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Partial Replacement of Chromium in Austenitic Stainless Steels by Molybdenum, Copper, and Vanadium

By S. C. Rhoads, S. J. Bullard, and M. L. Glenn



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	μa	microampere
cm^2	square centimeter	$\mu\text{a}/\text{cm}^2$	microampere per square centimeter
$^{\circ}\text{C}$	degree Celsius		
g	gram	min	minute
g/cm^3	gram per cubic centimeter	mpy	mil per year
		<u>N</u>	normal
h	hour	pct	percent
in	inch	ppm	parts per million
$\text{in}/\text{in}\cdot\text{min}^{-1}$	inch per inch per minute	V	volt
lb	pound	V/h	volt per hour
mL	milliliter	$V_{(\text{SCE})}$	volt versus saturated calomel electrode

PARTIAL REPLACEMENT OF CHROMIUM IN AUSTENITIC STAINLESS STEELS BY MOLYBDENUM, COPPER, AND VANADIUM

By S. C. Rhoads,¹ S. J. Bullard,¹ and M. L. Glenn²

ABSTRACT

The Bureau of Mines is investigating low-chromium alloy substitutes for type 304 stainless steel (type 304 SS). The purpose of the research is to reduce the chromium content in austenitic stainless steels used for corrosion-resistant applications. Nine Fe-9Cr-12Ni alloys containing additions of 0 to 5 pct Mo, 0 to 2 pct V, and 0 to 2 pct Cu were selected for evaluation.

All of the experimental alloys containing 5 pct Mo and an alloy containing 2Mo-2V-2Cu possessed structure and tensile strengths similar to those of type 304 SS. Alloys containing 5Mo-2V and 5Mo-2V-2Cu had acceptable welding properties as measured by the Varestraint test.

Alloys containing at least 2 pct Mo had corrosion resistance comparable to that of type 304 SS in solutions of nitric acid, phosphoric acid, acetic acid, and citric acid. In chlorides, all the experimental alloys were susceptible to localized corrosion and stress corrosion cracking similar to that of type 304 SS. The corrosion properties were established by weight-loss tests, electrochemical polarization tests, and stress-corrosion cracking tests.

An Fe-9Cr-12Ni-5Mo-2V alloy and an Fe-9Cr-12Ni-5Mo-2V-2Cu alloy had a combination of welding properties, tensile properties, and corrosion resistances that were most comparable to those of 304 SS.

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INTRODUCTION

Chromium is essential in high-temperature alloys, in many corrosion-resistant alloys, and in the common 300-series wrought stainless steels. A recent study (1)³ summarizes chromium uses and suggests alternatives to minimize the impact of a prolonged shortage. The results of this study indicate that partial substitution for chromium in the 300-series stainless steels, such as type 304 SS, is of immediate interest because 70 pct of the metallurgical chromium imported into the United States is used to produce these steels. The potential for chromium conservation is quite large if a suitable substitute can be found for type 304 SS. This Bureau of Mines research was directed toward replacing part of the chromium with other alloying elements to produce an alloy having mechanical and corrosion-resistant properties similar to those possessed by type 304 SS.

Because chromium is relatively inexpensive and currently available from foreign sources, only a few studies of lower chromium stainless steels have been made. The corrosion behavior of a number of 12-pct-Cr alloys in 1.0N H₂SO₄ and 1.0N NaCl was studied by Chen and Stephens (2).

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Their optimized alloy contained 12Cr-10Ni-1.5Si-1Al-2Mo and had corrosion-resistant characteristics similar to those of type 304 SS. A Bureau of Mines contract with International Nickel Co. (INCO) included an investigation by Floreen (3) of the corrosion rates of a number of Fe-9Cr-24Ni alloys in 1.0N H₂SO₄ and 1,000-ppm-Cl⁻¹ solutions. Floreen found that the corrosion resistance of some 9Cr-24Ni alloys, containing additions of Mo, Cu, and V, is comparable to that of type 304 SS in these environments. Floreen concluded that additions of Mo, Cu, and V are useful in producing a low-Cr austenitic alloy that possesses good corrosion resistance, good formability, good weldability, and reasonable mechanical properties.

Because the INCO research showed good potential for a low-Cr substitute, research was begun by the Bureau of Mines to investigate the potential of lower Ni content (12 pct) alloys containing Mo, Cu, and V additions. From the modified Schaeffler diagram (4), it was predicted that the selected 9Cr-12Ni alloys with Mo additions would be austenitic. The levels of Mo, V, and Cu additions were based upon anticipated effectiveness, relative cost, and domestic availability. The nine alloys studied and compared to type 304 SS are listed in table 1.

TABLE 1. - Chemical composition of alloys,¹ weight percent

Alloy	Nominal composition	Cr	Ni	Mo	V	Cu	Mn	Si	C	S
1.....	Fe-9Cr-12Ni.....	9.2	12.2	0	0	0.05	0.27	0.50	0.010	0.005
2.....	Fe-9Cr-12Ni-2Mo.....	8.7	12.0	2.0	0	0	.53	.22	.035	.020
3.....	Fe-9Cr-12Ni-2Mo-2V....	8.3	12.2	2.1	2.2	.06	1.15	.56	.020	.009
4.....	Fe-9Cr-12Ni-2Mo-1Cu...	9.1	12.1	2.1	0	1.0	.35	.35	.030	.007
5.....	Fe-9Cr-12Ni-2Mo-2V-2Cu	8.9	12.5	2.4	2.1	1.8	.92	.69	.026	.010
6.....	Fe-9Cr-12Ni-5Mo.....	8.3	11.8	5.1	0	0	.64	.31	.040	.007
7.....	Fe-9Cr-12Ni-5Mo-2V....	9.8	12.8	5.2	1.8	0	.87	.58	.038	.014
8.....	Fe-9Cr-12Ni-5Mo-2Cu...	8.5	12.1	5.0	0	2.0	1.60	.63	.046	.006
9.....	Fe-9Cr-12Ni-5Mo-2V-2Cu	9.7	11.3	4.9	1.8	1.7	.62	.59	.025	.013
304 SS	Fe-18Cr-8Ni.....	18.5	8.3	.15	.05	.21	.45	.30	.078	.007

¹Balance Fe.

Mechanical properties of the alloys were established from yield strengths, tensile strengths, and ductilities. Weldability of the alloys was evaluated for hot cracking susceptibility. The

corrosion properties of the Fe-9Cr-12Ni alloys were investigated by weight-loss tests, electrochemical polarization tests, and U-bend stress corrosion tests.

EXPERIMENTAL PROCEDURES

ALLOY PREPARATION

Alloys were prepared as 60-lb melts in a vacuum induction furnace. Charge materials were electrolytic grades of Cr, Ni, Fe, and Mn; high-purity Mo powder; conductor-grade Cu; high-purity V; high-purity ferrosilicon; and pig iron (for carbon additions). Carbon contents of the alloys were kept below 0.05 pct, as is done in commercial practice, to minimize the deleterious effects of chromium carbides in the grain boundaries (5). After the Fe, Cr, Ni, Mo, and V charge was melted, ferrosilicon, Mn, and Cu were added to the molten pool. The molten metal pool temperature was then brought to 1,600° C (about 5 min after the additions were made), and the metal was poured into a cast-iron ingot mold.

The cast ingots were inspected, the hot top and bottom were cropped, and the sides of ingots were machined to remove scale and small casting voids. Surfaced ingots were cut longitudinally into halves and homogenized for 20 h at 1,200° C in a vacuum furnace. At 1,100° C, the ingot halves were step-forged with 20-pct reductions to 1-in-thick slabs, to break up the grain structure. Forged slabs were hot-rolled, with 20-pct reductions, at 1,100° C to provide plate stock ~0.5 in thick. Sheet stock 0.14 in, 0.08 in, and 0.06 in thick was similarly hot-rolled from the plate stock.

MECHANICAL PROPERTY EVALUATION

Mechanical properties were determined on 0.125-in-thick standard flat tensile specimens according to ASTM E8-79. These standard test specimens were machined from the 0.14-in sheet parallel, transverse, and at 45° to the rolling direction. The properties were compared with wrought type 304 SS tensile

properties. Specimens were strained at 0.05 in/in·min⁻¹ by pacing the movement of the crosshead in a 60,000-lb-capacity hydraulic universal test machine. Strain was measured and recorded with an ASTM class A averaging separable extensometer. After the 0.2-pct yield strength was exceeded, the extensometer was removed, and the specimen was strained at the same rate until failure. Elongation and reduction in area were taken in the normal manner after the test.

WELDING EVALUATION

The occurrence of hot cracks in austenitic stainless steel welds is a major commercial problem. Therefore, it was necessary to evaluate the hot-cracking susceptibility of the experimental stainless steel substitutes. Although the cause of hot cracking is not fully understood, one explanation is that low-melting constituents segregate in the interdendritic areas and render these areas susceptible to cracking under thermal and solidification stresses that occur during cooling and shrinkage of the weld. Welds are not usually susceptible to hot cracking if they solidify with 5 to 10 pct delta ferrite, although they may be susceptible to corrosion or to embrittlement at elevated temperatures (6).

A subscale Vareststraint (Variable RESTRAINT) welding test apparatus was used to evaluate the hot-cracking sensitivity of these alloys. This apparatus simulates weld hot cracking in thick cross sections by straining a 0.125-in-thick specimen during welding (7). The apparatus bends the specimen over a mandril to provide a given strain during welding. The strained welds are then examined at X50 magnification for hot cracks. In these tests, welding conditions were adjusted for each alloy in

order to maintain a constant fusion zone width. By changing mandrills, the coupons were strained from 1 to 6 pct during welding. The tendency for hot cracking was determined by evaluating the number of hot cracks, the maximum crack length, and the sum of the lengths of these cracks as a function of augmented strain. A threshold strain level for onset of cracking was determined for each alloy.

Although comparable values may not be identical from laboratory to laboratory, the relative rankings of the hot-cracking susceptibility test values determined by the Vareststraint test are in good agreement. The subscale Vareststraint test results for two reference alloys, type 304 SS and Fe-10Cr-11Ni-5Si-0.5Mn, compared favorably with results obtained at the University of Tennessee.⁴

The weld specimens were also examined with a metallograph to determine their tendency to form martensite in the heat-affected zone.

CORROSION EVALUATION

Aqueous corrosion tests were carried out using conventional weight-loss tests and electrochemical polarization measurements. The main objective of the aqueous corrosion tests was to determine the corrosion rates of the experimental alloys in those acid solutions to which type 304 SS is known to be resistant (8).

Electrochemical polarization measurements also were used to determine the susceptibility of the experimental alloys to localized corrosion in high- and low-chloride solutions. U-bend stress-corrosion cracking tests in boiling 46-pct magnesium chloride solutions also were run.

⁴These results were courtesy of Dr. Carl Lundin, University of Tennessee, Knoxville, TN.

Weight-Loss Tests

For the conventional weight-loss tests, 0.08-in thick sheets were cut into 2- by 1-in coupons and annealed for 1 h at 1,100° C in argon. The coupons were wet-ground with 60-grit SiC paper and finished with 120-grit SiC paper to eliminate variations in the surface finish. Prior to immersion, the coupons were cleaned and degreased in Bransonic ultrasonic general purpose cleaner,⁵ rinsed in water, rinsed in acetone, dried in air, and weighed.

Weight-loss tests were conducted in Erlenmeyer flasks with extended necks and acorn condensers left open to the atmosphere. The test temperature was maintained at 50° C by immersing the flasks in a circulating water bath. Duplicate coupons were held in glass cradles to permit circulation of the corrosive medium in the flask by natural convection. Each flask contained 1,000 mL of acid, and the corrosive medium was not changed during the test. The weight-loss tests were run in 5-pct sulfuric acid, 6-pct acetic acid, 10- and 40-pct citric acid, and 2- and 86-pct phosphoric acid.

After exposure, coupons with no apparent visual changes were ultrasonically cleaned as previously described. The coupons with a visible corrosion layer were first scrubbed with a rubber stopper, then immersed in Bransonic ultrasonic oxide remover and rinsed with water. Then the coupons were cleaned in Bransonic ultrasonic general purpose cleaner for 5 min, rinsed first with water then with acetone, and air-dried. To determine whether the ultrasonic cleaning solutions removed solid metal, the above cleaning methods were tried on blank coupons. No loss in weight was detected.

⁵Reference to specific products does not imply endorsement by the Bureau of Mines.

After air drying, the coupons were weighed and the apparent corrosion rates were obtained using the following equation:

$$\text{Corrosion rate, mpy} = (KW)/(ATD),$$

where $K = 3.45 \times 10^6$, a constant,

W = mass loss, g,

A = area, cm^2 ,

T = time of exposure, h,

and D = density, g/cm^3 .

Electrochemical Polarization Tests

The specimens used for polarization measurements were 5/8-in-diam disks punched out from 0.06-in sheets. Surfaces of the disks were wet-ground first with 60-grit and then with 120-grit SiC paper. Immediately prior to running the polarization measurements, the specimens were polished again on 120-grit SiC paper, rinsed in water then in acetone, and dried in air.

An EG&G PARC model 331-1 corrosion measurement system with a flat specimen holder was used to perform the polarization measurements. The polarization measurements were plotted automatically, using the rapid-scan potentiodynamic technique developed by Morris and Scarberry (9-10). This technique utilizes forward and reverse scans that, for most environments, are started at $-0.9 V_{(SCE)}$, reversed at $+0.9 V_{(SCE)}$, and ended at the starting potential. The scans are started immediately after immersion without allowing the specimen time to equilibrate and yield the shape of the current-potential curve during the active-to-passive transition stage. At the completion of the reverse scan, the potentiostat is turned off until the freely corroding potential reaches steady state (15 to 60 min). A third cathodic scan is made from this steady state E_{corr} to $-0.9 V_{(SCE)}$. The plot of the composite polarization curve is termed a corrosion behavior diagram (CBD).

A CBD was run for each alloy. The corrosion current density, J_{corr} , was determined from the third cathodic scan using a graphical analysis extrapolation method. Polarization measurements were done at a scan rate of 60 V/h. Fresh solutions were used for each run, and the cell was left open to the atmosphere through a water-cooled condenser. To compare the weight-loss and electrochemical corrosion rates, electrochemical polarization tests were run at 50°C in 5-pct sulfuric acid, 40-pct citric acid, and 86-pct phosphoric acid. These tests showed excellent correlation between the weight-loss and electrochemical corrosion rates for the same alloy and medium. Additional electrochemical polarization tests were run in 5-pct sulfuric acid at 25°C , 40-pct citric acid at 80°C , 86-pct phosphoric acid at 80°C , glacial acetic acid at 50° and 80°C , and 25-pct nitric acid at 50°C .

Corrosion rates were calculated from the corrosion current densities by means of Faraday's law, using the following equation:

$$\text{Corrosion rate, mpy} = \frac{0.13(J_{corr})(EW)}{D},$$

where J_{corr} = corrosion current density, $\mu\text{A/cm}^2$,

EW = equivalent weight, g,

D = density, g/cm^3 ,

and 0.13 = conversion factor, $\frac{\text{mpy}}{\mu\text{A}\cdot\text{cm}}$.

Pitting Tests

Alloy susceptibility to localized corrosion was evaluated using electrochemical polarization measurements in 3.56- and 0.016-pct-sodium chloride solutions with pH's of 4.5 at 25°C . The 5/8-in-diam disk specimens were prepared as described in the electrochemical corrosion test section. A CBD for each alloy was made as previously described except the scan rate was 6 V/h. The freely corroding potential, E_{corr} , was recorded 30 min after the completion of the

reverse scan. Results from these scans are reported in terms of the pitting potentials ($E_{p|+}$), protection potentials (E_{prot}), and steady state corrosion potentials (E_{corr}).

Stress-Corrosion Cracking Tests

Stress-corrosion cracking tests were run in boiling 46-pct magnesium chloride solutions (155° C) using U-bend specimens in accordance with ASTM standard G36-73. Specimens of the experimental alloys and type 304 SS were machined to a length of 4.750 in, a width of 1.000 in, and a thickness of 0.0625 in. Using a plunger

and die, the specimens were bent into a U-shape having a 0.250-in radius of curvature in the longitudinal direction. Insulated Inconel bolts were used to maintain the stress. The stressed area of the specimens was immersed in the boiling magnesium chloride solution until failure or for a total of 30 days. At that time, the unruptured specimens were removed and inspected for cracks with a microscope at X50. Some of the specimens that survived 30 days without failure showed cracks. Lengths of these cracks are given as a percentage of the thickness of the specimen to allow comparison with the 9Cr-24Ni alloys evaluated by INCO (3).

RESULTS AND DISCUSSION

MECHANICAL PROPERTY EVALUATION

Results of tensile tests are summarized in table 2. The austenitic alloys, 5-9, displayed yield and tensile strengths comparable to those of type 304 SS. Although the alloys were designed to be austenitic, some of the alloys were shown by metallography and Magne-Gage readings to be partially martensitic (i.e., ferrite number >29) before tensile tests. These alloys had high yield and tensile strengths, which are characteristic of their partially martensitic microstructures. The properties of all the alloys were generally isotropic.

Magne-Gage readings of the failed sections of the austenitic tensile specimens indicated significant amounts of a ferromagnetic phase were developed during straining. This is due to partial transformation of the austenitic matrix to strain-induced martensite.

WELDING EVALUATION

Weldability of the alloys was evaluated by Vareststraint tests and by examination of weld microstructures. Vareststraint welding results for hot cracking are shown in table 3. Alloys having the best resistance to hot cracking were alloys 7

and 9 which had threshold strains between 1 and 2 pct. The 2 to 4-pct threshold strain for type 304 SS is slightly better than the thresholds for alloys 7 and 9. Welding hot-cracking sensitivities and welding cracking thresholds for the other alloys are significantly worse than for alloys 7 and 9, and for type 304 SS. Probably alloys 7 and 9 were most resistant to hot cracking because they had a residual delta ferrite content of 2 to 3 pct, which is known to impart hot-cracking resistance in austenitic stainless steels. All of these 9Cr-12Ni alloys had better hot-cracking resistance than did the 9Cr-24Ni alloys investigated by INCO (3) with the Vareststraint test.

Metallographic examination of the welds revealed both acceptable and unacceptable weld microstructures. Alloys 5-9 contained primary and secondary austenite, which is an acceptable microstructure. Alloys 1-4 had unacceptable microstructures that contained martensite in the heat-affected zone.

These results indicate that only alloys 7 and 9 had acceptable hot-cracking resistance and suitable microstructures for a weldable stainless steel substitute.

TABLE 2. - Tensile properties of annealed sheet in longitudinal, transverse, and 45° orientation

Alloy	Strength, psi		Ductility, pct		Ferrite number ² before test
	Yield	Tensile	$\frac{\Delta l}{l}$	RA ¹	
LONGITUDINAL DIRECTION ³					
1.....	91,640	119,280	12	64	>29
2.....	78,880	124,910	13	62	>29
3.....	33,820	95,480	38	72	>29
4.....	62,500	109,660	18	67	>29
5.....	30,610	71,215	72	77	1
6.....	29,500	87,830	53	74	18
7.....	32,270	83,150	68	77	3
8.....	31,570	73,870	63	74	.4
9.....	28,650	84,890	58	72	12
304 SS	⁴ 35,000	⁴ 85,000	⁴ 55	⁴ 65	NA
TRANSVERSE DIRECTION ⁵					
1.....	89,630	117,800	13	62	>29
2.....	76,270	126,310	12	48	>29
3.....	35,670	97,940	35	65	>29
4.....	62,290	109,890	19	64	>29
5.....	27,450	71,910	65	73	1
6.....	30,900	87,200	54	66	21
7.....	31,430	82,540	69	72	4
8.....	30,190	72,980	65	63	1.1
9.....	33,950	86,750	54	70	11
304 SS	NA	NA	NA	NA	NA
45° DIRECTION ⁵					
1.....	94,580	120,175	13	64	>29
2.....	76,750	122,450	13	62	>29
3.....	30,670	98,730	35	70	>29
4.....	61,500	110,230	18	65	>29
5.....	28,930	71,630	66	75	2
6.....	29,370	86,900	53	73	17
7.....	26,850	82,690	72	75	4
8.....	29,340	71,690	70	75	1.9
9.....	30,620	87,210	52	75	12
304 SS	NA	NA	NA	NA	NA

NA Not available.

¹RA is reduction in area.

²Ferrite number approximates ferrite or martensite percent; values were determined by Magne-Gage on unstrained alloy.

³Longitudinal yield and tensile values are averaged from four annealed specimens.

⁴American Society for Metals (11).

⁵Transverse and 45° yield and tensile values are averaged from 2 annealed specimens.

CORROSION EVALUATION

Weight-loss Tests

Weight-loss test results of the nine experimental alloys and type 304 SS at 50° C are summarized in table 4 for 5-pct sulfuric acid, 6-pct acetic acid, 10- and 40-pct citric acid, and 2- and 86-pct phosphoric acid. The corrosion rate classification employed by NACE in the "Metals Section Corrosion Data Survey" (12) is used for evaluating the aqueous corrosion resistance of the alloys. The corrosion rate classification is defined as follows:

"Good" resistance: corrosion rates less than 2 mpy.

"Useful" resistance: corrosion rates less than 20 mpy.

"Doubtful" utility: corrosion rates between 20 and 50 mpy.

"Severe" corrosion: corrosion rates over 50 mpy.

In 5-pct sulfuric acid, type 304 SS coupons had a corrosion rate of less than 1 mpy, and the nine experimental alloys had corrosion rates that ranged from 50 to 3,000 mpy. The alloys containing 2Mo-2V-2Cu, 5Mo-2V-2Cu, and 5Mo-2Cu had the lowest corrosion rates.

All the specimens exhibited "good" to "useful" corrosion resistance in 6-pct acetic acid, 10- and 40-pct citric acid, and 2-pct phosphoric acid. In 86-pct phosphoric acid, all the specimens except alloy 1 exhibited "good" to "useful" corrosion resistance. Alloy 1, which had no Mo, Cu, or V additions, severely corroded at a rate of 1,400 mpy in 86-pct phosphoric acid. In general, all the alloys containing Mo, Cu, or V additions had corrosion resistances comparable to that for type 304 SS in all the environments except 5-pct sulfuric acid.

TABLE 3. - Welding summary evaluation

Alloy	Varestraint threshold strain for weld cracking, pct	Weld bead ferrite number	Structure in heat-affected zone
1.....	0-1	>29	Martensite + austenite.
2.....	0-1	>29	Do.
3.....	0-1	23	Do.
4.....	0-1	>29	Do.
5.....	0-1	1.0	Austenite.
6.....	0-1	.5	Do.
7.....	1-2	2.0	Do.
8.....	0-1	.5	Do.
9.....	1-2	2.0	Do.
304 SS...	2-4	2.7	Do.

Electrochemical Polarization Tests

Polarization characteristics and corrosion rates for the nine experimental alloys and type 304 SS are summarized in table 5 for 5-pct sulfuric acid at 25° and 50° C, 40-pct citric acid at 50° and 80° C, 86-pct phosphoric acid at 50° and 80° C, glacial acetic acid at 50° and 80° C, and 25-pct nitric acid at 50° C. Electrochemical polarization tests performed at 50° C in 5-pct sulfuric acid, 40-pct citric acid, and 86-pct phosphoric acid were conducted at the same conditions used for the weight-loss tests for comparison of the electrochemical and weight-loss corrosion rates. The electrochemical corrosion rates obtained correlated well with the weight-loss corrosion rates for the same alloy and medium. Only the results from the remaining environments will be discussed.

In 5-pct sulfuric acid at 25° C, three of the experimental alloys had corrosion rates in the "useful" resistance range. Two of these alloys contained Mo, V, and Cu, and the third contained a combination of 5 pct Mo and 2 pct Cu. The remaining experimental alloys exhibited "severe" corrosion.

In 40-pct citric acid at 80° C, all the alloys except alloy 1, which had no Mo, V, or Cu additions, exhibited "useful" resistance. Alloy 1 exhibited "severe" corrosion.

In 86-pct phosphoric acid at 80° C, all except three of the experimental

alloys exhibited "useful" resistance. Two of these alloys contained a combination of Mo, V, and Cu and were in the "doubtful" utility range. The third alloy, alloy 1 without additions of Mo, V, or Cu, severely corroded in this environment.

All nine experimental alloys exhibited "good" corrosion resistance in glacial acetic acid at 50° and 80° C and in 25-pct nitric acid at 50° C.

Type 304 SS exhibited "good" resistance in all the environments.

In evaluating the potential of these alloys as substitutes for type 304 SS, the test results show that 9Cr-12Ni alloys containing a minimum of 2 pct Mo have general corrosion resistance comparable to that of type 304 SS in all the environments used except 5-pct sulfuric acid. Alloys with additions of Cu, V, and increased amounts of Mo showed no appreciable gain in corrosion resistance, except in 5-pct sulfuric acid.

Pitting Tests

The results of the pitting scans are shown in table 6. The following evaluations were used to determine the alloys' susceptibility to localized corrosion:

1. The presence of a well-defined hysteresis loop indicates susceptibility to localized corrosion.

TABLE 4. - Summary of weight-loss tests at 50° C

Alloy	Time, h	Weight loss, g	Corrosion rate, mpy	Time, h	Weight loss, g	Corrosion rate, mpy	Time, h	Weight loss, g	Corrosion rate, mpy
	5-pct sulfuric acid			2-pct phosphoric acid			86-pct phosphoric acid		
1.....	72	4.420	1,000	96	.004	<1	96	7.840	1,400
	2.5	.169	1,100	96	.004	<1	96	8.365	1,400
2.....	24	4.487	2,700	96	.002	<1	NA	NA	NA
	1.5	.285	3,100	96	.002	<1	NA	NA	NA
3.....	24	1.670	1,100	96	.001	<1	96	.002	<1
	2.5	.176	1,100	96	.001	<1	96	.002	<1
4.....	24	1.583	1,100	96	<.001	<1	96	.025	4.2
	2.5	.199	1,200	96	<.001	<1	96	.026	4.1
5.....	72	.265	55	96	<.001	<1	144	.004	<1
	96	.413	64	96	.001	<1	144	.004	<1
6.....	24	.774	480	96	.001	<1	144	.002	<1
	92	2.139	440	96	.001	<1	144	.002	<1
7.....	24	.262	160	96	.001	<1	144	.002	<1
	72	.863	180	96	.001	<1	144	.003	<1
8.....	72	.283	66	96	.001	<1	144	.002	<1
	96	.297	53	96	.001	<1	144	.002	<1
9.....	72	.254	50	96	<.001	<1	144	.003	<1
	96	.333	51	96	<.001	<1	144	.003	<1
304 SS	72	<.001	<1	96	.001	<1	96	.001	<1
	96	<.001	<1	96	<.001	<1	96	.001	<1
	6-pct acetic acid			10-pct citric acid			40-pct citric acid		
1.....	96	<0.001	<1	72	0.039	8.7	96	.049	8.7
	96	<.001	<1	72	.038	8.8	96	.051	8.2
2.....	96	.004	<1	72	.005	1	NA	NA	NA
	96	.006	1	72	.003	<1	NA	NA	NA
3.....	96	<.001	<1	72	.001	1	96	.008	<1
	96	<.001	<1	72	.001	<1	96	.007	<1
4.....	96	.001	<1	72	.002	<1	96	.014	2.4
	96	.001	<1	72	.003	<1	96	.013	2.2
5.....	96	<.001	<1	72	.001	<1	96	.001	<1
	96	<.001	<1	72	.001	<1	96	<.001	<1
6.....	96	.004	<1	72	.004	<1	96	.009	1.5
	96	.002	<1	72	.004	<1	96	.012	1.6
7.....	96	<.001	<1	72	.002	<1	96	.003	<1
	96	<.001	<1	72	.002	<1	96	.004	<1
8.....	96	.001	<1	72	.002	<1	96	.005	<1
	96	.001	<1	72	.001	<1	96	.005	<1
9.....	96	<.001	<1	72	.001	<1	96	.005	<1
	96	.001	<1	72	.001	<1	96	.004	<1
304 SS	96	.001	<1	72	<.001	<1	96	<.001	<1
	96	.001	<1	72	<.001	<1	96	<.001	<1

NA Not available.

TABLE 5. - Summary of electrochemical polarization characteristics

Alloy	J_{crit} , $\mu\text{a}/\text{cm}^2$	E_{pp} , V(SCE)	E_{corr} , V(SCE)	Corrosion rate, mpy	J_{crit} , $\mu\text{a}/\text{cm}^2$	E_{pp} , V(SCE)	E_{corr} , V(SCE)	Corrosion rate, mpy
	5-pct sulfuric acid at 25° C				5-pct sulfuric acid at 50° C			
1.....	30,500	-0.19	-0.435	170	39,000	-0.19	-0.419	1,000
2.....	13,500	-.18	-.384	280	14,000	-.21	-.372	2,800
3.....	3,400	-.21	-.365	170	3,300	-.22	-.347	1,100
4.....	5,000	-.12	-.337	85	5,200	-.11	-.329	1,200
5.....	2,050	-.10	-.291	14	1,500	-.11	-.290	66
6.....	2,700	-.18	-.343	170	2,300	-.11	-.335	400
7.....	1,600	-.18	-.315	54	1,050	-.22	-.319	190
8.....	1,850	-.09	-.281	13	2,000	-.06	-.272	71
9.....	1,900	-.11	-.294	15	1,300	-.09	-.270	52
304 SS.....	620	-.31	-.096	<1	540	-.28	-.090	<1
	40-pct citric acid at 50° C				40-pct citric acid at 80° C			
1.....	1,100	-0.18	-0.318	34	3,600	-0.12	-0.316	99
2.....	1,050	-.08	-.150	2.5	1,900	-.13	-.208	10
3.....	340	-.11	-.119	1.9	600	-.17	-.124	4.0
4.....	640	-.06	-.181	5.2	900	-.09	-.170	5.6
5.....	280	-.03	-.050	<1	320	-.08	-.100	3.3
6.....	460	-.09	-.114	2.3	630	-.09	-.125	2.4
7.....	360	-.12	-.063	<1	325	+0.10	-.106	3.7
8.....	315	-.01	-.068	<1	620	-.06	-.130	2.4
9.....	400	-.10	-.001	<1	360	-.09	-.070	2.4
304 SS.....	158	-.18	+0.001	<1	290	-.21	+0.015	<1
	86-pct phosphoric acid at 50° C				86-pct phosphoric acid at 80° C			
1.....	3,300	-0.22	-0.338	611	12,500	-0.26	-0.326	3,200
2.....	1,700	-.16	-.105	2.0	1,525	-.17	-.120	8
3.....	860	-.16	-.113	4.0	620	-.16	-.144	17
4.....	960	-.14	-.162	4.6	1,025	-.15	-.148	12
5.....	470	-.16	-.038	<1	750	-.12	-.196	36
6.....	500	-.15	-.034	<1	650	-.12	-.123	13
7.....	480	-.14	+0.026	1.1	600	-.13	-.136	19
8.....	940	-.03	+0.061	<1	520	-.11	-.122	9
9.....	340	-.03	+0.040	<1	600	-.11	-.176	34
304 SS.....	400	-.27	+0.020	<1	350	-.09	+0.011	<1
	Glacial acetic acid at 50° C				Glacial acetic acid at 80° C			
1.....	(1)	(1)	+0.080	<1	(1)	(1)	+0.454	<1
2.....	(1)	(1)	-.002	<1	(1)	(1)	+0.396	<1
3.....	(1)	(1)	+0.254	<1	(1)	(1)	+0.468	<1
4.....	(1)	(1)	+0.066	<1	(1)	(1)	+0.473	<1
5.....	(1)	(1)	+0.116	<1	(1)	(1)	+0.459	<1
6.....	(1)	(1)	+0.225	<1	(1)	(1)	+0.477	<1
7.....	(1)	(1)	+0.161	<1	(1)	(1)	+0.474	<1
8.....	(1)	(1)	+0.103	<1	(1)	(1)	+0.450	<1
9.....	(1)	(1)	+0.223	<1	(1)	(1)	+0.484	<1
304 SS.....	(1)	(1)	+0.002	<1	(1)	(1)	+0.452	<1
	25-pct nitric acid at 50° C							
1.....	(1)	(1)	+0.573	<1				
2.....	(1)	(1)	+0.566	<1				
3.....	(1)	(1)	+0.634	<1				
4.....	(1)	(1)	+0.605	<1				
5.....	(1)	(1)	+0.548	<1				
6.....	(1)	(1)	+0.553	<1				
7.....	(1)	(1)	+0.535	<1				
8.....	(1)	(1)	+0.641	<1				
9.....	(1)	(1)	+0.607	<1				
304 SS.....	(1)	(1)	+0.654	<1				

[†]Passive--no values obtained for J_{crit} and E_{pp} .

NOTE.-- J_{crit} = critical current density; E_{pp} = primary passivation potential; E_{corr} = steady state corrosion potential.

2. If steady state $E_{corr} > E_{prot}$, localized corrosion can occur (13). In general, localized corrosion can propagate at potentials more noble than the point where the hysteresis loop is completed (E_{prot}) (14).

3. The more noble E_{pit} is, compared to steady state E_{corr} , the less susceptible the alloy is to initiation of localized corrosion (14).

TABLE 6. - Summary of pitting polarization measurements at 25° C and pH 4.5

Alloy ¹	E_{corr}	E_{pit}	E_{prot}
3.56-pct NaCl			
1.....	-0.382	-0.12	-0.39
2.....	-.405	-.09	-.36
3.....	-.172	+.03	-.31
4.....	-.208	-.13	-.34
5.....	-.035	+.06	-.22
6.....	-.243	-.02	-.32
7.....	-.193	+.01	-.26
8.....	-.103	+.04	-.21
9.....	-.210	+.15	-.21
304 SS.....	-.088	+.10	-.24
0.016-pct NaCl			
1.....	-0.188	+0.25	-0.26
2.....	-.113	+.24	-.27
3.....	+.006	+.41	-.19
4.....	-.047	+.34	.23
5.....	+.015	+.38	-.07
6.....	-.078	+.37	-.20
7.....	-.017	+.41	-.13
8.....	-.020	+.50	-.10
9.....	+.065	+.37	-.07
304 SS.....	+.006	+.48	-.01

¹All the alloys exhibited well-defined hysteresis loops in both NaCl solutions.

NOTE.-- E_{corr} = steady state corrosion potential; E_{pit} = pitting potential; E_{prot} = protection potential.

All the experimental alloys and type 304 SS exhibited well-defined hysteresis loops, and E_{corr} was greater than or equal to E_{prot} for all alloys in both 3.56-pct and 0.016-pct sodium chloride solutions, indicating susceptibility to localized corrosion. The difference between E_{pit} and E_{corr} was greater for all experimental alloys and type 304 SS in 0.016-pct sodium chloride than in

3.56-pct sodium chloride. This indicates that the susceptibility of these alloys to initiation of localized corrosion would be less in 0.016-pct sodium chloride than in the more concentrated solution. All experimental alloys and type 304 SS demonstrated susceptibility to localized corrosion in both chloride solutions.

Stress-Corrosion Cracking Tests

The results of the stress-corrosion cracking tests are shown in table 7. Alloy 1 was resistant to stress-corrosion cracking in boiling magnesium chloride solution. This observation is in

TABLE 7. - Results of U-bend stress corrosion tests in boiling magnesium chloride

Alloy	Test length, days	Cracked	Length of crack after test, pct ¹
1.....	30	No	0
2.....	30	No	0
	² 24	No	0
3.....	15	Yes	100
	30	Yes	25
4.....	30	No	0
	30	Yes	100
5.....	30	Yes	100
	30	No	0
6.....	30	Yes	25
	30	No	0
7.....	30	Yes	100
	30	Yes	100
8.....	26	Yes	100
	30	Yes	90
9.....	30	Yes	90
	30	No	0
304 SS ³ ...	12	Yes	100
	30	Yes	90
304 SS ³ ...	12	Yes	100
	16	Yes	100

¹Expressed as percentage of the thickness of the specimen.

²Test terminated early owing to equipment failure.

³The composition of this 304 SS was Fe-18.5Cr-9.5Ni

agreement with a conclusion of Staehle (15) that a comparable alloy in the composition range of Fe-(10-15)Cr-(10-15)Ni has improved resistance to chloride stress-corrosion cracking. For the remaining eight experimental alloys, the additions of Mo promoted susceptibility

to stress-corrosion cracking. The deleterious effect of Mo at the 2-pct level was not as pronounced as at the 5-pct level. The eight experimental alloys containing Mo are susceptible to stress-corrosion cracking similar to that demonstrated by type 304 SS.

CONCLUSIONS

GENERAL CONCLUSIONS

The results indicate that it is possible to produce an acceptable wrought 9Cr-12Ni stainless steel, with additions of Mo, Cu, and V, that has mechanical properties comparable to the conventional type 304 SS. All the 9Cr-12Ni alloys with additions of at least 2 pct Mo have corrosion resistance comparable to those of type 304 SS in all the acids tested except 5-pct sulfuric acid. Additions of Cu, V, or more Mo provided little additional corrosion resistance. However, only two of the alloys possessed welding properties sufficient for them to substitute for type 304 SS. Overall, it is necessary to add 5Mo-2V-2Cu or 5Mo-2V to the 9Cr-12Ni alloy to achieve a combination of structure, tensile strength, yield strength, weldability, and corrosion resistance that is comparable to that of type 304 SS.

SPECIFIC CONCLUSIONS

1. The 9Cr-12Ni alloys containing additions of 5Mo-2V-2Cu or 5Mo-2V are most comparable to type 304 SS.

2. Sheet tensile properties of the austenitic alloys that contain 5Mo or a

combination of 2Mo-2V-2Cu are comparable to those of type 304 SS. The remaining alloys are partially martensitic and have mechanical properties typical of martensitic stainless steels.

3. Welds of the 9Cr-12Ni-5Mo-2V alloy and the 9Cr-12Ni-5Mo-2V-2Cu alloy have acceptable weld microstructures and have reduced but acceptable hot-cracking characteristics. The remaining alloys are unacceptable for welding because of either poor hot-cracking characteristics or martensite in the microstructure.

4. The 9Cr-12Ni alloys containing a minimum of 2 pct Mo have corrosion resistance comparable to that of type 304 SS in 6-pct and glacial acetic acid, 10- and 40-pct citric acid, 2- and 86-pct phosphoric acid, and 25-pct nitric acid. None of these alloys appear to be acceptable for use in 5-pct sulfuric acid. Alloying additions of Cu, V, or more Mo provide no substantial change in corrosion resistance.

5. All of these alloy substitutes are susceptible to localized corrosion.

6. Molybdenum additions are detrimental in stress-corrosion cracking.

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