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NEW ALLOYS TO CONSERVE CRITICAL ELEMENTS

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ABSTRACT

Based on availability of domestic reserves, chromium is one of the most critical elements within the U.S. metal industry. At NASA-Lewis Research Center, new alloys having reduced chromium contents which offer potential as substitutes for higher chromium containing alloys currently in use are being investigated. This paper focuses primarily on modified Type 304 stainless steels having one-third less chromium, but maintaining comparable oxidation and corrosion properties to that of Type 304 stainless steel, the largest single use of chromium. Substitutes for chromium in these modified Type 304 stainless steel alloys include silicon and aluminum plus molybdenum.

INTRODUCTION

There is a growing awareness among those in industry and in government that the U.S. can expect to face shortages of critical materials on a repeated basis. The oil crisis of 1973, the gas shortage in parts of the U.S. in 1977, and the coal shortage of 1978 have all served to emphasize the importance of having an adequate supply of raw materials to meet demand or to have a contingency plan if a materials shortage does occur. The aforementioned shortages have been due to cartel actions, low reserves, and strikes. In general, these shortages have been of relatively short duration and have involved materials of which the U.S. has some reserves (oil and gas) or adequate reserves such as coal. The metal industry also faces shortages of critical elements due to possible cartel action, from the aluminum producing countries for example, as well as from other causes. Several surveys and conferences have been conducted by government and industry to identify those metals that should be considered to be in a shortage or critical category (refs. 1-3). The results of these conferences and other surveys of materials availability have identified chromium as one of the more critical elements within the metals industry. 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. 4). 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 (ref. 5). These and other activities have established that the bulk of Cr is consumed in the making of stainless steels - specifically Type 304 stainless steel.

To investigate alternatives for possible contingency plans to conserve Cr, a program was undertaken at the NASA-Lewis Research Center to investigate means of reducing chromium in commercial stainless steels by substituting more abundant or less expensive elements with the intent of maintaining properties common to Type 304 stainless steel (304SS). The purpose of this paper is to present some of the oxidation and corrosion properties of new stainless steels with only 12% Cr, which represents a potential savings of 33% of the chromium consumed in the production of 304SS.

THE CRITICALITY OF CHROMIUM

As a basis for deciding which elements may be considered critical to the U.S. metal industry, domestic reserves were selected as the primary indicator. Reserves are defined as known, identified ore deposits from which minerals can be extracted profitably with existing technology and under present economic conditions. A lack of reserves obviously necessitates importing metals from foreign sources. The amounts of several selected elements that the United States imports (ref. 6) are shown in figure 1 along with the major foreign sources for each element. As indicated, chromium and cobalt imports exceed 90 percent and are imported primarily from countries outside the Western Hemisphere. Further complicating the chromium picture is the fact that mining of Cr in the United States stopped in 1961, and the outlook for future mining is dim due to scarcity of even low-grade ores. Reclamation of Cr from scrap is the only viable domestic source for this critical element at this time.

Another factor leading to the identification of Cr as one of the more critical elements is the price trend of various metals over the past several years. In figure 2, the percent increase in price of several selected aerospace elements is shown (ref. 7). The price of Cr increased almost 300% over the time period 1969 to 1976 while the price increase of the remaining seven elements ranged from 90 to 175%. This price trend suggests that more domestically abundant elements may be economically substituted for chromium in years to come.

A final factor influencing the identification of Cr as a critical element is the importance of this metal to the United States economy. A break down by percent is shown in figure 3 for the primary usage of Cr. According to the findings of the National Materials Advisory Board Committee on Cr utilization, Cr is an essential element in the plating industry and in the chemical industry for such applications as pigments for paints and in leather tanning. The largest use of Cr, however, is for metallurgical applications in the manufacture of ferrous and non-ferrous alloys. Two-thirds of the metallurgical use of Cr is in the production of stainless steels where the excellent corrosion and oxidation resistance imparted by Cr when alloyed in Fe-Ni alloys makes Cr a very critical element. Stainless steels are used industry wide from such applications as aerospace, chemical and petro-chemical processing, to food handling and in homes for tableware and other uses. As figure 3 indicates, 304SS is the single largest use of Cr, comprising over 30 percent of the total United States consumption of Cr (ref. 8). In attempting to conserve this critical element, finding substitutes for Cr in 304SS would have one of the largest impacts in achieving this conservation measure.

SUBSTITUTES FOR CHROMIUM

Commercial 304SS which has 18 percent Cr was used as a baseline to compare with the oxidation and corrosion properties of experimental alloys developed in this program. The effects on oxidation and corrosion of removing Cr from 304SS in 2% increments to as low as 8 percent Cr was explored followed by substituting the more domestically abundant elements or less expensive elements listed in figure 4. Some alloying elements which were substituted for Cr in 304SS were selected on the basis of their potential for protective oxide formation during high temperature oxidation. These included Al, Si, Ti, Y, and misch metal which is 99.7 percent rare earth metals containing 50 to 55 percent cerium. 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 18Cr-8Ni stainless steels (ref. 9). A preliminary investigation of the corrosion and oxidation properties of the modified composition 304SS indicated that 12 percent Cr was the minimum amount of Cr that would permit retention of corrosion and oxidation resistance comparable to that of 304SS (ref. 10). Results further showed that to achieve these comparable results, Si or Al plus Mo were effective substitutes for Cr.

Figures 5 through 7 illustrate the effects on corrosion and oxidation resistance of removing Cr from 304SS. Corrosion testing was conducted according to ASTM specification A262-70. Practice E under A262-70 is used in the aerospace industry to qualify commercial stainless steels and was selected as the corrosion test for the preliminary corrosion testing in this program. The test involved embedding specimens in copper shot, and then exposing them to a boiling solution of $CuSO_4$-H_2SO_4 for 48 hours. After exposure, the specimens were evaluated by their general appearance, by examination of the surface of specimens undergoing a 180° bend test, and by metallography. Figure 5 shows the general surface appearance of the alloys with decreased Cr content. At levels of 18 (standard 304SS), 16, and 14 Cr, no apparent attack occurred, and the specimens were ductile in bend testing after corrosion. However, at a 12 Cr level slight attack was noted, and cracks were observed upon bend testing. At the 10 and 8 Cr levels, severe and even catastrophic failure occurred during corrosion testing. These results support earlier work (ref. 11) where it was noted that above about 12 to 13 Cr, a dramatic decrease in corrosion rate occurs in Fe-10Ni-Cr alloys because of the formation of a protective, chromium-rich oxide film on the surface of the alloys. Microstructures of selected alloys are shown in figure 6 where the corrosion ranking, R_c, is given based on the evaluation criteria described previously. Also shown in figure 6(d) is the effect of adding 2.65 Si to the 12 Cr alloy which produces corrosion resistance in this series of alloys comparable to the 304SS baseline alloy shown in figure 6(a). The oxidation resistance of 304SS and alloys with reduced Cr contents is shown in figure 7. Specimens were normally cycled at 870°C for 15 hours followed by a minimum 20 minute cool-down time interval until a total of 200 hours was accumulated on the specimens. Chromium removal is noted to have a drastic effect on cyclic oxidation resistance of 304SS.

A subsequent program aimed at optimizing the composition with special emphasis on austenite stability as well as electrochemical corrosion properties led to further modification of the alloy composition involving the elements Ni and Mn. Alloy compositions of 304SS, the first generation alloys with 12 percent Cr, and the second generation alloys having more optimized compositions for corrosion, oxidation, and structure properties are listed in Table I.

EVALUATION OF NEW ALLOYS

Oxidation Resistance

The oxidation resistance of the modified composition 304SS alloys was evaluated by cyclic oxidation testing at 870°C for 200 hours as described above. Although 870°C exceeds the normal use temperatures of 304SS, it was chosen to characterize the oxidation resistance of the various alloys in a reasonable length of time since oxidation of 304SS occurs quite rapidly near this temperature. The procedure used to analyze the specific 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. 12) to equation (1):

$$\frac{\Delta W}{A} = K_1^{\frac{1}{2}} t^{\frac{1}{2}} - K_2 t \pm SEE \qquad (1)$$

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.

The specific weight change data for first and second generation Si modified alloys are shown in figure 8 as a function of cyclic oxidation time at 870°C. Under these oxidation conditions, the austenitic 18Cr-8Ni, 304SS exhibited a slight increase in weight with increase in oxidation time up to about

100 hours. Beyond 100 hours of oxidation 304SS lost weight, exhibiting a weight loss of 50mg/cm^2 after 190 hours of testing. The effect of reducing the Cr level to 12% is also shown in figure 8 where it should be noted that this alloy immediately began to lose weight upon oxidation testing. Weight loss exceeded 50mg/cm^2 after only 90 hours exposure. The results of cyclic oxidation testing of the first and second generation Si modified alloys shows that these alloys compare quite favorably with the commercial 304SS. The first generation, ferritic alloy gained weight with cyclic oxidation time for the first 100 hours followed by a total weight loss of 26mg/cm^2 after 200 hours. The second generation, austenitic alloy behaved in a similar fashion with a total weight loss of 35mg/cm^2 after 200 hours testing. Since the ferrite content is about 45% for the first generation alloy, it is considered not to be a substitute for the austenitic 304SS. In contrast, the second generation alloy with nickel content of 10% also possesses an austenitic structure and thus is considered to be a potential substitute for 304SS having comparable oxidation resistance.

The results of testing a second series of alloys with Al and Mo substituted for Cr are shown in figure 9 along with the results shown previously for 304SS and the 12Cr alloy. The first generation, ferritic alloy exhibited a slight weight gain with increase in oxidation time for the total 200 hours of cyclic exposure at 870°C. The second generation, austenitic alloy exhibited an increase in weight with oxidation time for the first 100 hours followed by a total weight loss of about 49mg/cm^2 after 200 hours of cyclic testing. The first generation alloy has a ferrite content of 53% and based on this property is not considered to be an adequate substitute for 304SS. However, the second generation alloy with 10%Ni and Al, Mo, Mn, and Si adjusted properly possesses an austenitic structure with comparable oxidation resistance to 304SS and thus is considered to be a potential substitute for this commercial alloy.

Corrosion Resistance

The corrosion resistance of the modified composition 304SS alloys was evaluated by investigating the anodic polarization behavior of the alloys using a potentiodynamic technique. The alloy specimens were forced to act as an anode so that they would corrode or form a protective oxide film. The anodic current density was measured as the potential impressed on the specimen was made increasingly more noble. All potentials were measured against a Standard Calomel Electrode (SCE). Corrosion tests were conducted in a 1N H_2SO_4 solution at 21°C and at a scan rate of 0.2mv/sec. An anodic polarization curve for 304SS is shown in figure 10 which also indicates the meaning of the corrosion terms critical current density (I_c), passive current density (I_p), the primary passivation potential (E_p), the passivation breakdown potential E_b, and the corrosion potential E_c. An alloy such as 304SS which develops its corrosion resistance by forming a protective film on the surface usually exhibits a typical S-shape anodic polarization curve as shown in figure 10. An effective method generally used to improve the corrosion resistance of active-passive metals is to increase the ease of passivation of the matrix by alloying to reduce the critical current density (I_c) or to shift the primary passive potential (E_p) to a more active potential. Preliminary anodic polarization corrosion data for first and second generation Si modified 304SS alloys are presented in figure 11 along with data for commercial 304SS and the 12Cr alloy. It should be noted that reducing Cr from 18% in 304SS to 12% increases I_c by about ten fold. The first generation, ferritic alloy with 2.65Si decreased the critical current density I_c only slightly. The second generation austenitic alloy with 12Cr-10Ni-3Si further reduced I_c at about the same primary passive potential. However, the critical current density for the modified second generation alloy is not as low as 304SS. Preliminary anodic polarization corrosion data for the first and second generation Al+Mo modified 304SS alloys are compared in figure 12 with the baseline 304SS alloy and with this alloy having Cr content reduced to 12%. The first generation, ferritic alloy has a much lower critical current density than does the 12Cr alloy while the second generation austenitic alloy exhibits a critical current density about equal to 304SS and at the same primary passive potential. In addition, the range of passivation is about the same for 304SS and the second generation alloy. These results indicate comparable corrosion resistance between the commercial 304SS and the second generation alloy.

Prognosis

Based on the cyclic oxidation data and anodic polarization corrosion data presented herein, modified composition 304SS alloys with 12%Cr possess comparable properties to the baseline 304SS. Second generation Si modified alloys possess slightly superior oxidation resistance than 304SS while corrosion resistance of the modified alloy is somewhat inferior to the baseline 304SS. Second generation Al+Mo modified 304SS possesses oxidation and corrosion resistance comparable to the baseline alloy. More research is required to fully characterize these new alloys and further refine their compositions, as well as learning more about their fabricability and weldability. Results to date suggest that the potential exists to substitute the modified alloys for 304SS where oxidation and corrosion resistance is desired.

CONCLUDING REMARKS

This paper has presented some of the initial data on new alloys currently under laboratory development which offer potential of conserving the critical element chromium. In the case of the low Cr modified composition 304 stainless steels, a program was undertaken to investigate the potential of reducing Cr in this alloy by substituting more domestically abundant metals. Based on oxidation and corrosion properties presented here, second generation alloys offer comparable properties to the 304SS baseline alloy as well as possessing a semi-austenitic structure. The compositions of these second generation alloys are not fully optimized, but the results to date suggest that new alloys based on the compositions described here offer the potential of conserving one-third the Cr currently used in 304SS.

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Alloy	Nominal Chemical Composition, wt.%							
	Cr	Ni	Mn	Si	Al	Mo	C	Fe
304 Stainless Steel	18	8	1.1	0.65	--	--	0.06	Bal.
12%Cr-Si (Ferritic)	12	8	1.1	2.65	--	--	0.06	Bal.
12%Cr-Al-Mo (Ferritic)	12	8	1.1	0.65	2	2	0.06	Bal.
12%Cr-Si (Austenitic)	12	10	1.1	3.65	--	--	0.06	Bal.
12%Cr-Al-Mo (Austenitic)	12	10	5.1	1.65	2	2	0.06	Bal.

TABLE I. Composition of Modified 304 Stainless Steel Alloys.
Ferritic - 1st Generation, Austenitic - 2nd Generation

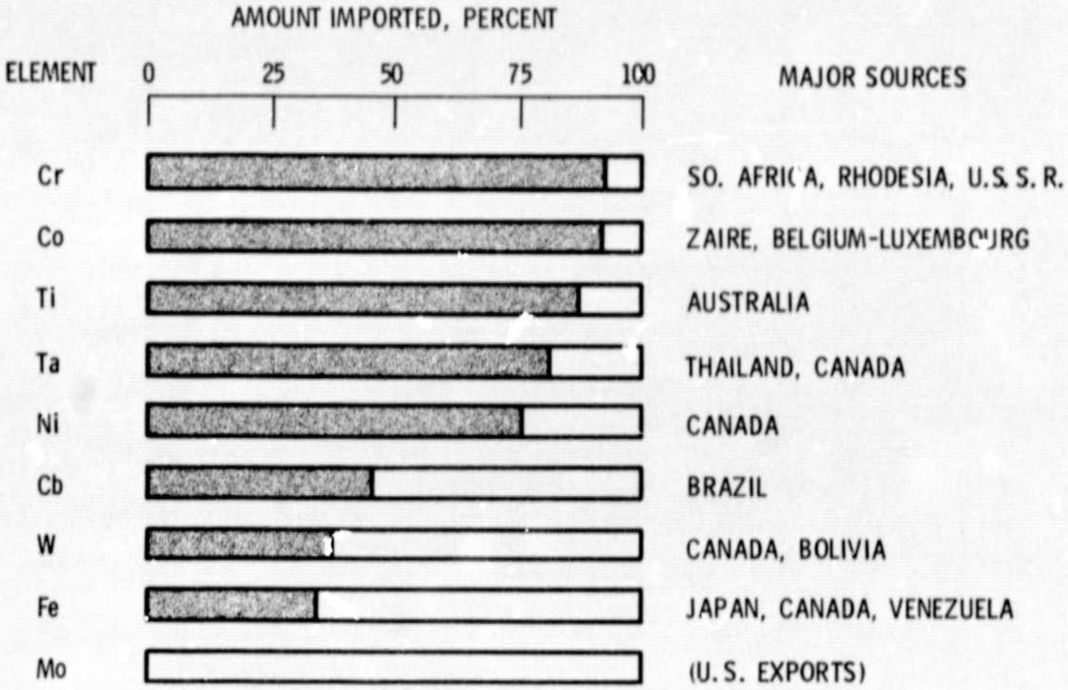


Figure 1. - Sources of critical elements and the amount imported by the United States in 1977 (ref. 6).

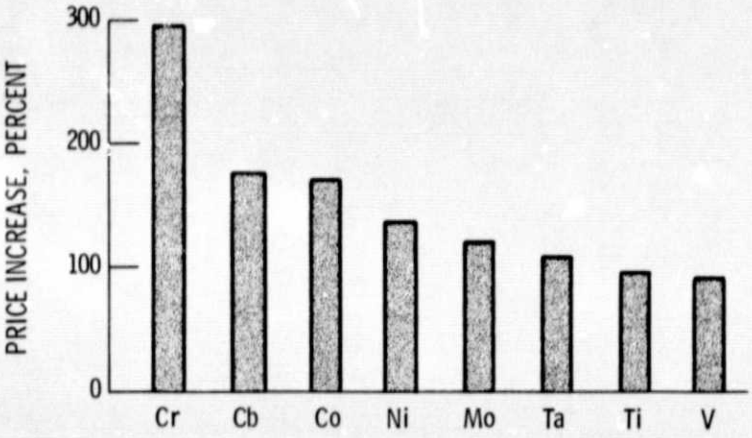


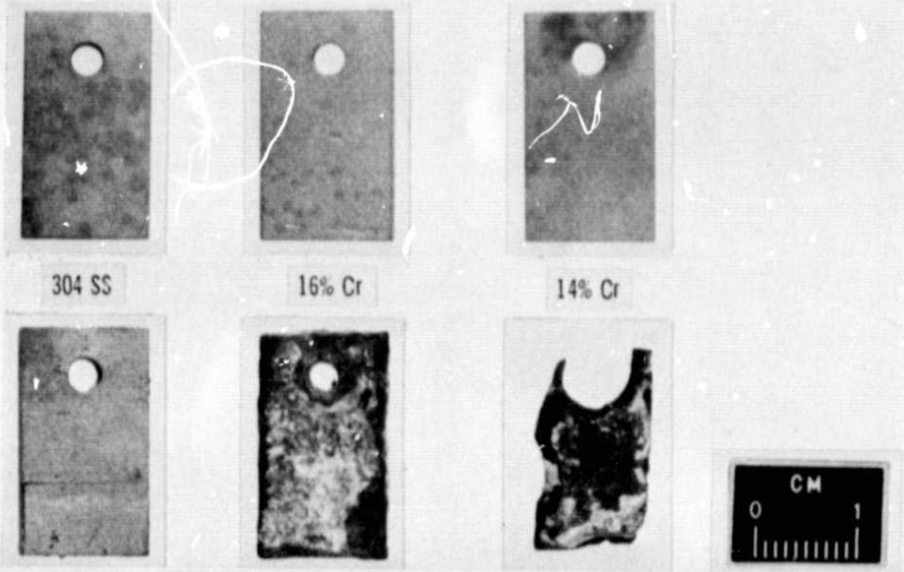
Figure 2. - Critical element price increase, 1969-1976 (ref. 7).

	PERCENT
PLATING	2
CHEMICAL	8
REFRACTORY	12
METALLURGICAL	78
TOOL STEELS	1
NON-FERROUS ALLOYS	4
CAST IRON AND STEELS	12
WROUGHT ALLOY STEELS	16
STAINLESS STEELS (40% AS 304 SS)	67

Figure 3. - Usage of chromium.

OXIDATION	CORROSION
Al	Mn
MISCH METAL	Mo
Si	V
Ti	
Y	

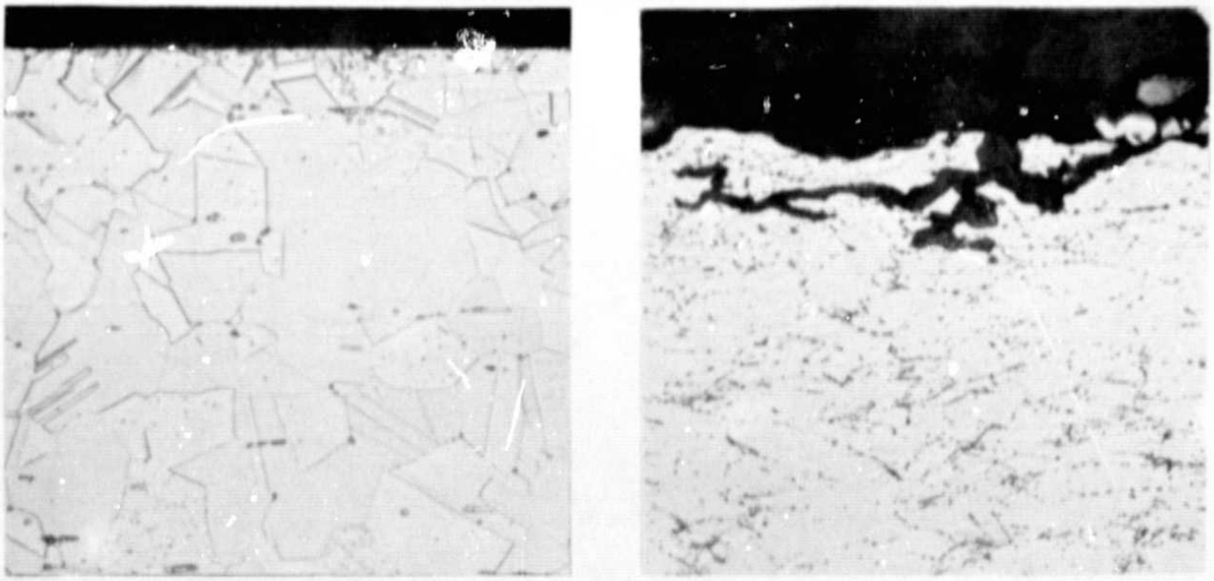
Figure 4. - Alloy substitutes for Cr in 304 SS.



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.



(a) Standard 304 SS. 18% Cr. $R_c = 1$. No apparent attack.

(b) Modified 304 SS. 12% Cr. $R_c = 2$. Slight attack.

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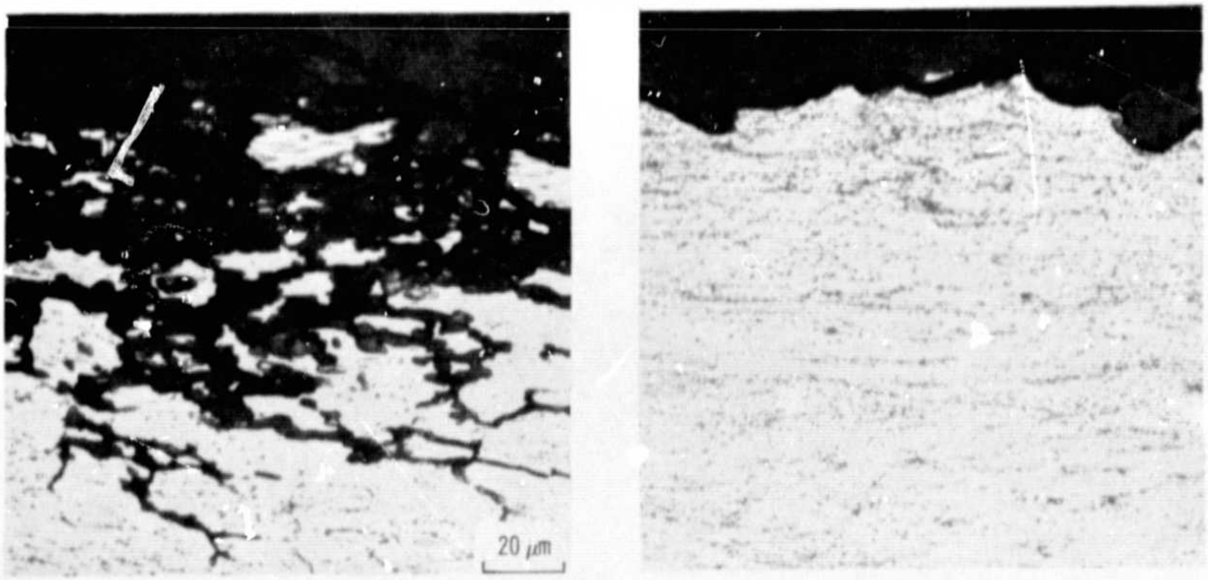

(c) Modified 304 SS. 10% Cr. $R_c = 3$. Severe attack.

(d) Modified 304 SS. 12% Cr. 2.65% Si $R_c = 1$. No apparent attack.

Figure 6. - 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.

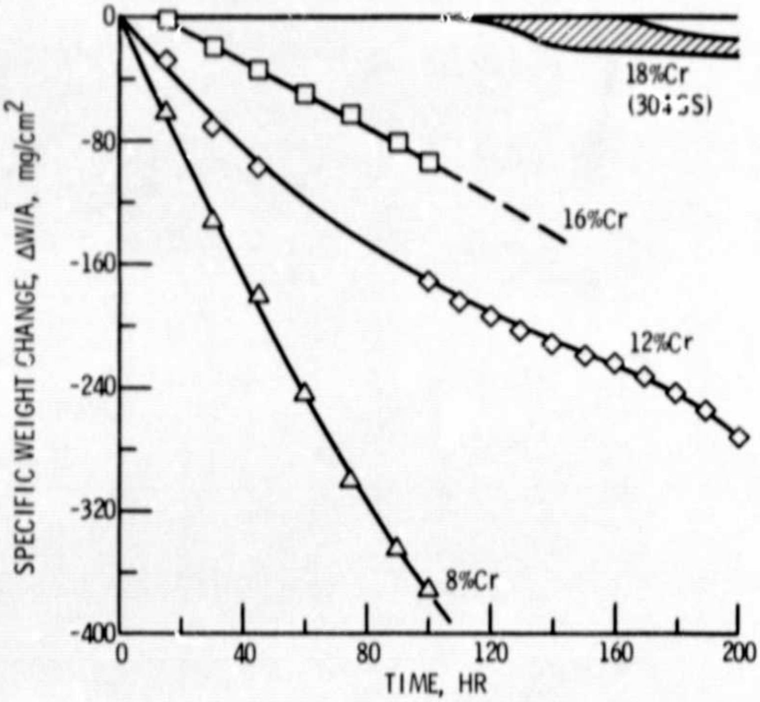

Figure 7. - Effects of partial removal of Cr from 304 SS on specific weight change during cyclic oxidation at 870° C.

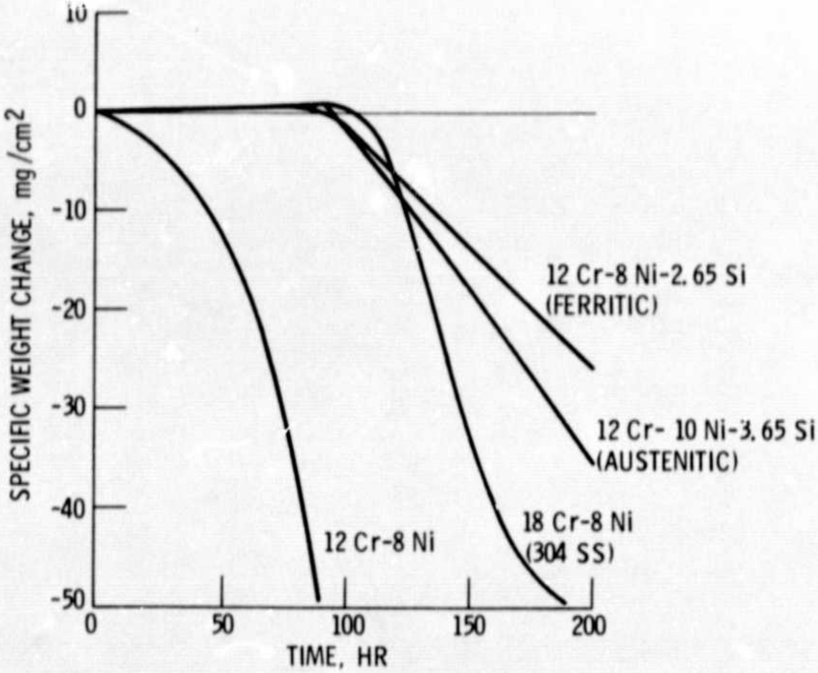

Figure 8. - Specific weight change data for Si modified 304 SS alloys. Cyclic oxidation temperature, 870° C.

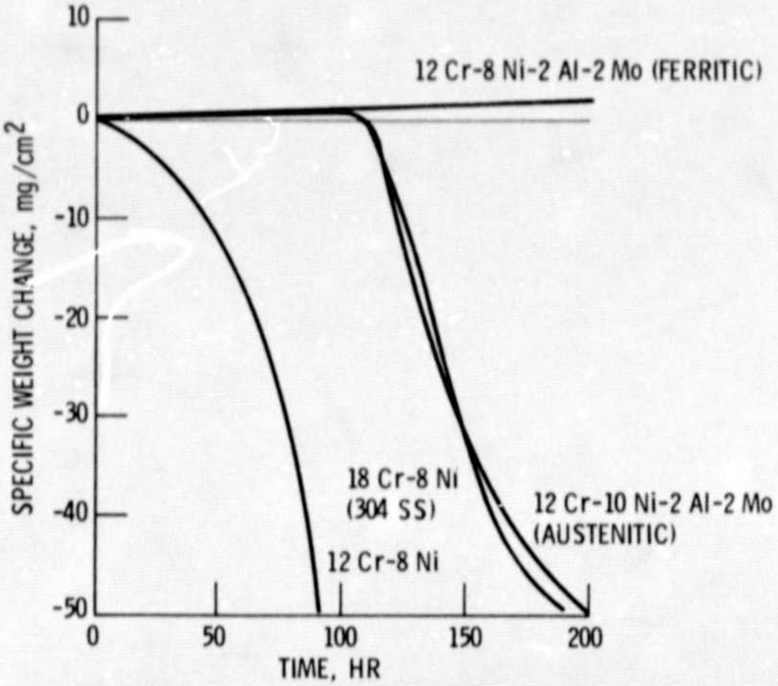

Figure 9. - Specific weight change data for Al-Mo modified 304 SS alloys. Cyclic oxidation temperature, 870° C.

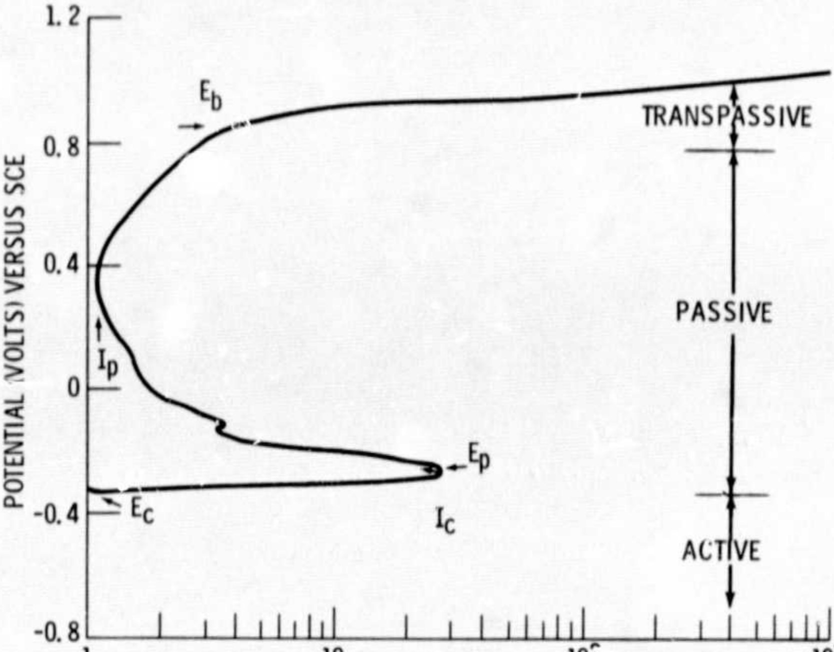

Figure 10. - Anodic polarization curve of 304 SS in 1N H_2SO_4 at 21° C.

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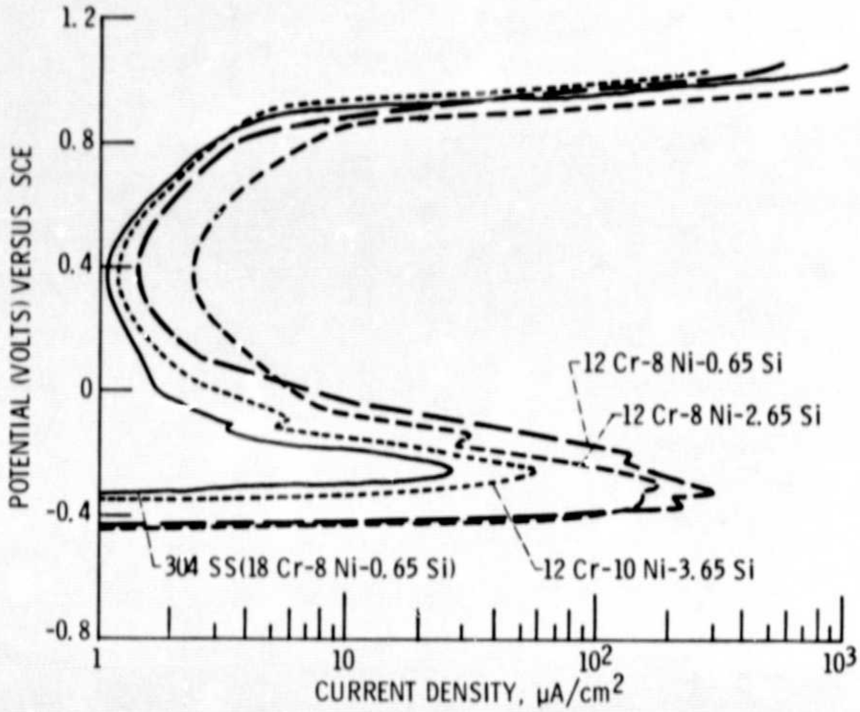

Figure 11. - Anodic polarization curves of Si modified 304 SS in 1N H_2SO_4 at 21° C.

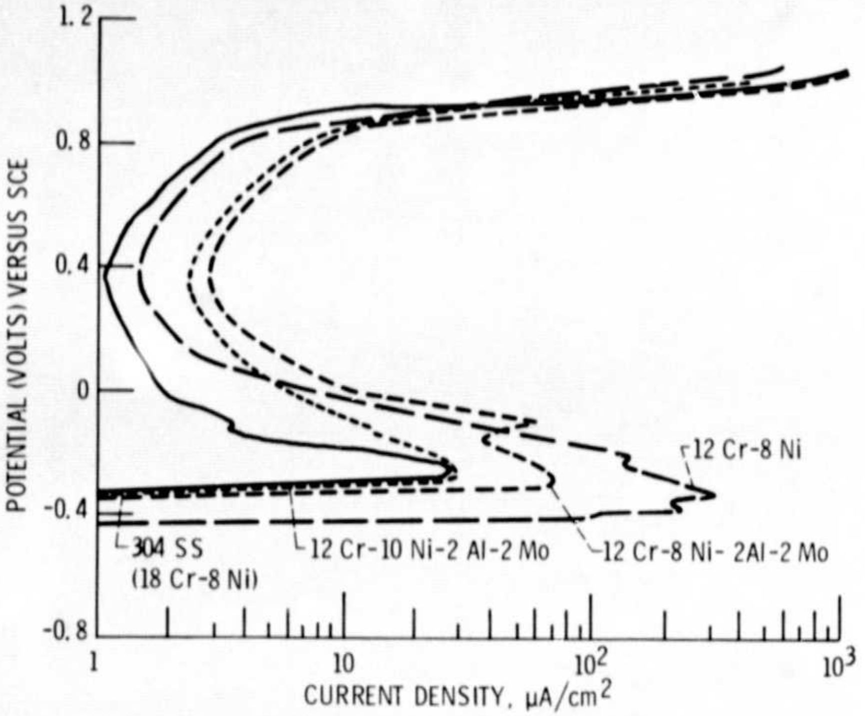

Figure 12. - Anodic polarization curves of Al-Mo modified 304 SS in 1N H_2SO_4 at 21° C.