (1).

$$\frac{\Delta W}{A} = k_1^{1/2} t^{1/2} - k_2 t \pm \mathrm{SEE} \tag{1}$$

where k_1 is an oxide growth constant comparable to a parabolic oxidation scaling constant, k_2 is an oxide spalling constant, and SEE is the standard error of estimate.

Corrosion testing. - Corrosion testing was conducted according to ASTM specification A262-70 (ref. 8). Practice E under A262-70 is used in the aerospace industry to qualify commerical stainless steels and was selected as the standard corrosion test for the experimental alloys of this investigation. The corrosion test involved embedding test specimens in copper shot, and then exposing them to a boiling solution of $CuSO_4$ - H_2SO_4 for 48 hours. Figure 2 is a schematic of the corrosion test apparatus. Since smaller specimens (2.2 cm long compared with 7.6 cm long in ASTM A262-70) were used for these tests, one standard 304 SS specimen and all the modified alloys in an alloy series, normally six specimens, were tested in the flask simultaneously.

After exposure the specimens were evaluated by their general appearance and by examination of the surface of specimens after undergoing a 180° bend test. Bend testing was conducted at 25° C in a screw-driven tensile testing machine at a crosshead rate of approximately 25 millimeters per minute. A bend radius equal to the specimen thickness and a total bend angle of approximately 120° (the limit of the bend fixture) were used for all tests. After completing the bend test, all the ductile specimens were further bent in a vise to a total bend angle of 180° before they were examined for corrosion attack. Specimens were also observed metallographically to determine the nature and extent of the attack.

Corrosion-test specimens were rated according to their corrosion resistance on a scale from 1 to 4 (no apparent corrosion attack to catastrophic failure as evidenced by dissolution of the specimen) and also to their bend ductility on a scale from 1 to 3 (ductile bend behavior to brittle fracture before yielding). Incorporated in this rating scheme was the appearance of the specimen after corrosion testing, the amount of corrosion attack, and evidence of cracks or brittle failure during bend tests of corrosion tested specimens.

RESULTS

Oxidation Resistance

The relative oxidation resistance of the alloys at 870° C was evaluated for a total cyclic exposure of 200 hours. Specimens were characterized by specific weight change as a function of time, by spalling tendencies, and by X-ray diffraction of the scale after oxidation testing.

Weight change and spalling. - Final weight change data and spalling tendencies are summarized in table II for the oxidation test specimens. The spall classifications may be somewhat qualitative, since in some cases spall was lost and crossspalling occurred even though precautions were taken to prevent this. Spalling tendencies were rated as follows:

Rating	Total collected spall, mg
Negligible	<5.0
Light	5 to 100
Moderate	100 to 500
Heavy	500 to 1000
Massive	>1000

In appearance, the negligible exhibits only a few discernable specks in the cup, while for a massive rating the spall in some instances overflowed the 3-centimeter-diameter by 2-centimeter high spall cups.

The final weight change data along with the spalling tendencies of the specimens presented in table II combine to give a qualitative indication of the oxidation resistance of the individual alloys. Usually a large weight loss and excessive spalling indicate poor oxidation resistance. Most alloys were tested for the full 200 1-hour cycles. In extreme cases oxidation testing was terminated before 200 cycles because of excessive spalling. A low positive specific weight change of under approximately 3 milligrams per square centimeter, coupled with negligible or light spalling and minimal specimen distortion or growth, indicates good oxidation resistance. A few of the specimens showed fairly large final positive weight changes ranging from 38 to 142 milligrams per square centimeter. These specimens underwent severe growth and distortion and in most cases exhibited little spall, probably due to growth relieving stresses that permit the oxide scale to remain on the specimen.

The individual specimen specific weight changes data are plotted as a function of cyclic oxidation time in figure 3 for selected alloys. Most of the curves follow a typical growth-spall behavior previously designated as paralinear (ref. 9). Characteristic of this behavior is an initial weight gain followed by a steady weight loss when significant spalling occurs.

The effects of decreasing Cr content on the oxidation resistance of modified 304 SS alloys as indicated by weight change are shown in figure 3(a). (The range of weight change data for 11 tests of the standard 304 SS alloy is also shown in fig. 3 for comparison. This material exhibited typical paralinear behavior.) After 200 hours of cyclic oxidation, a total specific weight loss ranging from approximately 12 to 25 milligrams per square centimeter was noted for the standard 304 SS (fig. 3(a)). But as Cr content was reduced from 18 percent, weight loss increased dramatically (also shown in fig. 3(a)). Based on extrapolations to 200 hours (using eq. (1)) for levels of 16, 12, and 8 percent Cr, the total cyclic oxidation weight loss increased to 210, 273, and 830 milligrams per square centimeters, respectively.

The effects of 2-percent Al additions on the modified 304 SS alloys with 16, 12, and 8 percent Cr are shown in figure 3(b). A 16-percent Cr - 2 percent Al modified alloy exhibited a slight weight gain (1.5 mg/cm^2) after 200 hours of cyclic oxidation testing (fig. 3(b)); the 12-percent Cr - 2-percent Al modified alloy exhibited a weight loss near 60 milligrams per square centimeter. At the 8-percent Cr level, the addition of 2-percent Al was somewhat beneficial in improving oxidation resistance, the weight loss being comparable to the 12-percent Cr alloy without Al. (Compare figs. 3(a) and (b).)

The effects of Y additions on the oxidation resistance of modified 304 SS alloys are shown in figure 3(c). For a 16-percent Cr - 0.2-percent Y alloy, oxidation resistance appears to be superior to the standard 304 SS, which suggests that an 11-percent Cr saving could be realized by substituting 0.2 percent Y for 2 percent Cr. Although 0.2 percent Y was also beneficial in the alloys with the 12 and 8 percent Cr levels (compare figs. 3(a) and (c)) total weight losses after the 200-hour test were greater than that observed for the standard 304 SS.

A combination of Al and Mo was very beneficial in improving the oxidation resistance of modified alloys based on total weight change. Figure 3(d) shows that at 16 and 12 percent Cr with 2 percent Al plus 2 percent Mo, slight weight gains of less than 2 milligrams per square centimeter were observed after 200 hours testing, again compared to a 25-milligram-per-square-centimeter weight loss for 304 SS. These were the best results of all alloys studied here. At the 8 percent Cr level a weight loss of approximately 380 milligrams per square centimeter was experienced after 200 hours, or about 45 percent of the extrapolated 830-milligram-per-square-centimeter weight loss of the 8 percent Cr modified alloy without Al and Mo additions.

It is apparent from examination of figures 3(a) to (d) that 8 percent Cr alloys are markedly inferior in oxidation resistance to the standard 18 percent Cr 304 SS. To achieve oxidation resistance comparable to 304 SS, near 12 percent Cr will probably be required. Figure 3(e) shows a comparison of the oxidation resistance of several modified alloys containing 12 percent Cr along with the data band for 304 SS, which represents the extremes in weight loss as functions of time for 11 specimens tested during the course of the program. Lowering the Cr of the standard alloy to 12 percent resulted in a large weight loss after only a short time of cyclic oxidation testing. But the small additions of the other alloying elements shown in this figure improved the oxidation resistance of the 12 percent Cr alloys. Based on weight losses, improvements in oxidation resistance in increasing order were afforded by additions of 2 percent Ti, 0.2 percent Y, 2 percent Al, 2.65 percent Si (modified alloys with this addition fall within the scatter band for 304 SS), and 2 percent Al + 2 percent Mo (where the average of four results are indicated by the line shown in fig. 3(e)).

The weight change data suggest that a 33-percent Cr saving can be accomplished by substituting 2 percent Si (0.65 percent Si is in standard 304 SS) or 2 percent Al + 2 percent Mo for 6 percent Cr in 304 SS without sacrificing its excellent oxidation resistance.

X-ray diffraction. - The X-ray diffraction data for the retained surface oxide and accumulated collected spall are also summarized in table II for each specimen tested. In most cases results are for specimens that have undergone 200 hours cyclic oxidation testing unless, as indicated, the test was terminated early because of excessive scale spalling. The major oxides formed at 870° C on the basically Fe-Cr alloys are Cr_2O_3 and Fe_2O_3. These sesquioxides are isomorphic and form a complex series of solid solutions. The strongest lattice spacing a_0 value is 2.67 for Cr_2O_3, compared with 2.69 for Fe_2O_3. Because of these similarities, it was difficult to differentiate the two oxides. Based on the results listed in table II, it appears that 18 percent Cr is required in 304 SS alloys to produce the protective Cr_2O_3 oxide. Reducing the Cr content to 16 percent or lower results only in formation of Fe_2O_3/Fe_3O_4 oxides.

In general, the higher Cr content alloys initially formed Cr_2O_3, with the formation of Fe_2O_3 increasing with increasing exposure time. Also forming on the modified 304 SS alloys was a spinel oxide with a_0 ranging from 8.45 to 8.30. The lower values of a_0 (8.30 to 8.40) are thought to be magnetite (Fe_3O_4), which, along with Fe_2O_3, appears to be spall-prone and which has poor oxidation resistance. In contrast, the higher a_0 values appear to be $FeO \cdot (Cr, Fe, Ni)_2O_3$, which, along with Cr_2O_3, spall much less and are associated with the more oxidation-resistant alloys.

The simple monoxides, such as FeO or NiO, were not detected on any of the modified 304 SS alloys studied here. This type of oxide is common in superalloy oxidation and is associated with severe spalling (ref. 10). The only other oxides detected in this study were those resulting from specific alloy additions. For example, alloys containing high concentrations of Al (4 to 6%) formed a protective sesquioxide, α-Al_2O_3, which is also isomorphic with Cr_2O_3 and Fe_2O_3. High Mn additions may form Mn_2O_3 in addition to Fe_2O_3 and spinel, and high V alloys may form traces of tapiolite (ref. 10) along with the normal oxides; however, neither appears protective. It also appears that Ti tends to increase the stability of Cr_2O_3 in relation to the Fe_2O_3 in the Ti-modified series.

Ranking of experimental alloys. - Previous use of regression analysis (ref. 6) yielded a reasonably good fit of oxidation data to equation (1). Most data in this study could also be correlated by this relation. However, the fit was poor for alloys that underwent growth and distortion. Because of the poor fit for about one-third of the specimens, a ranking as a function of composition was emphasized in the present study.

After oxidation testing each specimen was rated on a scale from 1 (excellent cyclic oxidation resistance) to 5 (catastrophic oxidation resistance). Incorporated into each rating category was the general appearance of the specimen after testing, the nature of the scale on the specimen, the amount and type of spall as determined by X-ray diffraction, and the nature of the specimen specific weight change with respect to time. The oxidation rank R_0 assigned to each experimental alloy is included in table II.

Oxidized specimens are shown in figure 4, which illustrates the ranking of oxidation resistance used in this report. Included in the photographs are the two most promising alloys based on specific weight change, as shown in figure 3(e): the 12 percent Cr modified 304 SS with either 2 percent Al + 2 percent Mo or a 2.65 percent Si. These alloys were given a rank R_o of 2.5 or slightly poorer than the $R_o = 2$ for standard 304 SS. Also shown in figure 4 are two $R_o = 5$ specimens. These alloys are typical of those that undergo catastrophic failure either by extreme weight loss (8% Cr) or oxide growth and extreme weight gain (8% Cr - 2.65% Si).

Corrosion Resistance

Corrosion testing was conducted on all specimens in a boiling solution of $CuSO_4$-H_2SO_4. Since the specimens were not given a sensitization heat treatment, the corrosion test measured bulk corrosion resistance as well as localized grain boundary attack.

Surface appearance and bend test results. - The effects of modifying the composition of 304 SS on corrosion resistance and subsequent bend ductility are summarized in table III. The corrosion data were evaluated in a manner similar to the oxidation data, with the corrosion test specimens being rated on a scale from 1 (no apparent corrosion attack) to 4 (catastrophic corrosion failure).

Figure 5 shows the effect of decreasing the Cr content on the corrosion resistance of the modified 304 SS. At levels of 18 (standard 304 SS), 16, and 14 percent Cr, no apparent attack occurred, and the specimens were ductile in bend testing after corrosion. However, at 12 percent Cr slight attack was noted, and cracks were observed upon bend testing. At the 10 or 8 percent Cr levels, severe and even catastrophic failure occurred during corrosion testing of the modified 304 SS alloys.

Based on the summary by Cowan and Tedman (ref. 4), these results were expected. Above about 12 to 13 percent Cr a dramatic decrease in the corrosion rate occurs in Fe - 10 percent Ni-Cr alloys. According to these authors, this occurs because of the formation of a protective, chromium-rich oxide film on the surface of alloys with 12 percent Cr.

Modified 304 SS alloys with Cr contents of 16, 12, and 8 percent were selected as base materials for evaluating the effects of various alloying additions on corrosion resistance.

Photographs of corrosion-tested specimens from selected groups of alloys are shown in figures 6 to 9. The beneficial effect of Si additions on corrosion resistance is shown in figure 6. No attack was evident in the 12 percent Cr alloys with either 1.65 or 2.65 percent Si. Even at 8 percent Cr content, increasing the amount of Si to 1.65 or 2.65 percent improved the corrosion resistance (from severe to slight attack, respectively) compared with catastrophic failure of the 8% Cr-0.65% Si alloy (fig. 5).

Substitution of small amounts of Al and Ti for Cr improved the corrosion resistance of the alloys to some extent, as summarized in table III, but these additions were not as beneficial as Si. Except for the 16 percent Cr - 2 percent Al alloy, all the Al-modified series of alloys failed in a brittle manner in bending. This may be due to the ferrite forming tendencies of Al, since brittle behavior was observed in these alloys before corrosion testing.

The effects of misch metal (MM) on corrosion resistance are shown in figure 7. At 16 percent Cr no visible surface attack occurred; however, these alloys exhibited cracks during bend testing after corrosion. Metallographic examination revealed grain boundary corrosion, which may have initiated cracks during subsequent bend testing. At 12 percent Cr content, severe corrosion occurred in the MM-modified alloys. And at 8 percent Cr content, catastrophic failure occurred with complete dissolution of the specimens. It is concluded from these results that misch metal (primarily Ce) is detrimental to the corrosion resistance of modified 304 SS alloys. Additions of Y had similar effects on corrosion resistance.

Alloy additions of V, Mn, and Mo were substituted for Cr on a one-for-one basis in weight percent; their effects on corrosion resistance are compared in figure 8. At the 16 percent Cr levels, no detrimental corrosion effects were observed. At 12 percent Cr levels no attack was visible on the V- and Mn modified alloys, and the corrosion tested specimens of these alloys were ductile in bending. In contrast, a 12 percent Cr alloy of the 304 SS composition (fig. 5) and the Mo-modified 12 percent Cr alloy (fig. 8) exhibited slight corrosion and cracking during bending. At 8 percent Cr levels, the V-modified alloy exhibited the best corrosion resistance observed for alloys of the 304 SS composition with such a low Cr content. Only slight attack was observed in this alloy (fig. 8). In contrast, catastrophic failure of the 8 percent Cr-10 percent Mn alloy and severe attack of the 8 percent Cr-10 percent Mo alloy occurred (fig. 8).

Because of the good oxidation resistance of Al-modified alloys and the previously reported excellent corrosion resistance imparted by Mo additions (ref. 5), these two elements were combined in an attempt to form a modified 304 SS with attractive corrosion and oxidation properties. Figure 9 and table III show that this combination imparted excellent corrosion resistance and good ductility at 12 or 16 percent Cr levels. This behavior, coupled with the outstanding oxidation resistance of the 12 percent Cr + 2 percent Al + 2 percent Mo alloy, suggests that this system is worthy of more detailed evaluation.

An attempt was made to improve the ductility of Al-modified alloys by simultaneously adding Mn, an austenite-stabilizing element. This approach was not successful: severe corrosion occurred at the 12 percent Cr level and brittle failure characterized all of the alloys in the series.

Metallographic observations. - Metallographic examination of corrosion test specimens revealed that there were basically two types of corrosion attack: (1) grain-boundary attack and (2) bulk corrosion characterized by surface roughening. The nature and extent of the corrosion attack in the standard 304 SS alloy and in alloys with Cr levels reduced to 12 and 10 percent are shown in figure 10. Based on surface appearance (see table III), the standard 304 SS alloy appeared to be resistant to attack by the $CuSO_4$-H_2SO_4 solution. The photomicrograph shown in figure 10(a) supports this observation as evidenced by lack of either grain-boundary attack or bulk corrosion. In contrast, with a reduced Cr level of 12 percent, a modified 304 alloy exhibited grain-boundary attack near the surface of the specimen (fig. 10(b)) corresponding to slight corrosion attack based on surface appearance. At a 10 percent Cr level grain-boundary attack penetrated to a depth of at least 0.15 millimeter (fig. 10(c)). This specimen was judged to have undergone severe corrosion attack based on surface appearance (table III). In addition to grain-boundary attack being observed in the reduced-Cr alloys (without special additions), this type of corrosion attack also was observed in alloys containing Al, misch metal, Y, Mn, and Mn + Al. A typical example of this type of attack is shown in figure 11 for a 12-percent-Cr-plus-Y-modified alloy.

Examples of bulk corrosion are shown in figure 12 by Si-containing alloys. A 12-percent Cr - 2.65-percent Si alloy (fig. 12(a)) exhibits just a slight hint of bulk corrosion as indicated by the small pits near the specimen surface. Figure 12(b) illustrates severe bulk corrosion with the surface reaction going much deeper in an 8 percent Cr-2.65 percent Si alloy. Alloys that exhibited this type of bulk corrosion behavior in addition to the Si-modified alloys included those containing Mo, V, Al + Mo, or Ti. Figure 13 illustrates the good corrosion resistance of the 8 percent Cr-10 percent V alloy.

DISCUSSION

Results from the 59 experimental alloy compositions investigated in this program showed a wide variation in oxidation and corrosion resistance, depending on the Cr content and elements substituted for Cr. In order to conserve Cr, it is desirable to develop an alloy with as low a Cr content as possible and still maintain the excellent oxidation and corrosion resistance of the standard 304 SS alloy. As noted previously, a nominal Cr content near 12 percent appears to be near the minimum concentration for adequate oxidation and corrosion resistance. Examination of the 19 alloys in table II with 12 percent Cr indicates that the observed oxidation ranking R_o ranges from 1 to 5, with most alloys having a rank between 3 and 5. We arbitrarily set an upper limit of 2.5 for acceptable oxidation resistance. Six alloys with 12 percent Cr fall into the acceptable category, including those with 4 or 6 percent Al, 2.65 Si, 2 percent Al + 2 percent Mo, 4 percent Al + 4 percent Mn, and 6 percent Al + 7 percent Mn. A similar examination of R_c in table III indicates a range from 1 to 3 for alloys with 12 percent Cr. Consideration of only those alloys equivalent to the standard 304 SS, that is, arbitrarily setting an upper limit of 1 for the corrosion rank, eliminates all but 6 of the 19 alloys. These six include those with 1.65 or 2.65 percent Si, 6 percent V, 6 percent Mn, 2 percent Al + 2 percent Mo, or 2 percent Al + 4 percent Mo. Two 12 percent Cr modified 304 SS alloys meet both of these criteria: they contain 2.65 percent Si or 2 percent Al + 2 percent Mo. Based on the nominal 12 percent Cr content of these two alloys and considering the minimum of the range of Cr (18 to 20% Cr) specified for 304 SS, the potential Cr savings is 33 percent for these two experimental alloys. Other alloys that slightly exceed the combined limits set for oxidation and corrosion resistance include those with 1.65 percent Si or 0.1 percent Y.

Some insight into the beneficial effects produced by the additions of Si or Al + Mo to the 12 percent Cr modified 304 SS alloy may be gained by consideration of the nature of the oxides and corrosion attack. Although the oxides detected by X-ray diffraction for Si additives included only Fe_2O_3 and Fe_3O_4, the low weight gain and moderate spalling tendencies similar to the standard 304 SS suggest that SiO_2 may be playing an important role in the oxidation behavior of this alloy, similar to the role observed in an Fe - 19 percent Cr - 13 percent Ni - 3 percent Si alloy (ref. 11). Good scaling resistance was attributed in part to the uniform layer of SiO_2 at the interface of surface oxide and metal acting as a barrier to cation diffusion. The Al + Mo modified alloy promoted the formation of Cr_2O_3 found on the standard 304 SS plus a protective spinel which had a low spalling tendency. During corrosion testing in a $CuSO_4$-H_2SO_4 solution, both 12 percent Cr + 2.65 percent Si and 12 percent Cr + 2 percent Al + 2 percent Mo modified 304 SS alloys prohibited grain-boundary attack found in the 12 percent Cr alloy without other additions. The absence of such attack suggests that a passive oxide-film characteristic of 304 SS (ref. 4) was formed on these alloys. Although other alloying elements (such as Ti) prohibited grain-boundary corrosion attack and promoted formation of Cr_2O_3 during oxidation, oxide spalling tendencies were high, thus reducing the attractiveness of Ti-bearing alloys.

It is also desirable to consider modified 304 SS alloys with Cr contents only slightly lower than 304 SS, such as a 16 percent Cr alloy. By using the oxidation and corrosion ranking criteria employed for the 12 percent Cr alloys, it is possible to identify the 16 percent Cr alloys that are attractive enough for further investigation. Of the 19 alloys investigated, 12 alloys meet the oxidation ranking criterion of 2.5 combined with the corrosion ranking of 1.0. These alloys include additions of 2, 4, or 6 percent Al, 0.2 percent misch metal, 1.65 or 2.65 percent Si, 1 or 2 percent Ti, 0.1 or 0.2 percent Y, 2 percent Al + 2 percent Mo, and 2 percent Al + 4 percent Mo. It should be noted, however, that three of these alloys were brittle during bend testing and thus are not being considered for further examination. These alloys include the 4 and 6 percent Al and the 2 percent Al + 4 percent Mo additions (table III).

The ranking systems for oxidation and corrosion provide an effective means of identifying more promising alloys for future characterization and study. In order to relate oxidation and corrosion behavior to alloy composition so that alloying contents can be optimized, a linear regression analysis was used. The estimating equations used are described in the appendix, and calculated R_o and R_c values are given in tables II and III. In general, agreement between observed and calculated rankings is quite good, which indicates that the linear regression analysis technique can be used for future alloy modifications. In addition, the effects of alloying elements on the mechanical properties and austenite stability will have to be incorporated in future alloying considerations.

CONCLUSIONS

Based on a study of the oxidation and corrosion resistance of 59 experimental alloys of a modified 304 stainless steel composition, the following conclusions are drawn:

1. Less strategic elements can be substituted for part of the chromium without appreciably degrading the excellent oxidation and corrosion resistance of 304 stainless steel.

2. An approximate lower limit for chromium for maintenance of acceptable oxidation and corrosion resistance is nominally 12 weight percent, which represents a potential 33 percent saving in the use of chromium.

3. Two experimental 12 percent chromium alloys were identified that offer both oxidation and corrosion resistance comparable to that of 304 stainless steel; these alloys contain 12 percent Cr + 2 percent Al + 2 percent Mo or 12 percent Cr + 2.65 percent Si plus the other normal constituents of 304 stainless steel.

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National Aeronautics and Space Administration,
Cleveland, Ohio, December 17, 1976,
505-01.

APPENDIX - MULTIPLE LINEAR REGRESSION ANALYSIS OF TEST RESULTS

Oxidation test results. - The relationship of cyclic oxidation resistance to composition can be determined by multiple linear regression using the following estimating equation:

$$\begin{aligned}\text{Oxidation rank, } R_o = {} & b_0 + b_1\,\%\,\mathrm{Cr} + b_2\,\%\,\mathrm{Al} + b_3\,\%\,\mathrm{Y} + \ldots \\ & + b_{1.1}(\%\,\mathrm{Cr})^2 + b_{2.2}(\%\,\mathrm{Al})^2 + b_{3.3}(\%\,\mathrm{Y})^2 + \ldots \\ & + b_{1.2}(\%\,\mathrm{Cr}\cdot\%\,\mathrm{Al}) + b_{1.3}(\%\,\mathrm{Cr}\cdot\%\,\mathrm{Y}) + \ldots \\ & + b_{1.2.6}(\%\,\mathrm{Cr}\cdot\%\,\mathrm{Al}\cdot\%\,\mathrm{Mo}) \\ & + b_{1.2.7}(\%\,\mathrm{Cr}\cdot\%\,\mathrm{Al}\cdot\%\,\mathrm{Mn}) + b_{2.6}(\%\,\mathrm{Al}\cdot\%\,\mathrm{Mo}) \pm \mathrm{SEE} \qquad (\mathrm{A1})\end{aligned}$$

This relation uses all first-order terms in the nine compositional variables, their square terms, interaction terms involving Cr and other addition elements, and Al-Mo, Al-Mn, Cr-Al-Mo, and Cr-Al-Mn interaction terms. The equation involves a constant (i. e., intercept) and 30 variables. Ninety-six test results (including 20 replicate sets) were computer-correlated according to this relation (using the NEWRAP program (ref. 7)) with a rejection level of 0. 90. This means that any coefficient not significant in a F-test compared with the pooled residual error with the proper degrees of freedom is automatically dropped and the relationship recalculated. In this program, the entire equation is computed initially and the terms successively dropped and recalculated step by step starting from the lowest probability coefficient term. This is continued until only terms >0. 90 probability remain.

The final equation relating oxidation resistance to composition was determined as follows:

$$\begin{aligned}R_o = {} & 7.86 - 0.30\%\,\mathrm{Cr} - 0.73\%\,\mathrm{Al} - 0.48\%\,\mathrm{Si} - 0.51\%\,\mathrm{V} - 2.01\%\,\mathrm{Mo} \\ & - 0.33\%\,\mathrm{Ti} + 0.12\%\,\mathrm{Mo}^2 + 0.02\%\,\mathrm{Cr}\cdot\%\,\mathrm{Al} - 0.06\%\,\mathrm{Cr}\cdot\%\,\mathrm{Y} + 0.05\%\,\mathrm{Cr}\cdot\%\,\mathrm{V} \\ & + 0.12\%\,\mathrm{Cr}\cdot\%\,\mathrm{Mo} - 0.09\%\,\mathrm{Cr}\cdot\%\,\mathrm{Al}\cdot\%\,\mathrm{Mo} + 1.16\%\,\mathrm{Al}\cdot\%\,\mathrm{Mo} \pm 0.52 \qquad (\mathrm{A2})\end{aligned}$$

The fraction explained variation due to the regression equation (i. e., the coefficient of variation) is close to 0. 90. It should be noted that 17 of the original 30 terms drop out of the equation. The equation was considered valid because the lack of fit was insignificant. This was based on the F-test for the residual variance broken into lack-of-fit and replication mean squares, with 54 and 28 degrees of freedom, respectively:

$$F = \frac{MS_{(LOF)54}}{MS_{(REPS)28}} = \frac{0.3084}{0.2277} = 1.355$$

which was insignificant to the 0.90 probability level. This shows that most of standard error of estimate value of 0.53 is made up of a replication error of 0.48. Most of the observed data seem consistent with this estimating equation. (See table II where the observed rating of the oxidized specimens and the calculated rank R_0, using eq. (A2), are compared.)

One could then use the estimating equation to make certain generalizations that are consistent with and extend the previous generalizations of the results. For example, Mn and misch metal (MM) are not significant in either direction, and V does not appear to improve oxidation resistance at Cr levels of 10 percent or greater. Both Ti and Si appear beneficial in a simple linear manner. As expected, Cr and Al are both beneficial but are not additive because of the Cr · Al interaction term. The most complex element is Mo whose immediate benefit is not obvious from the equation - particularly when both Cr and Al are present in the alloy. It should be pointed out this equation appears valid particularly for interpolation between the various alloy levels.

Extrapolations beyond the compositional levels involve more risk.

Corrosion test results. - The corrosion data were correlated in a similar manner as the oxidation data with the corrosion test specimens being rated on a scale from 1 (no apparent corrosion attack) to 4 (catastrophic corrosion failure). (Note that a brittleness rating was not included.) A 30-term equation similar to equation (A2) was used for the corrosion data. Seventy data sets were analyzed, including 11 replicates of 304 SS. The final estimating equation for correlating corrosion resistance to composition was determined as follows:

$$\begin{aligned} R_c = {} & 6.85 - 0.58\%\ Cr + 12.13\%\ Y - 1.74\%\ Si - 0.13\%\ V - 0.09\%\ Mo + 1.91\%\ Mn \\ & - 0.18\%\ Ti_2 + 7.69\%\ MM + 0.02\%\ Cr^2 + 0.44\%\ Si^2 - 0.09\%\ Mn^2 - 0.01\%\ Cr \cdot \%\ Al \\ & - 0.88\%\ Cr \cdot \%\ Y - 0.13\%\ Cr \cdot \%\ Mn - 0.47\%\ Cr \cdot \%\ MM + 0.02\%\ Cr \cdot \%\ Al \cdot \%\ Mn \\ & - 0.04\%\ Al \cdot \%\ Mo - 0.19\%\ Al \cdot \%\ Mn \pm 0.33 \end{aligned} \qquad \text{(A3)}$$

Twelve of the first 30 terms were dropped from the corrosion estimating equation. The final coefficient of variation was just over 0.94. Table III compares the observed rating of the corrosion test specimens and the calculated rank R_c using equation (A3), where again agreement is quite good. Here, a lack-of-fit estimate was not made because replicate modified alloys were not tested.

The estimating equation is more complicated for corrosion than oxidation, involving not only more terms but also more higher-order terms.

Combined test results. - The simplest approach to combining the oxidation and corrosion test results is to simply add both equations and use a combined ranking which includes both oxidation and corrosion resistance. In this case values will be compared with 304 SS, which is rated 2.0 in oxidation resistance on a scale from 1.0 to 5.0 and 1.0 in corrosion resistance on a scale from 1.0 to 4.0. Because the computed equation is quite complex, it is easier to present it graphically for alloy levels of interest. Figure 14 shows equations (A2) plus (A3) as a function of the Cr and Al contents for a fixed $R_o + R_c$ level of 3.0, which represents the combined oxidation/corrosion resistance of 304 SS. This is an isoattack contour plot: every area to the right of the solid line is predicted to have at least the resistance of 304 SS. Other contours are also shown for various Mo and/or Ti levels which sum to 4.0 percent. For comparison some of the experimentally observed combined $R_o + R_c$ values are also shown for other alloys.

The plots indicate that without Al, the minimum Cr content is about 13 to 14 percent plus 1 percent Ti or greater with adequate Mo levels. With about 2 percent Al, the Cr level can be dropped to about 12 percent with 1 percent Mo and 3 percent Ti. Twelve percent Cr appears to be the practical lower limit without a high degree of embrittlement of the alloy. The plot indicates, for example, that a 10 percent Cr alloy would require about 6 percent Al along with 0.5 percent Mo and 3.5 percent Ti to have comparable oxidation and corrosion resistance to 304 SS. However, such an alloy would be strongly ferritic and probably quite brittle.

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TABLE I. - CHEMICAL ANALYSIS OF MODIFIED COMPOSITION 304 STAINLESS STEEL ALLOYS

Alloy	Analyzed solute content, wt %				
Standard 304 and master alloys	Cr	Ni	Mn	Si	C
304 stainless steel (standard)	18.68	8.65	1.13	0.65	0.061
304 master alloy -18Cr	18.20	8.76	1.10	.62	.057
Modified 304 master alloy -16Cr	14.16	8.15	1.08	.62	.058
Modified 304 master alloy -12Cr	11.13	8.10	1.09	.63	.066
Modified 304 master alloy -8Cr	7.90	8.06	1.03	.63	.061
Cr modified	Cr				
-16Cr	14.82				
-14Cr	12.82				
-12Cr	11.22				
-10Cr	9.38				
-8Cr	7.48				
Cr and Al modified	Cr	Al			
-16Cr - 2Al	15.51	2.21			
- 4Al	15.20	4.25			
- 6Al	14.83	6.87			
-12Cr - 2Al	11.70	2.30			
- 4Al	11.47	4.23			
- 6Al	11.24	7.07			
-8Cr - 2Al	7.33	1.99			
- 4Al	7.07	4.07			
- 6Al	7.05	6.29			
Cr and misch metal (MM) modified	Cr	MM			
-16Cr - 0.1MM	15.97	0.10			
- 0.2MM	15.93	.38			
-12Cr - 0.1MM	12.00	.18			
- 0.2MM	11.90	.33			
-8Cr - 0.1MM	7.96	.16			
- 0.2MM	7.71	.34			
Cr and Si modified series	Cr	Si			
-16Cr - 1.65Si	15.58	1.57			
- 2.65Si	15.34	2.62			
-12Cr - 1.65Si	11.87	1.62			
- 2.65Si	11.63	2.59			
-8Cr - 1.65Si	7.92	1.62			
- 2.65Si	7.68	2.55			
Cr and Ti modified	Cr	Ti			
-16Cr - 1Ti	15.12	0.95			
- 2Ti	14.99	2.01			
-12Cr - 1Ti	11.54	1.42			
- 2Ti	11.41	1.91			
-8Cr - 1Ti	7.63	.98			
- 2Ti	7.67	1.96			

Alloy	Analyzed solute content, wt %		
Cr and Y modified	Cr	Y	
-16Cr - 0.1Y	15.91	0.07	
- 0.2Y	15.82	.18	
-12Cr - 0.1Y	12.04	.06	
- 0.2Y	12.00	.18	
-8Cr - 0.1Y	9.04	.05	
- 0.2Y	7.94	.14	
Cr and Mn modified	Cr	Mn	
-16Cr - 3Mn	14.60	2.91	
-12Cr - 7Mn	10.65	7.05	
-8Cr - 11Mn	6.93	10.50	
Cr and Mo modified	Cr	Mo	
-16Cr - 2Mo	14.53	2.06	
-12Cr - 6Mo	10.43	6.05	
-8Cr - 10Mo	6.76	9.52	
Cr and V modified	Cr	V	
-16Cr - 2V	16.80	2.11	
-12Cr - 6V	12.40	6.02	
-8Cr - 10V	7.88	10.40	
Cr, Al, and Mo modified	Cr	Al	Mo
16Cr - 2Al - 2Mo	15.05	1.99	1.72
- 4Mo	15.00	2.00	3.81
12Cr - 2Al - 2Mo	11.31	2.06	2.06
- 4Mo	10.91	2.02	4.91
8Cr - 2Al - 2Mo	7.57	1.98	1.97
- 4Mo	7.40	2.01	3.63
Cr, Al, and Mn modified	Cr	Al	Mn
-16Cr - 4Al - 4Mn	14.67	3.95	3.88
-12Cr - 4Al - 4Mn	11.03	4.01	3.94
-8Cr - 4Al - 4Mn	7.32	4.00	3.70
16Cr - 6Al - 7Mn	13.85	5.89	6.46
-12Cr - 6Al - 7Mn	10.45	5.91	5.97
-8Cr - 6Al - 7Mn	6.94	5.91	6.18

TABLE II. - OXIDATION TEST RESULTS FOR MODIFIED COMPOSITION 304 STAINLESS STEEL ALLOYS

[Cyclic oxidation test: 200 hr at 870° C.]

Alloy modification nominal composition, wt %	Number of cycles	Final observed weight change, $\Delta w/A$, mg/cm^2	Spall appearance	X-ray diffraction results[a] (oxides identified in scale and spall)	Oxidation range, R_o	
					Observed	Calculated[b]
304 Stainless steel (standard)	200	-23.25	Moderate	$Cr_2O_3/Fe_2O_3/Fe_3O_4$	2.0	2.0
		-25.16	↓	↓	↓	↓
		-15.95	↓	↓	↓	↓
		-14.45	↓	↓	↓	↓
		-15.30	↓	↓	↓	↓
		-15.01	↓	↓	↓	↓
		-13.91	↓	↓	↓	↓
		-19.35	↓	↓	↓	↓
		-17.90	↓	↓	↓	↓
		-17.97	↓	↓	↓	↓
		-12.03	↓	↓	↓	↓
Cr modified						
- 16Cr	100	-93.16	Moderate	Fe_2O_3/Fe_3O_4	3.5	3.2
- 14Cr	100	-165.77	Heavy	↓	4	3.7
- 12Cr	200	-273.0	Massive	↓	4.5	4.2
- 10Cr	100	-265.0	Massive	↓	5	4.8
- 8Cr	100	-371.5	Massive	↓	5	5.3
Cr and Al modified						
-16Cr - 2Al	200	1.52	Negligible	Cr_2O_3/Fe_3O_4	1.5	2.1
-16Cr - 4Al	↓	.76	Negligible	$Cr_2O_3/\alpha Al_2O_3/Fe_3O_4$	1	1.4
-16Cr - 6Al	↓	.25	Negligible	$Cr_2O_3/\alpha Al_2O_3$	1	.4
-12Cr - 2Al	↓	62.01	Moderate	$Cr_2O_3/Fe_2O_3/Fe_3O_4$	4	3.0
-12Cr 4Al	↓	2.22	Negligible	Cr_2O_3/Fe_3O_4	1.5	2.1
-12Cr - 6Al	↓	.35	Negligible	αAl_2O_3	1	.8
-8Cr - 2Al	60	-134.54	Heavy	Fe_2O_3/Fe_3O_4	4.5	4.2
-8Cr - 4Al	175	-34.31	Moderate	Fe_2O_3/Fe_3O_4	4	3.1
-8Cr - 6Al	200	-.03	Negligible	$\alpha Al_2O_3/Cr_2O_3$	1	1.8
Cr and misch metal (MM) modified						
-16Cr - 0.1MM	200	-161.69	Heavy	Fe_2O_3/Fe_3O_4	3.5	2.8
-16Cr - 0.2MM	200	-1.57	Light		2	2.8
-12Cr - 0.1MM	↓	-181.2	Heavy[c]	Fe_2O_3/Fe_3O_4	4.5	4.0
-12Cr - 0.2MM	↓	-62.50	Heavy[c]	↓	5	4.0
-8Cr - 0.1MM	100	-361.16	Massive[c]	↓	5	5.2
-8Cr - 0.2MM	100	-448.42	Heavy	↓	5	5.3
Cr and Si modified						
-16Cr - 1.65Si	200	-14.18	Moderate	Fe_2O_3/Fe_3O_4	2.5	2.5
-16Cr - 2.65Si	↓	-.20	Light	↓	2.5	2.1
-12Cr - 1.65Si	↓	-129.6	Massive	↓	3.5	3.6
-12Cr - 2.65Si	↓	-26.00	Moderate	↓	2.5	3.2
-8Cr - 1.65Si	↓	-70.47	Heavy[c]	↓	5	4.7
-8Cr - 2.65Si	↓	38.55	Moderate[c]	↓	4.5	4.4
Cr and Ti modified						
-16Cr - 1Ti	200	0.96	Negligible	Cr_2O_3/Fe_3O_4	2	2.8
-16Cr - 2Ti	↓	-11.74	Moderate	$Cr_2O_3/Fe_2O_3/Fe_3O_4$	2.5	2.4
-12Cr - 1Ti	↓	-37.73	Heavy	Cr_2O_3/Fe_2O_3	4	3.7
-12Cr - 2Ti	↓	-66.86	Heavy	Cr_2O_3/Fe_3O_4	4	3.5
-8Cr - 1Ti	↓	142.52	Moderate[c]	$Cr_2O_3/Fe_2O_3/Fe_3O_4$	4.5	5.0
-8Cr - 2Ti	↓	-113.78	Massive	$Cr_2O_3/Fe_2O_3/Fe_3O_4$	4.5	4.6

TABLE II. - Concluded.

[Cyclic oxidation test: 200 hr at 870° C.]

Alloy modification nominal composition, wt %	Number of cycles	Final observed weight change, $\Delta w/A$, mg/cm^2	Spall appearance	X-ray diffraction results[a] (oxides identified in scale and spall)	Oxidation range, R_o	
					Observed	Calculated[b]
Cr and Y modified						
-16Cr - 0.1Y	200	-3.69	Light	Cr_2O_3/Fe_2O_3/Spinel-8.45	2	2.8
-16Cr - 0.1Y	↓	-.08	Negligible	Cr_2O_3/Fe_2O_3/Spinel-8.45	1.5	2.7
-12Cr - 0.1Y		-121.60	Heavy[c]	Fe_2O_3/Fe_3O_4	3	3.9
-12Cr - 0.2Y		-36.42	Light[c]	↓	4.5	3.9
-8Cr - 0.1Y	90	-306.54	Massive[c]		5	4.8
-8Cr - 0.2Y	90	-308.47	Massive		5	5.1
Cr and Mn modified						
-16Cr - 3Mn	200	-201.51	Heavy	Fe_2O_3/Fe_3O_4	4	3.2
-12Cr - 7Mn	200	-375.3	Massive	$Cr_2O_3/Fe_2O_3/Fe_3O_4/Mn_2O_3$	4.5	4.4
-8Cr - 11Mn	200	-512.2	Massive	$Cr_2O_3/Fe_2O_3/Fe_3O_4/Mn_2O_3$	5	5.5
Cr and Mo modified						
-16Mo - 2Mo	200	-131.42	Moderate	Fe_2O_3/Fe_3O_4	3	3.1
-12Cr - 6Mo	115	-170.28	Massive	Fe_2O_3/Fe_3O_4	4	3.9
-8Cr - 10Mo	115	-102.26	Massive	Fe_2O_3/Fe_3O_4	5	4.5
Cr and V modified						
-16Cr - 2V	200	-94.84	Heavy	Fe_2O_3/Fe_3O_4	4	3.4
-12Cr - 6V	145	-222.32	Heavy	Fe_2O_3/Fe_3O_4/Tapiolite	4.5	4.9
-8Cr - 10V	145	-127.57	Heavy	Fe_2O_3/Fe_3O_4/Tapiolite	4.5	4.4
Cr, Al, and Mo modified						
-16Cr - 2Al - 2Mo	200	2.02	Negligible	Cr_2O_3/Spinel-8.45	2	1.4
	↓	2.43	Negligible	↓	1	1.4
-16Cr - 2Al - 4Mo		1.71	Negligible		1	1.3
		2.20	Negligible		1.5	1.3
-12Cr - 2Al - 2Mo		.91	Light		2.5	2.8
		.93	Light		2.5	2.8
-12Cr - 2Al - 4Mo	145	-236.77	Massive	Fe_2O_3/Fe_3O_4	4	4.1
	200	-206.10	Massive	↓	4.5	4.1
-8Cr - 2Al - 2Mo	100	-187.30	Massive		4.5	4.2
	100	-176.51	Massive		5	4.2
-8Cr - 2Al - 4Mo	200	-161.66	Massive[c]		5	5.1
	200	103.73	Light[c]		4.5	5.1
Cr, Al, and Mn modified						
-16Cr - 4Al - 4Mn	200	2.20	Negligible	Fe_2O_3/Spinel-8.45	1.5	1.6
-12Cr - 4Al - 4Mn	↓	2.46	Negligible	$Mn_2O_3/Fe_2O_3/Fe_3O_4$	1.5	2.3
-8Cr - 4Al - 4Mn		-133.04	Massive	Fe_2O_3/Fe_3O_4	3.5	3.1
-16Cr - 6Al - 7Mn		.36	Negligible	α-Al_2O_3/Fe_2O_3	1.5	.9
-12Cr - 6Al - 7Mn		.43	Negligible	α-Al_2O_3	1.5	1.5
-8Cr - 6Al - 7Mn		-.09	Light	α-$Al_2O_3/Mn_2O_3/Fe_3O_4$	2	2.1

[a] Oxides identified in scall and spall.

[b] See eq. (A2).

[c] Growth of specimen observed during test.

TABLE III. - CORROSION TEST RESULTS FOR MODIFIED COMPOSITION 304 STAINLESS STEEL ALLOYS

[Corrosion test: 48 hr in boiling Cu rich $CuSO_4$-H_2SO_4 solution.]

Alloy modification nominal composition, wt %	Apparent corrosion resistance				Bend test results			Corrosion rank, R_c	
	No apparent attack	Slight attack	Severe attack	Catastrophic failure	Ductile	Cracks	Failure	Observed	Calculated[a]
304 stainless steel (standard)	X				X			1.0	1.0
Cr modified									
-16Cr	X				X			1	1.4
-14Cr	X				X			1	1.8
-12Cr		X	X[c]			X		2.5	2.2
-10Cr			X			X		3	2.8
-8Cr				X				4	3.6
Cr and Al modified									
-16Cr - 2Al	X				X			1	1.2
-16Cr - 4Al	X						X	1	1.2
-16Cr - 6Al	X						X	1	1.2
-12Cr - 2Al		X					X	2	1.9
-12Cr - 4Al		X					X	2	1.8
-12Cr - 6Al		X					X	2	1.7
-8Cr - 2Al			X				X	3	3.4
-8Cr - 4Al			X[d]	X[d]			X	3.5	3.3
-8Cr - 6Al			X				X	3	3.0
Cr and misch metal (MM) modified									
-16Cr - 0.1MM	X					X		1	1.2
-16Cr - 0.2MM	X					X		1	1.3
-12Cr - 0.1MM			X			X		3	2.3
-12Cr - 0.2MM			X			X		3	2.7
-8Cr - 0.1MM				X				4	4.0
-8Cr - 0.2MM				X				4	4.9
Cr and Si modified									
-16Cr - 1.65Si	X				X			1	0.5
-16Cr - 2.65SI	X				X			1	.7
-12Cr - 1.65Si								1	1.3
Cr and Si modified series									
-12Cr - 2.65Si	X				X			1	1.5
-8Cr - 1.65Si			X		X			3	2.7
-8Cr - 2.65Si		X[c]	X[c]		X			2.5	2.9
Cr and Ti modified									
-16Cr - 1Ti	X				X			1	1.1
-16Cr - 2Ti					X			1	1.0
-12Cr - 1Ti		X				X		2	1.8
-12Cr - 2Ti						X		2	1.8
-8Cr - 1Ti						X		3	3.3
-8Cr - 2Ti			X			X		3	3.1

TABLE III. - Concluded.

[Corrosion test: 48 hr in boiling Cu rich $CuSO_4$-H_2SO_4 solution.]

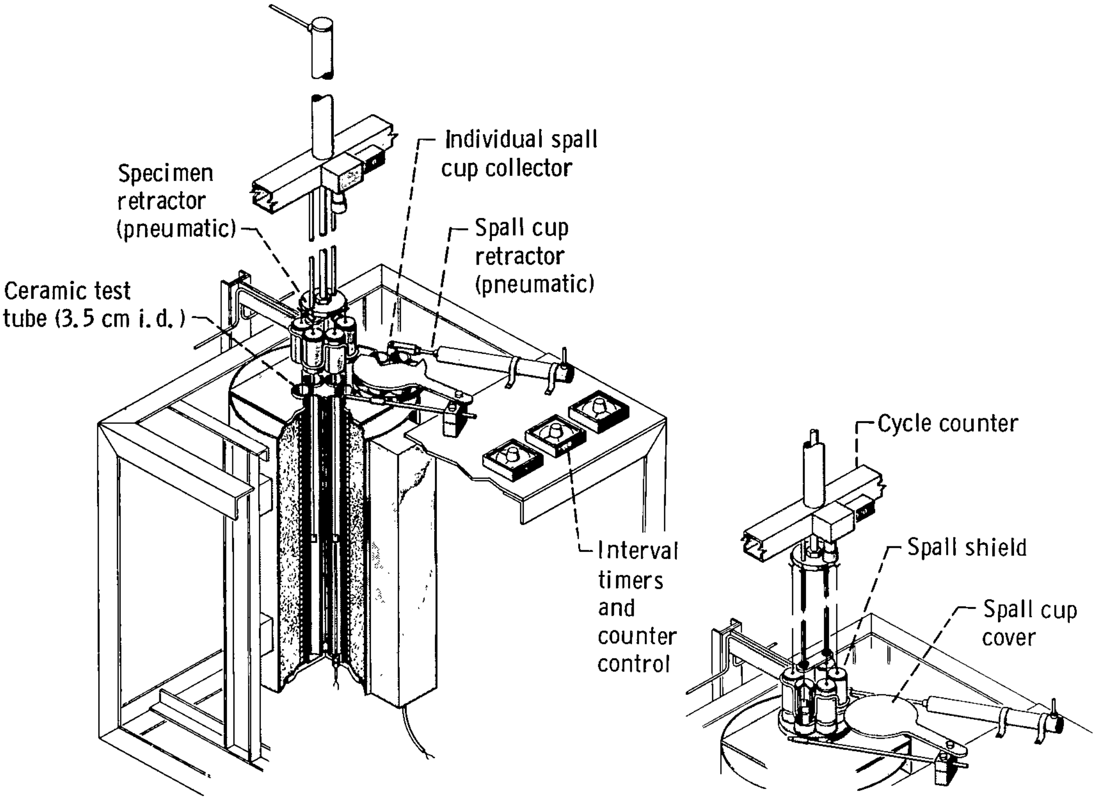
Alloy modification nominal composition, wt %	Apparent corrosion resistance				Bend test results			Corrosion rank, R_c	
	No apparent attack	Slight attack	Severe attack	Catastrophic failure	Ductile	Cracks	Failure	Observed	Calculated[a]
Cr and Y modified									
-16Cr - 0.1Y					X			1	1.1
-16Cr - 0.2Y	X				X			1	.9
-12Cr - 0.1Y		X				X		2	2.1
-12Cr - 0.2Y		X					X	2	2.2
-8Cr - 0.1Y			X					4	3.2
-8Cr - 0.2Y			X					4	4.1
Cr and V modified									
-16Cr - 2V	X				X			1	0.8
-12Cr - 6V	X				X			1	1.1
-8Cr - 10V		X				X		2	2.0
Cr and Mn modified									
-16Cr - 2Mn	X				X			1	0.8
-12Cr - 6Mn	X				X			1	1.9
-8Cr - 10Mn				X				4	3.9
Cr and Mo modified									
-16Cr - 2Mo	X				X			1	1.2
-12Cr - 6Mo		X				X		2	1.9
-8Cr - 10Mo			X			X		3	3.0
Cr, Al, and Mo modified									
-16Cr - 2Al - 2Mo	X				X			1	1.0
-16Cr - 2Al - 4Mo	X					X		1	.6
-12Cr - 2Al - 2Mo	X				X			1	1.7
-12Cr - 2Al - 4Mo	X				X			1	1.3
-8Cr - 2Al - 2Mo			X			X		3	3.0
-8Cr - 2Al - 4Mo			X			X		3	2.7
Cr, Al, and Mn modified									
-16Cr - 4Al - 4Mn		X					X	2	1.6
-16Cr - 6Al - 7Mn		X					X	2	2.2
-12Cr - 4Al - 4Mn			X				X	3	2.7
-12Cr - 6Al - 7Mn			X				X	3	3.0

[a] From eq. (A3).

[b] Eleven samples.

[c] Slight to severe attack.

[d] Severe attack to catastrophic failure.



(a) Specimens at test temperature.

(b) Specimens cooled to ambient temperature.

Figure 1. - Schematic representation of high-temperature test apparatus for measuring cyclic oxidation resistance of experimental alloys (ref. 6).

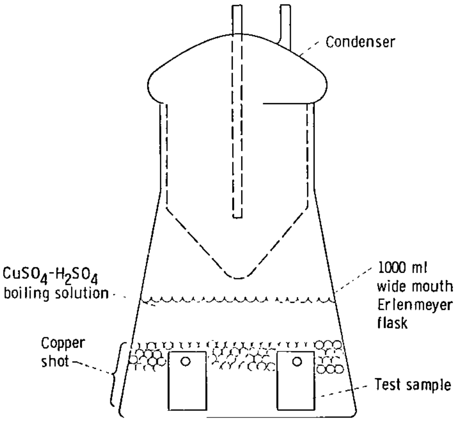
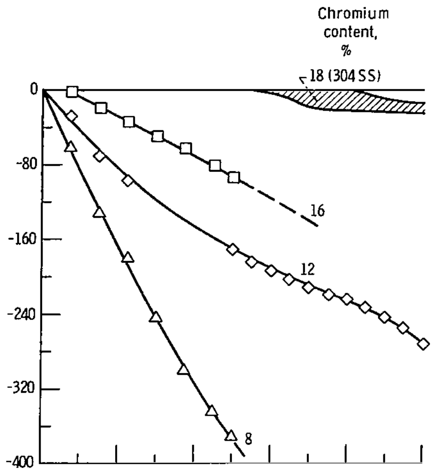
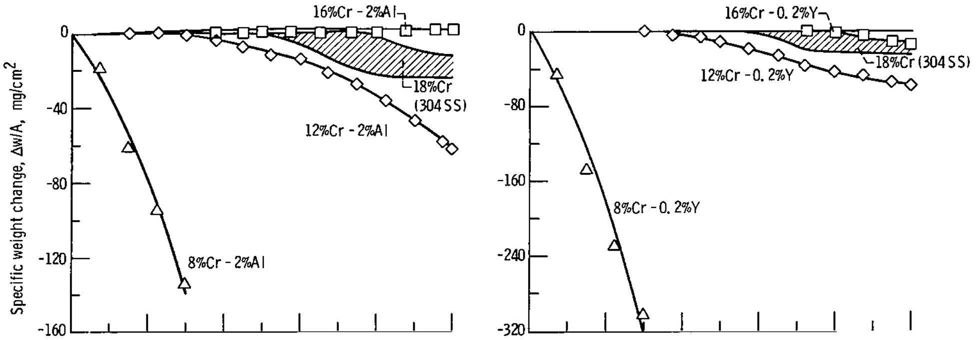


Figure 2. - Schematic representation of copper - copper sulfate - sulfuric acid test for detecting susceptibility to intergranular attack in experimental alloys.

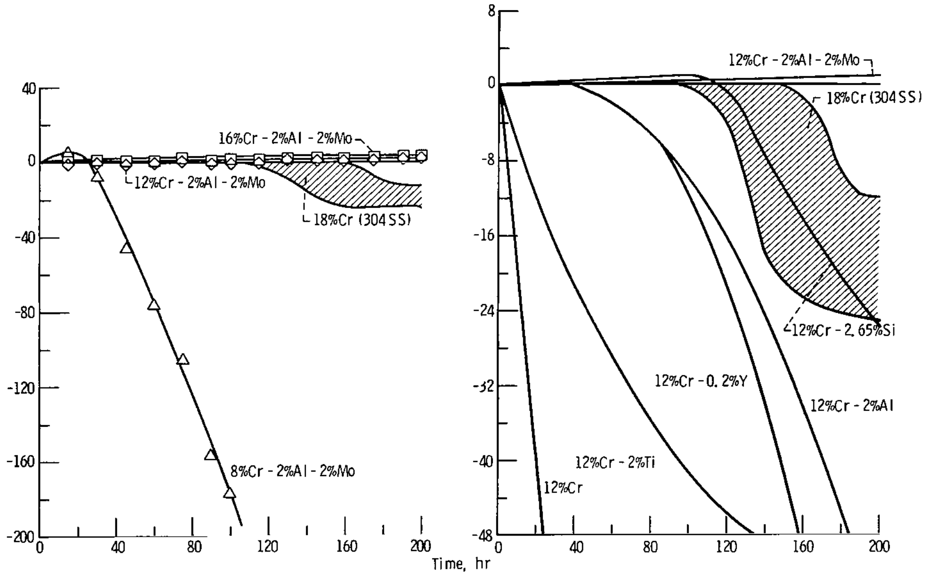


(a) Effect of partial removal of chromium from 304 stainless steel.



(b) Effect of 2 percent aluminum additions to reduced-chromium 304 stainless steel.

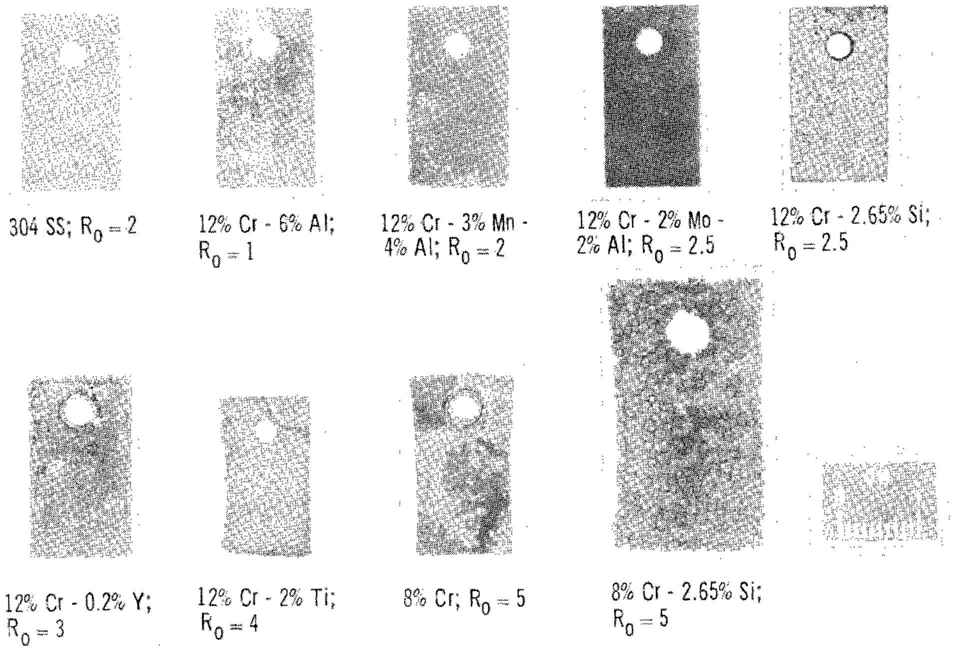
(c) Effect of 0.2 percent yttrium additions to reduced-chromium 304 stainless steel.



(d) Effect of 2 percent aluminum plus 2 percent molybdenum additions to reduced-chromium 304 stainless steel.

(e) Effect of selected alloying additions to 12 percent chromium content 304 stainless steel.

Figure 3. - Specific weight change data as function of cyclic oxidation time. Oxidation temperature, 870° C.



304 SS; $R_0 = 2$

12% Cr - 6% Al; $R_0 = 1$

12% Cr - 3% Mn - 4% Al; $R_0 = 2$

12% Cr - 2% Mo - 2% Al; $R_0 = 2.5$

12% Cr - 2.65% Si; $R_0 = 2.5$

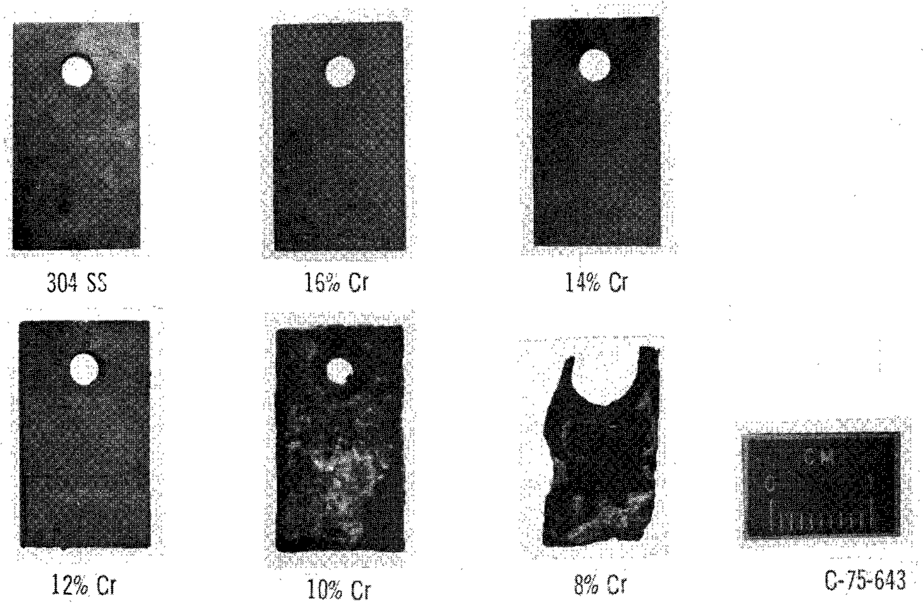
12% Cr - 0.2% Y; $R_0 = 3$

12% Cr - 2% Ti; $R_0 = 4$

8% Cr; $R_0 = 5$

8% Cr - 2.65% Si; $R_0 = 5$

Figure 4. - Typical appearance of cyclic-oxidation-tested modified 304 stainless steel specimens representative of five categories of oxidation resistance R_0, ranging from $R_0 = 1$ (best) to $R_0 = 5$ (poorest).



304 SS

16% Cr

14% Cr

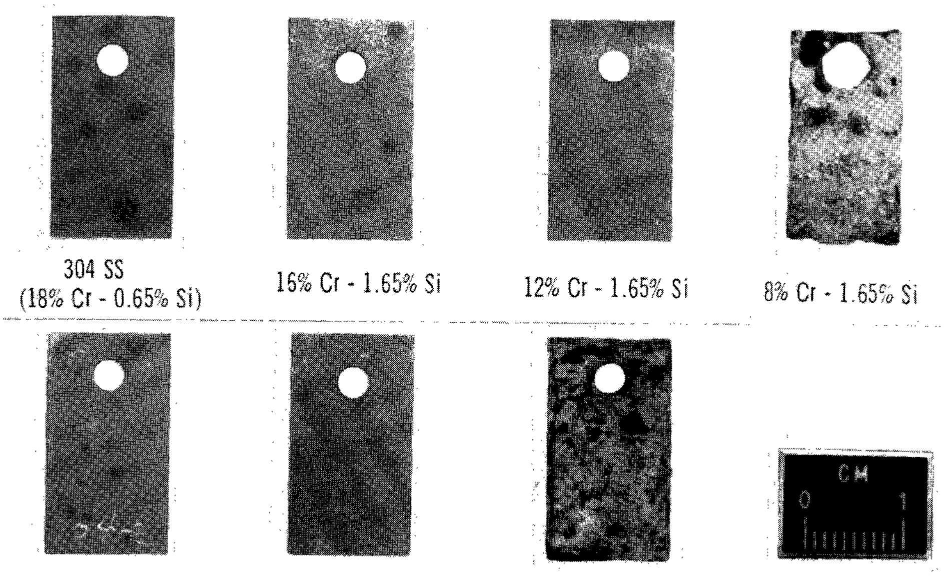
12% Cr

10% Cr

8% Cr

C-75-643

Figure 5. - Surface appearance of chromium modified 304 stainless steel alloys after corrosion testing in boiling $CuSO_4$-H_2SO_4.



304 SS (18% Cr - 0.65% Si)

16% Cr - 1.65% Si

12% Cr - 1.65% Si

8% Cr - 1.65% Si

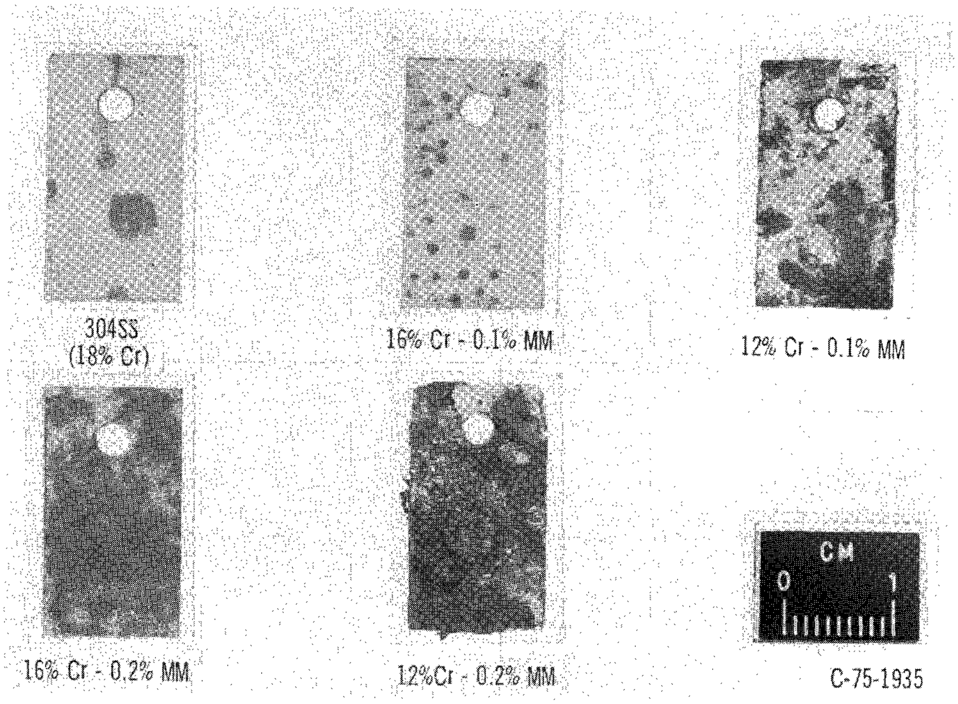
16% Cr - 2.65% Si

12% Cr - 2.65% Si

8% Cr - 2.65% Si

C-75-1016

Figure 6. - Surface appearance of chromium-silicon modified 304 stainless-steel alloys after corrosion testing in boiling $CuSO_4$-H_2SO_4.



304SS (18% Cr)

16% Cr - 0.1% MM

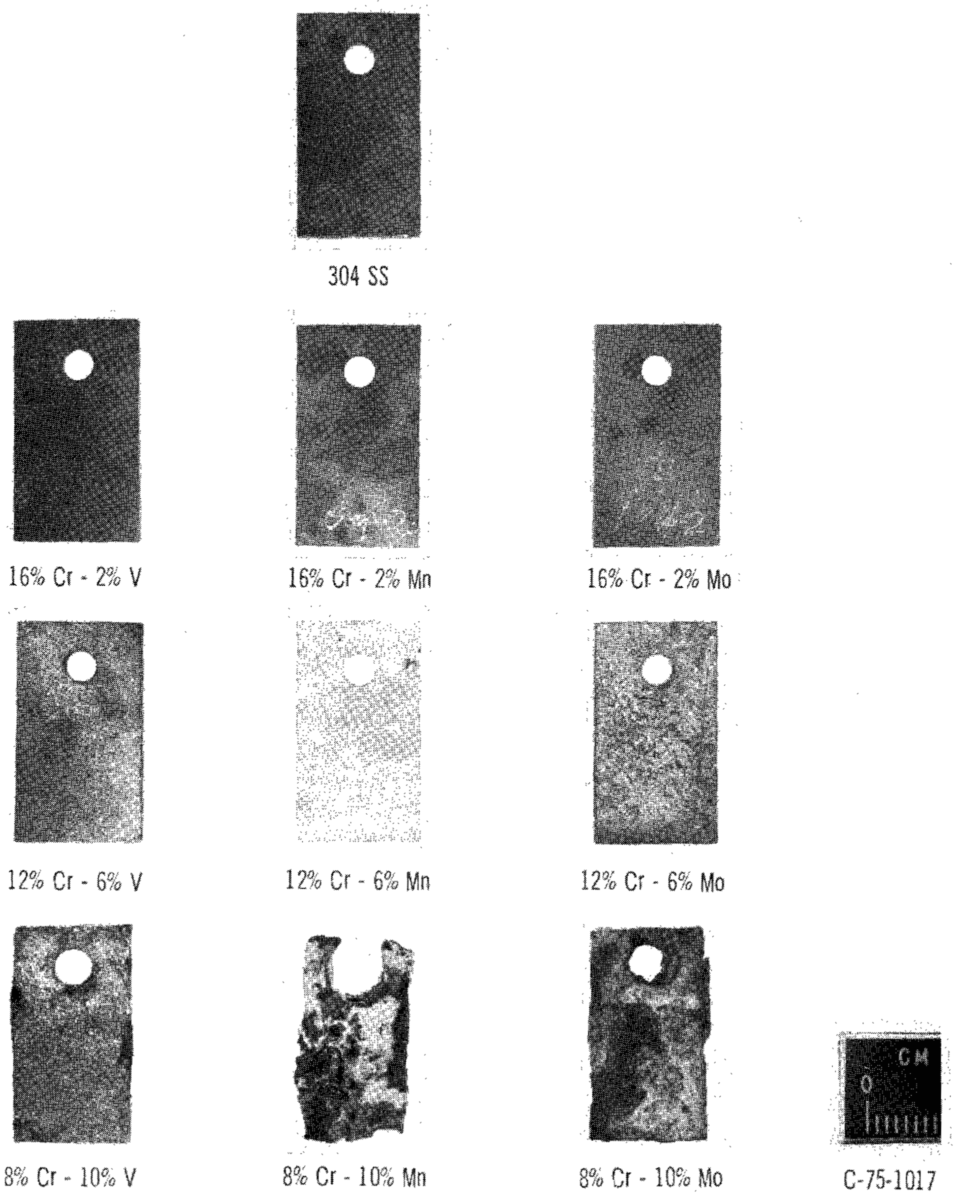
12% Cr - 0.1% MM

16% Cr - 0.2% MM

12%Cr - 0.2% MM

C-75-1935

Figure 7. - Surface appearance of chromium and misch metal modified 304 stainless steel alloys after corrosion testing in boiling $CuSO_4$-H_2SO_4.



304 SS

16% Cr - 2% V

16% Cr - 2% Mn

16% Cr - 2% Mo

12% Cr - 6% V

12% Cr - 6% Mn

12% Cr - 6% Mo

8% Cr - 10% V

8% Cr - 10% Mn

8% Cr - 10% Mo

C-75-1017

Figure 8. - Surface appearance of chromium-vanadium, chromium-manganese, and chromium-molybdenum modified 304 stainless steel alloys after corrosion testing in boiling $CuSO_4$-H_2SO_4.

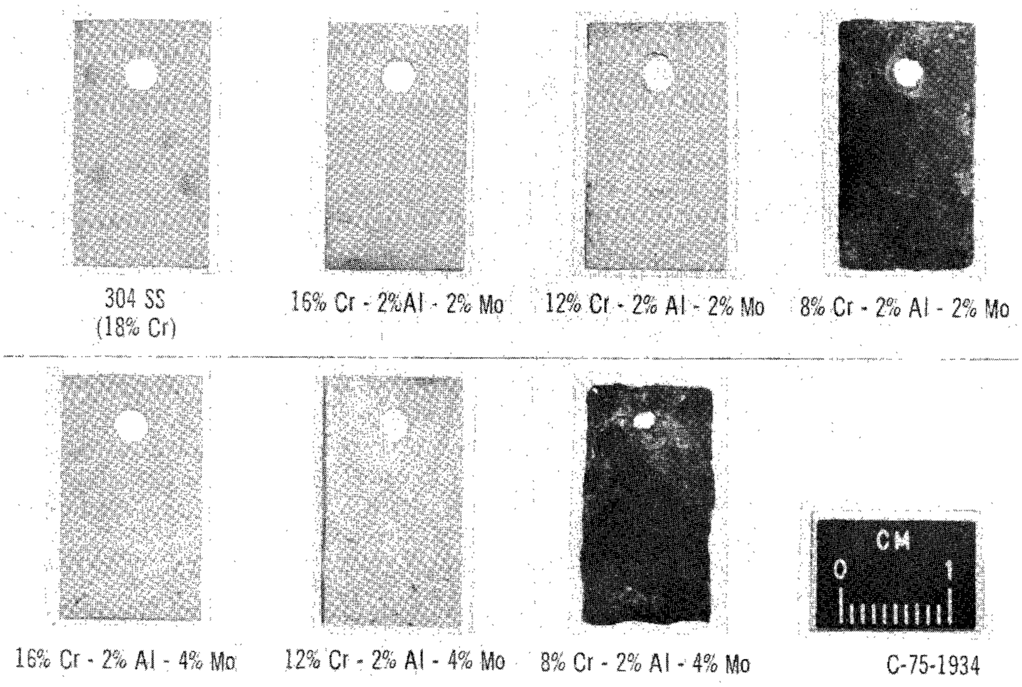
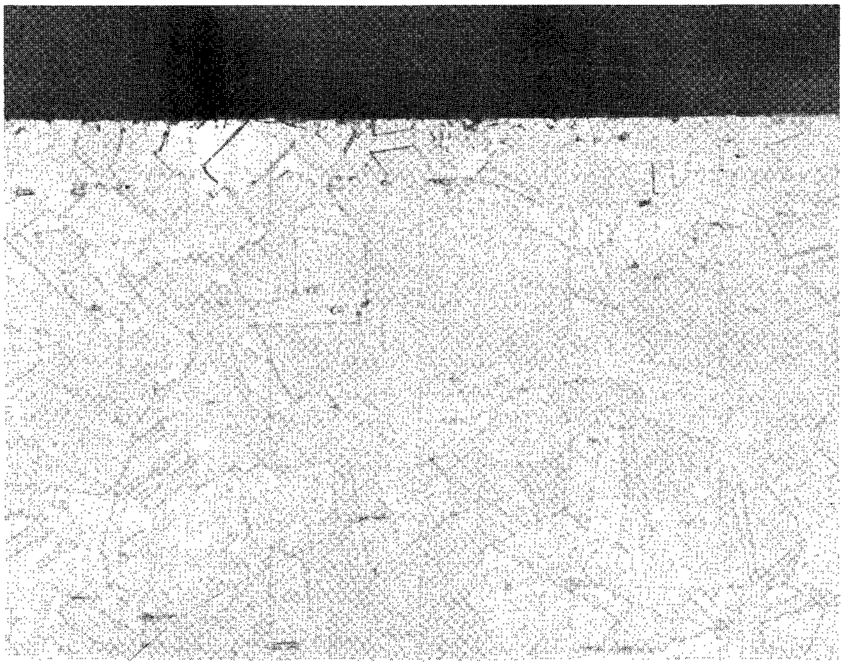
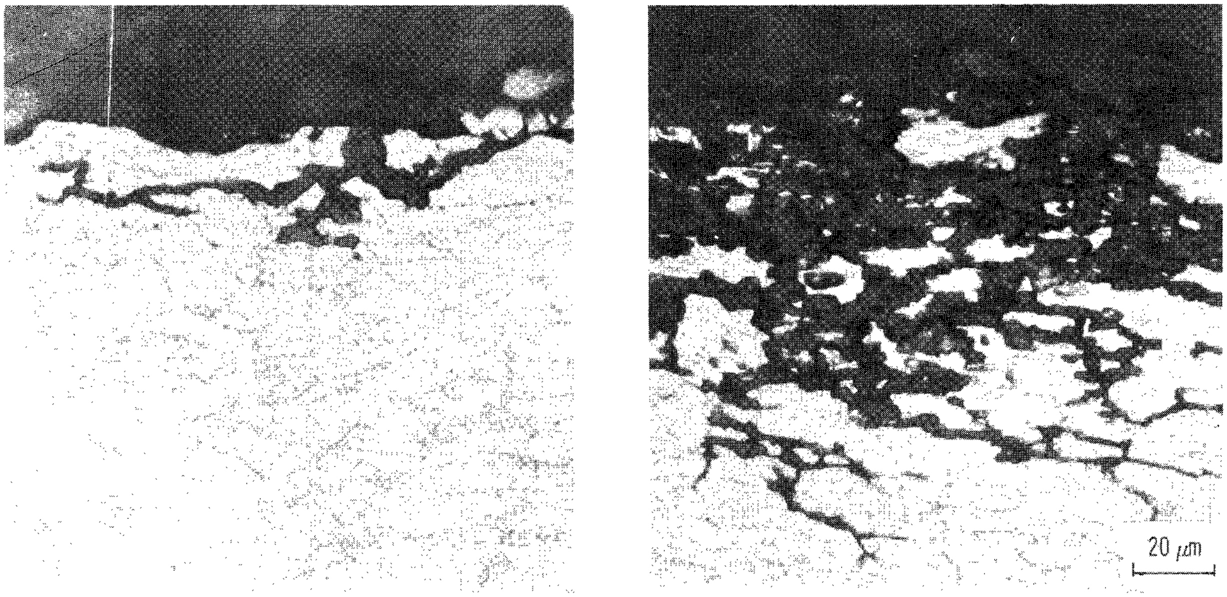


Figure 9. - Surface appearance of chromium-aluminum-molybdenum modified series of 304 stainless steel alloys after corrosion testing in boiling $CuSO_4$-H_2SO_4.



(a) Standard 304 stainless steel alloy (18% Cr). No apparent attack.



(b) Modified 304 stainless steel: 12% Cr. Slight attack.

(c) Modified 304 stainless steel: 10% Cr. Severe attack.

Figure 10. - Comparison of microstructures of standard 304 stainless steel alloy and 12 and 10 percent chromium modified alloys after corrosion testing in boiling $CuSO_4$-H_2SO_4. Etchant, electrolytic 10 percent oxalic acid.

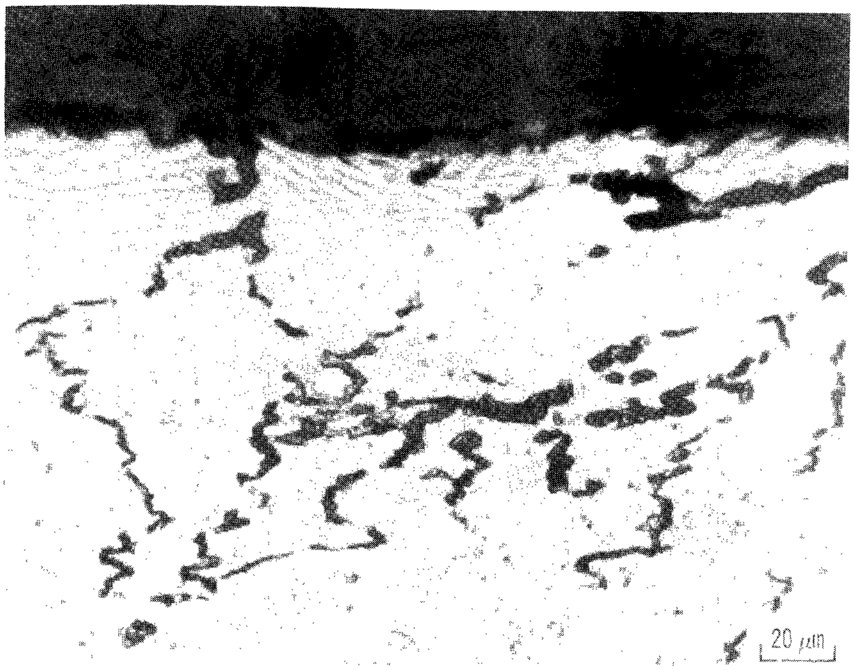
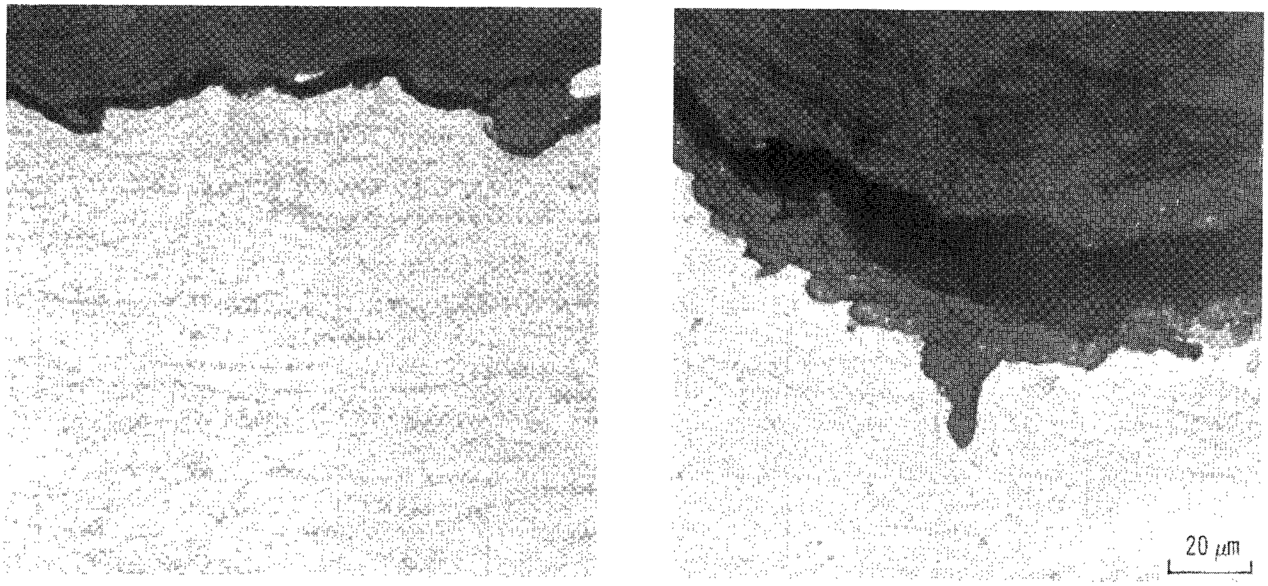


Figure 11. - Microstructure of chromium-yttrium modified 304 stainless steel alloy (12% Cr - 0.1% Y) illustrating grain boundary corrosion attack during testing in boiling $CuSO_4$-H_2SO_4. Etchant, electrolytic 10 percent oxalic acid.



(a) 12% Cr - 2.65% Si. No apparent attack.

(b) 8% Cr - 2.65% Si. Slight to severe attack.

Figure 12. - Microstructures of chromium-silicon modified series of 304 stainless steel alloys illustrating bulk corrosion attack during testing in boiling $CuSO_4$-H_2SO_4. Etchant, electrolytic 10 percent oxalic acid.

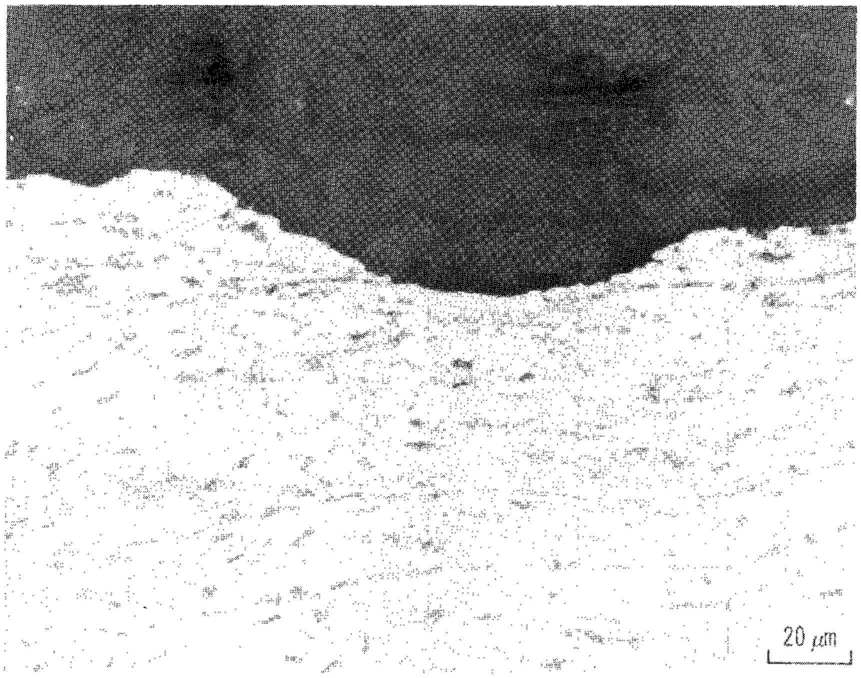


Figure 13. - Microstructure of an 8 percent Cr-10 percent V modified 304 stainless steel alloy after corrosion testing in boiling $CuSO_4$-H_2SO_4 illustrating slight attack. Etchant; electrolytic, 10 percent oxalic acid.

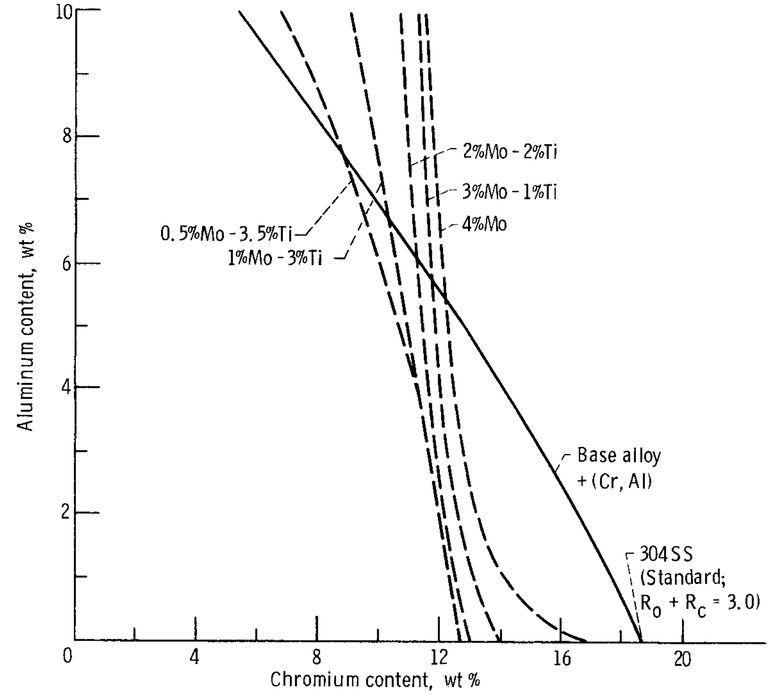


Figure 14. - Combined corrosion and oxidation resistance of modified 304 stainless steel for various alloy levels. Values to right of curves are equal or more resistant than 304 stainless steel.

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