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CORROSION RESISTANCE OF THE CHROMIUM-MANGANESE-NICKEL AND CHROMIUM-MANGANESE AUSTENITIC STAINLESS STEELS

by

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APPROVAL OF THESIS

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BY

FACULTY COMMITTEE

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JUNE, 1957

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ABSTRACT

The corrosion resistance of the chromium-manganese-nickel austenitic stainless steels has been established through a study of the available literature and unpublished data obtained from producers and users of these alloys. Several compositions are available as listed below.

DESIGNATION	COMPOSITION %				
	C	Mn	Cr	Ni	N
AISI 201	0.15	5.5/7.5	16.0/18.0	3.5/5.5	0.25
AISI 202	0.15	7.5/10.0	17.0/19.0	4.0/6.0	0.25
CM	0.15	13.0/18.0	14.0/17.0	1.0	0.25
Tenelon	0.10	14.5	17	-	0.40
TRC	0.08	16.5	15.0 min.	1.0	0.2
CMN	0.65	12	25	-	0.45
204	0.08	7.5/10.0	17.0/19.0	4.0/6.0	0.25

The AISI Type 201 and 202 alloys have been listed by the American Iron and Steel Institute.

The development and application of these alloys was necessary because of the increasing shortage of nickel and the wide use of the chromium-nickel austenitic stainless steels. The chromium-nickel steels are used in a wide variety of consumer items and are necessary for defense equipment. In times of national emergency the government restricts the use of nickel for consumer applications. The manganese substituted alloys are intended to fill the consumer shortage.

It has been found that the addition of manganese to the alloy will not seriously affect the corrosion resistance. In most environments,

manganese less than 10% has no effect, if the chromium and nickel remain constant. Above 10%, manganese decreases the corrosion resistance. This effect, however, is slight up to 18% manganese, the highest content reported.

More significant is the effect of lowering the nickel content. Reduction of nickel, particularly below 4%, will greatly reduce the corrosion resistance. It is the lowering of the nickel content rather than the addition of manganese that accounts for any reduction in corrosion resistance with the chromium-manganese-nickel austenitic stainless steels, since the chromium content is unchanged.

These alloys are subject to intergranular corrosion owing to the precipitation of chromium carbide as in the chromium-nickel alloys. They can not be stabilized with columbium or titanium. These elements will remove both carbon and nitrogen from the alloy with the formation of delta ferrite. It has been shown that by reducing carbon it is possible to prevent intergranular corrosion. The carbon limit has not been clearly established. It is reported to be either 0.025 or 0.060% depending upon the investigator.

The AISI Types 201 and 202 alloys appear to resist attack by a number of chemicals. Their resistance is similar to that of the Types 301 and 302 alloys. In a number of environments the resistance is better than Types 304 and 316 alloys. The oxidation resistance of the Types 201 and 202 alloys is equivalent to Type 304 up to about 1500°F. Above 1500°F the rate increases appreciably. These alloys are as susceptible to intergranular attack as the corresponding chromium-nickel alloys. The atmospheric corrosion resistance is good.

The alloys designated as 204 and 204L have a lower carbon content and should offer some improvement in corrosion resistance over the Types 201 and 202 but little data are available. The lower carbon content should make them less susceptible to intergranular attack.

The very low nickel, high manganese-chromium alloys have a corrosion resistance similar to that of the Type 430 alloys. They are resistant to only mild corrosives and would be used where the physical and mechanical properties are superior to the Type 430 alloy. The atmospheric corrosion resistance is good by both exposure tests and long time service tests. The alloy shows no promise for high temperature service where resistance to oxidation or sulfur is required.

A table of expected corrosion rates for the chromium-manganese-nickel and chromium-manganese alloys in a number of environments is presented. A complete bibliography of English language literature on the corrosion resistance of these alloys is included.

STATEMENT OF PROBLEM

Conduct an engineering correlation and evaluation of the corrosion resistance of the chromium-manganese-nickel and the chromium-manganese austenitic stainless steels. From a search of the published literature and from both published and unpublished data of producers and consumers establish the effect of manganese addition on the corrosion resistance of the alloys and present the expected corrosion rate in various environments. The data presented should provide a basis for the corrosion engineering of these alloys. Only foreign language articles of which English translations were available were used.

Obtain all unpublished data and permission to coordinate same from producers, consumers and interested organizations studying the Cr-Mn-Ni steels. Do this by surveys, correspondence and visitation to the extent needed.

Critically examine all corrosion data and tabulate same after examination and selection.

INTRODUCTION

The austenitic stainless steels are valuable construction materials because they combine corrosion resistance with ease of fabrication. The austenitic structure makes these alloys easy to fabricate. The alloying agents chromium and nickel, make the alloy passive in many environments. Because of these properties, the austenitic stainless steels are used in a large number of industries. Table I lists the end use of the austenitic stainless steels for the first half of 1956 by markets (1). The largest user is the automotive industry, with the aircraft and electrical industries following in that order. In 1956 the production of the common austenitic stainless steels amounted to 554,000 net tons or 5.3% of the total alloy steel production as reported by the American Iron and Steel Institute.

The wide use of the chromium-nickel austenitic stainless steels lead to the current problem. The defense need for nickel coupled with the limited supply (only two major Western sources) forced the government to restrict its use during national emergencies. Stock-piling of nickel for defense purposes during peace times prolonged the shortage. During World War II nickel was on allocation for defense use only.

TABLE 1

DISTRIBUTION OF STAINLESS STEEL BY MARKET CLASSIFICATIONS

FIRST HALF - 1956 (1)

MARKET	NET TONS	%
Automotive	52,884	14.5
Consumer Appliances	11,516	3.2
Utensils - Household & Cooking	10,713	2.8
Flatware - Cutlery & Table	9,901	2.7
Restaurant & Commercial	13,575	3.7
Plumbing, Heating & Air Conditioning	6,994	1.9
Builders Hardware, Architectural & Ornamental	9,253	2.5
Chemical Industry	7,982	2.2
Oil & Gas	4,360	1.2
Pulp and Paper Processing	4,700	1.3
Textile Processing	3,912	1.1
Dairy	7,033	1.9
Other Food & Beverage	7,220	2.0
Electrical	14,886	4.1
Metal Working	10,312	2.8
Farm	935	0.3
Railroads	2,516	0.7
Shipbuilding	2,926	0.8
Fasteners	12,603	3.4
Aircraft	30,240	8.3
Ordnance	3,892	1.1
Total Reported	228,353	62.5
Unreported	137,002	37.5
Total	365,355	100.0

During the Korean Emergency a directive, M-80 Schedule A, was issued by the National Production Authority prohibiting the use of stainless steels containing more than 1% nickel for a long list of industrial applications (2). These actions left the user of the austenitic stainless steels to look for a replacement alloy, preferably with similar physical and stainless properties.

Other than nickel, manganese is the only common metal which will retain an appreciable quantity of austenite in a chromium steel at room temperatures. Manganese has been used to form, with carbon, the austenitic "Hadfield" steels. In this steel carbon is about 1.1% and manganese is above 12%. However, at the lower carbon content required for corrosion resistance in the chromium steels, manganese is less efficient as an austenite stabilizer (3). Tests have shown manganese to be half as effective as nickel in stabilizing austenite (4). Figure 1 shows the structure present in steels of varying chromium and manganese content as quenched from 1800°F (1000°C) (5). It is clear that the chromium content must be below 15% at any manganese content if a wholly austenitic structure is to be obtained. Others (6,7) have placed a limit of 13% chromium to assure an austenitic structure. Unfortunately, lowering the chromium content to this level will adversely affect the corrosion resistance of the alloys.

To retain the chromium at 18% for corrosion resistance it is necessary to add nitrogen and/or nickel to obtain an austenitic structure. Considerable work was done by Franks, Binder and Thompson (8) to determine the structure of alloys containing various amounts of chromium, nickel, and manganese. The results of this study are summarized in

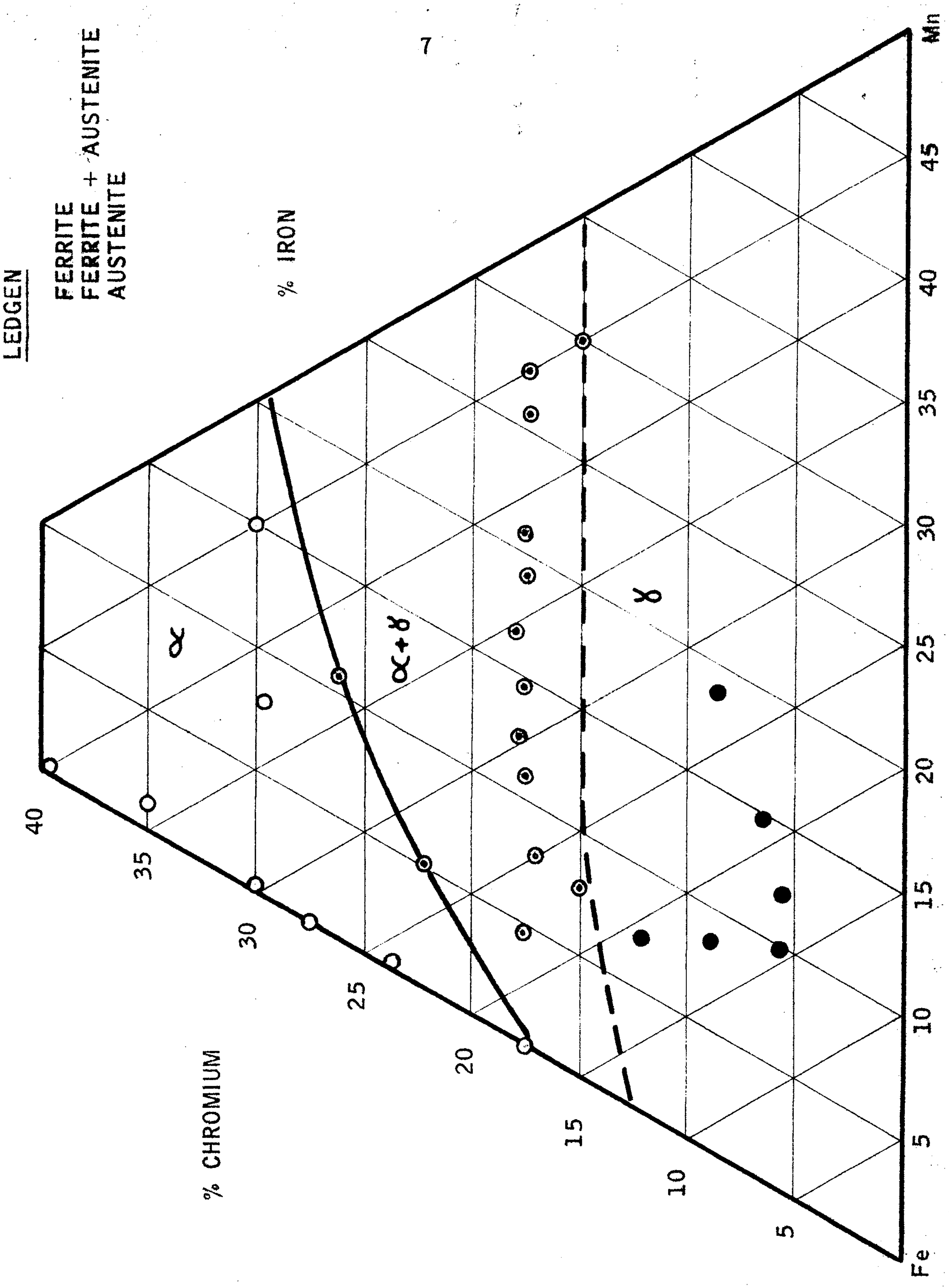


FIG. 1 PHASES PRESENT IN CHROMIUM - IRON ALLOYS. (5)
HEAT TREATMENT - QUENCHED FROM 1000°C.

Figure 2. This shows that the austenite region is greatly expanded by the addition of nickel. Increasing manganese above 6% at chromium levels above 15% causes a slight contraction in the austenite region. It was also found at the 18% chromium level that manganese functions primarily as a stabilizer of the austenite formed through the influence of carbon, nitrogen and nickel.

Carney has published (9) data on the structure of the very low nickel, high manganese alloys which shows the effect of nitrogen. His results, given in Figures 3 and 4, show that a fully austenitic structure can be obtained in the absence of nickel with as much as 18% chromium and 18% manganese provided the nitrogen content is 0.45%. This clearly shows the benefit of nitrogen as an austenite former. The data on the nitrogen-free alloys, Figure 1, indicated that the maximum chromium content was 15% at any manganese content to obtain an austenitic structure. By comparing these data with those in Figure 3, it can be seen that the austenitic region has been expanded by the addition of nitrogen. Likewise Figures 3 and 4 show that, in general, the austenitic region is reduced at the higher manganese contents. This points out the dual role of manganese as an austenite stabilizer at the lower concentrations and as a ferrite former at the higher concentrations. The beneficial effect of nickel as an austenite former is also shown by this data.

The American Iron and Steel Institute has assigned a type number to two chromium-manganese-nickel austenitic stainless steels. The designations are Types 201 and 202. The composition limits for these and for Types 301, 302 and 304 chromium-nickel austenitic stainless

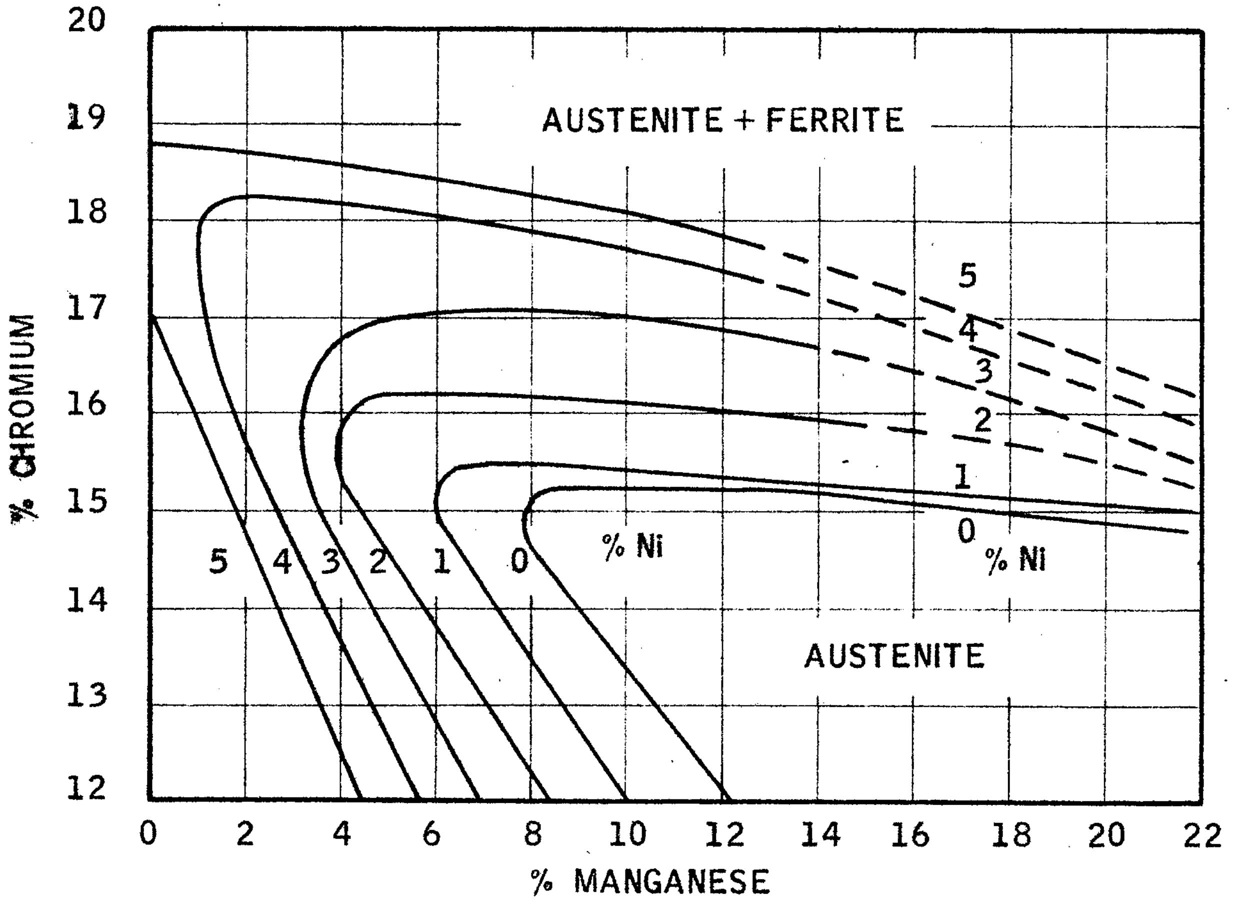
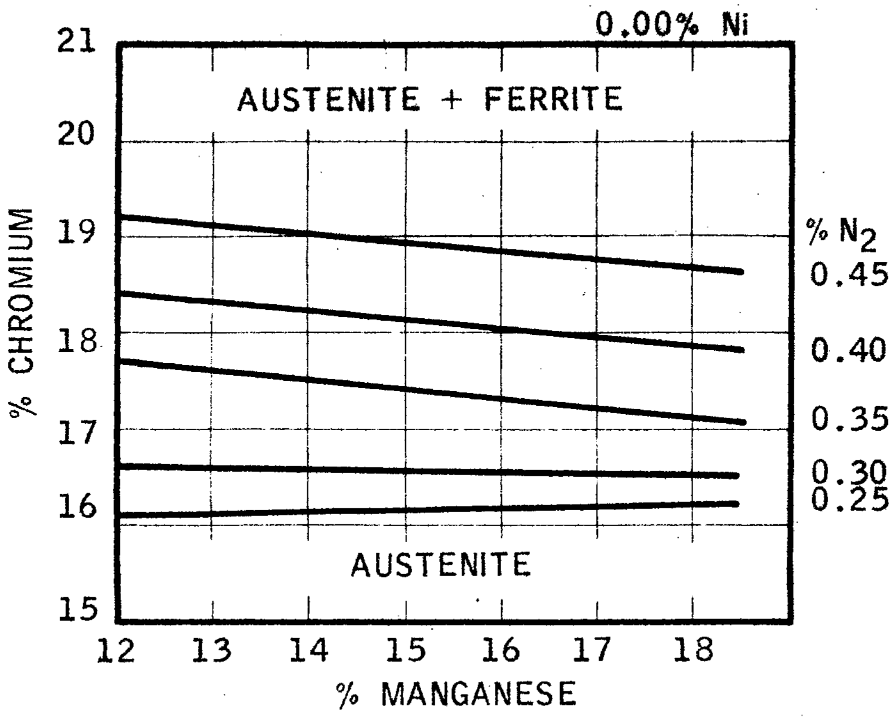


FIG. 2 STRUCTURE OF CHROMIUM - MANGANESE - NICKEL ALLOYS, HEATED TO 1075°C FOR 15 MINUTES AND AIR - COOLED. (8)



BASE COMPOSITION

% C	% Si	% P	% S
0.12 MAX.	1.00 MAX.	0.05 MAX.	0.05 MAX.

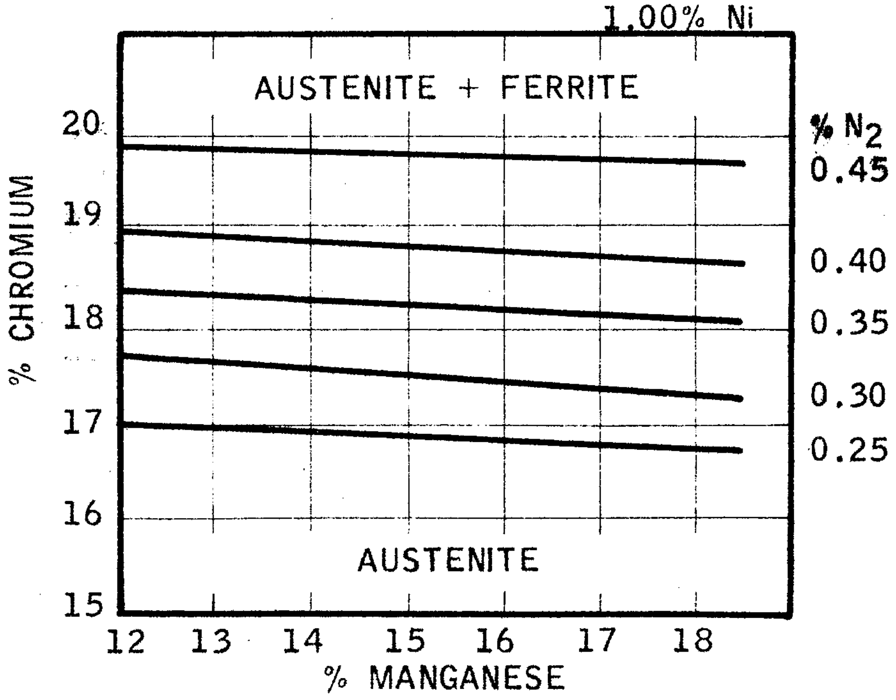
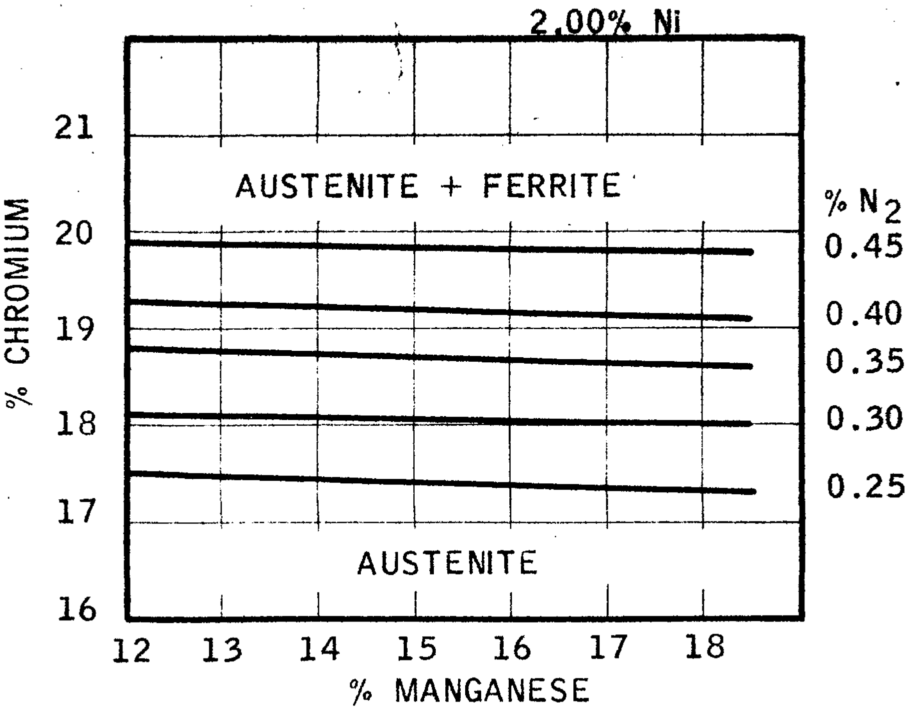


FIG. 3 EFFECT OF NITROGEN ON THE STRUCTURE OF CHROMIUM - MANGANESE - NICKEL ALLOYS. HEATED FOR 1 HOUR AT 2300°F AND WATER QUENCHED. (9)



BASE COMPOSITION

% C	% Si	% P	% S
0.12 MAX.	1.00 MAX.	0.05 MAX.	0.05 MAX.

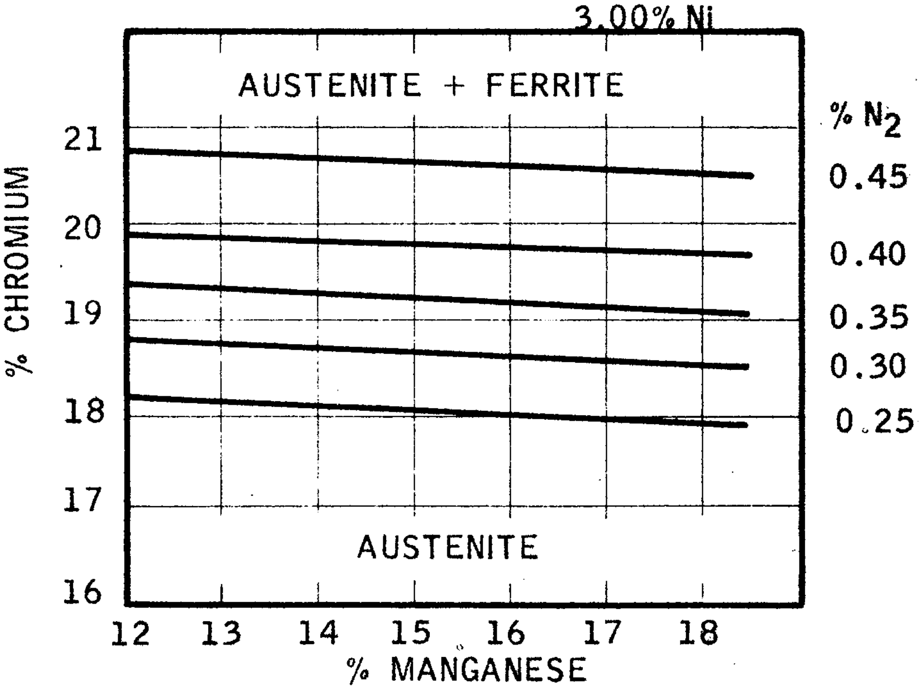


FIG. 4 EFFECT OF NITROGEN ON THE STRUCTURE OF CHROMIUM - MANGANESE - NICKEL ALLOYS. HEATED FOR 1 HOUR AT 2300°F AND WATER QUENCHED. (9)

steels are given below.

AISI TYPE	COMPOSITION (%)				
	C	Cr	Ni	Mn	N
201	0.15 max.	16/18	3.5/5.5	5.5/7.5	0.25 max.
202	0.15 max.	17/19	4.0/6.0	7.5/10.5	0.25 max.
301	0.08/0.20	16/18	6.0/8.0	2.0 max.	-
302	0.08/0.20	17/19	8.0/10.0	2.0 max.	-
304	0.08 max.	18/20	8.0/11.0	2,0 max.	-

As can be seen from the compositions, Type 201 is intended as a substitute for Type 301 and Type 202 for Type 302. Types 301 and 302 alloys are most commonly used for consumer applications, the one first cut off in time of short nickel supply. The Type 304 alloy because of its lower carbon and higher chromium and nickel is more resistant to corrosion and is used in applications where this property is most critical. Typical mechanical properties of Types 201 and 202 alloys are given in Table 2.

In addition to these alloys a number of others containing less than 1% nickel have been proposed by various producers. Compositions and trade names are give below.

DESIGNATION	COMPOSITION (%)					PRODUCER
	C	Cr	Ni	Mn	N	
CMN	0.65	25.0	-	12.0	0.45	Crucible Steel Co.
G-192	0.65	21/28	-	9.0	0.40	Allegheny Ludlum Steel Co.
TRC	0.08	15.0	1.0	16.5	0.20	Budd Co.
Tenelon	0.10	17.0	-	14.5	0.40	U. S. Steel Co.
CM	0.15	14/17	1.0	13/18	0.25	Allegheny Ludlum Steel Co.

TABLE 2

TYPICAL PROPERTIES OF THE MANGANESE AUSTENITIC STAINLESS STEELS (16,10,12,13)

TYPICAL ANNEALED MECHANICAL PROPERTIES

Material	Yield Strength (0.2% off set)	Tensile Strength	Elongation (in 2 in.) %
Type 301	40,000	110,000	60
Type 302	40,000	90,000	50
Tenelon	70,000	125,000	45
Type 201	50,000	115,000	60
Type 202	50,000	100,000	60
CM	50,000	100,000	50
G-192*	86,000	149,000	55

*Bar stock, others sheet

TYPICAL STRESS RUPTURE PROPERTIES

Material	Stress, 1000 psi, for Rupture in 1000 hr. at			
	900°F	1050°F	1200°F	1400°F
Type 302	49	32	17	6
Tenelon	68	41	28	-
Type 201	-	-	21	7
Type 202	-	-	21	7
CM	-	-	17	6.6
G-192	-	-	-	16.0*
Type 304	49	32	17	7

*1350°F

These steels are austenitic with the exception of TRC which contains some delta ferrite. Tenelon is austenitic through the balance of chromium, nitrogen and manganese in line with the data of Carney (9) mentioned earlier. The CMN and G-192 alloys however, contain too much chromium to attain an austenitic structure from nitrogen alone. The high carbon content together with the nitrogen will make these steels austenitic. However, by raising carbon to the level of 0.6%, the alloy loses some of its corrosion resistance. These steels are being used primarily where resistance to atmospheric corrosion is required. The mechanical properties are superior in some respects to the Types 301 and 302 alloys, Table 2, and the current fabrication techniques can be retained.

The acceptance of the manganese containing austenitic stainless steels is clearly shown by the production figures* for Types 201 and 202 over the last three years.

AISI TYPE	NET TONS		
	1954	1955	1956
201	Too small	1,190	11,050
202	to report	696	8,340

The applications of Types 201 and 202 alloys have been quite varied - from the exterior sheathing of Inland Steel's new office building in Chicago to a novel type of spring closure to replace men's shoe laces. Kitchen utensils and food processing equipment of Type 202 is extensively produced. Limited use is found in the chemical process and petroleum refining industries. The low nickel, high manganese alloys are being used

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*From AISI Production Reports

extensively for railroad cars and automotive truck trailers. A complete list of the uses of these alloys is given by Snair and Renshaw (14).

As these steels, although not really new, are still in their infancy, much corrosion data is being presented in the literature. Producers and consumers are actively conducting corrosion tests to evaluate them. There is a need for this corrosion data to be compiled and presented in a manner that will permit corrosion and material engineers to understand and apply the alloys correctly. Such a compilation will point out also the areas where data is lacking. This report will attempt to fill the need.

A search of the literature, back to 1920, was made to disclose articles relating to corrosion resistance of the chromium-manganese or chromium-nickel-manganese alloy steels. No foreign language literature was reviewed. A complete bibliography of all pertinent literature reviewed is given. The earliest articles appeared about 1930 when the value of the austenitic stainless steels containing chromium and nickel were first recognized. Without the knowledge that nitrogen would assist in forming austenite, work on the manganese containing alloys was discontinued in favor of the then cheaper and more satisfactory nickel bearing alloys.

In addition to the literature search, ten companies were contacted by letter in hope of obtaining unpublished data. One producer, Electro-Metallurgical Co., and two consumers, The Budd Co. and Esso Research & Engineering Co., provided data upon visiting their offices.

The discussion of corrosion resistance is divided into two sections. The first shows the effect of substituting manganese for nickel in various types of environments. The second covers the corrosion engineering of the manganese substituted austenitic stainless steels now marketed. Included is a table of the expected corrosion rates for these alloys in the various environments for which data has been obtained.

EFFECT OF MANGANESE AND NICKEL ON CORROSION RESISTANCE OF THE CHROMIUM AUSTENITIC STAINLESS STEELS IN VARIOUS ENVIRONMENTS

This is a discussion of the effect on corrosion resistance that results from the substitution of manganese for nickel in the austenitic stainless steels. The effect of both manganese and nickel are considered as they are the two variables. The effect of chromium content is noted in some environments to point out the need for maintaining the chromium content at 16 to 18%. It would be easier to maintain the austenitic structure at lower chromium contents.

The environments are representative of those in which these steels may be used. For each environment the discussion is limited to data on one reagent. Also included is a discussion of the susceptibility of these alloys to sensitization and intergranular corrosion.

Strong, oxidizing, inorganic acids - nitric acid. Most data for nitric acid was in boiling 65% solution. These conditions are a critical corrosion test for the austenitic stainless steels and are usually used to determine the resistance to intergranular corrosion (Huey Test). For this evaluation only data taken with fully annealed samples were used. In this condition the chromium-nickel austenitic stainless steels are very resistant to attack through the formation of a passive film on the surface of the alloy. Figure 5 shows the effect of adding 4 to 18% manganese to a 17-18% chromium - 4% nickel alloy. From 4 to 8% manga-

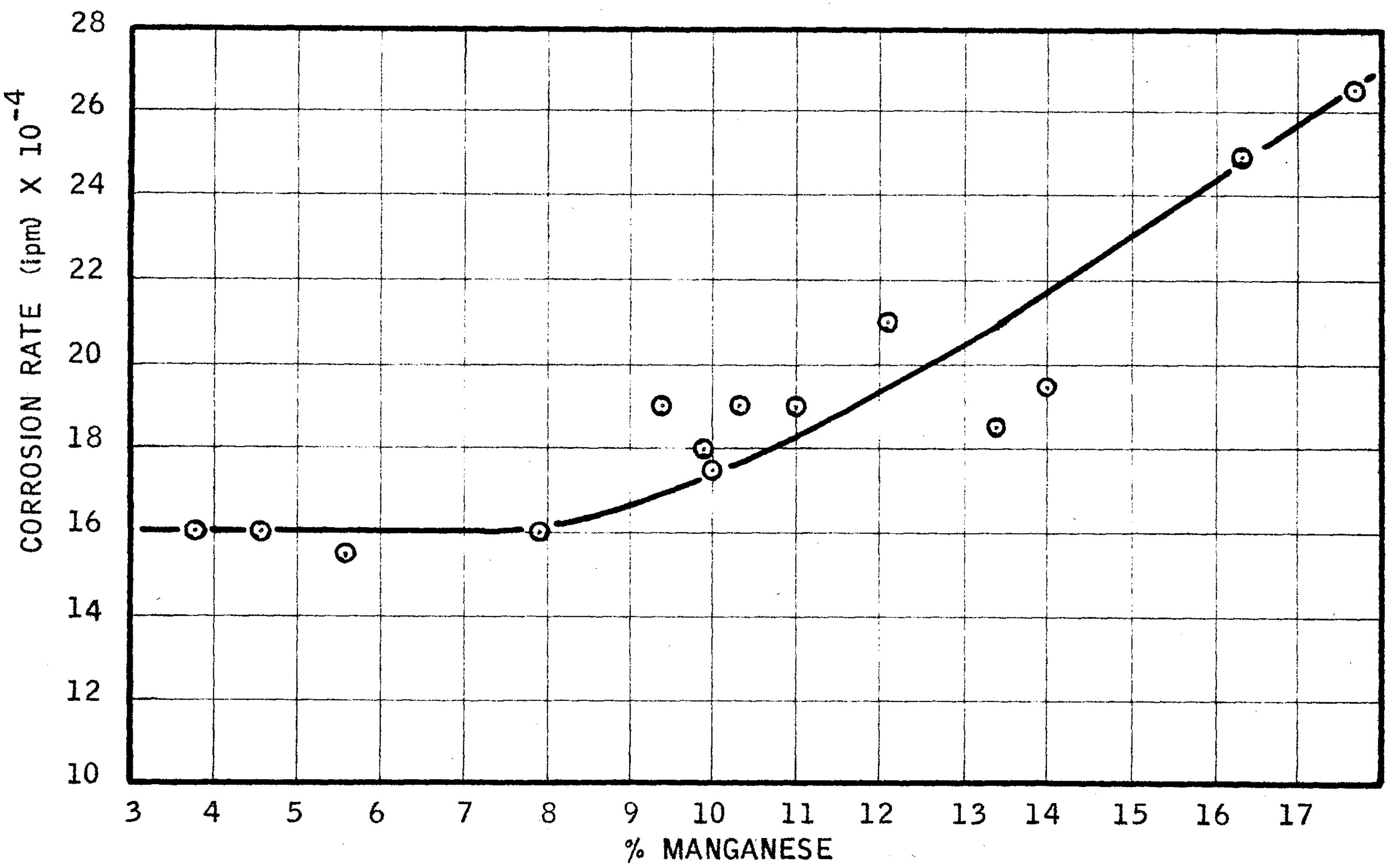


FIG. 5 EFFECT OF MANGANESE ON CORROSION IN BOILING 65% NITRIC ACID. (15)

ALLOY: 17 - 18% Cr, 4% Ni

nese no influence on the corrosion resistance. Above this manganese content the corrosion rate increases, but even at 18% manganese the increase is slight. In comparison, the beneficial role of nickel is illustrated in Figure 6. Increasing nickel from 1 to 7% decreases the corrosion rate from 0.005 to 0.001 inches per month (ipm). The increase of manganese from 4 to 18% only increased the corrosion rate from 0.0016 to 0.0027 ipm. This also justifies plotting data in Figure 6 neglecting manganese content. The difference in corrosion rates between Figures 5 and 6 for similar alloys is common when comparing the data of two investigators. Small variations in test procedure, sample preparation and cleaning techniques will account for the difference. It also points out the fallacy of using data from laboratory tests for predicting corrosion rates in operating equipment. This variation in data will be evident in a number of the comparisons presented. Figure 6 also shows that a high chromium content is beneficial. The effect is, however, less than that of nickel in the range reported.

From these data, it would be expected that an alloy containing at least 3.5% nickel and sufficient manganese and nitrogen to maintain an austenitic structure at 18% chromium would have a corrosion resistance equivalent to the 18% chromium - 8% nickel steels. Data on the commercial alloys show those containing higher nickel have a better corrosion resistance but that none of the manganese containing alloys are as resistant as the chromium-nickel alloys in boiling 65% nitric acid.

Weak, oxidizing, inorganic acid - phosphoric acid. The resistance to 10% boiling phosphoric acid was investigated by Renshaw and Lula (15). Figure 7 shows that manganese below 9% has no effect on the

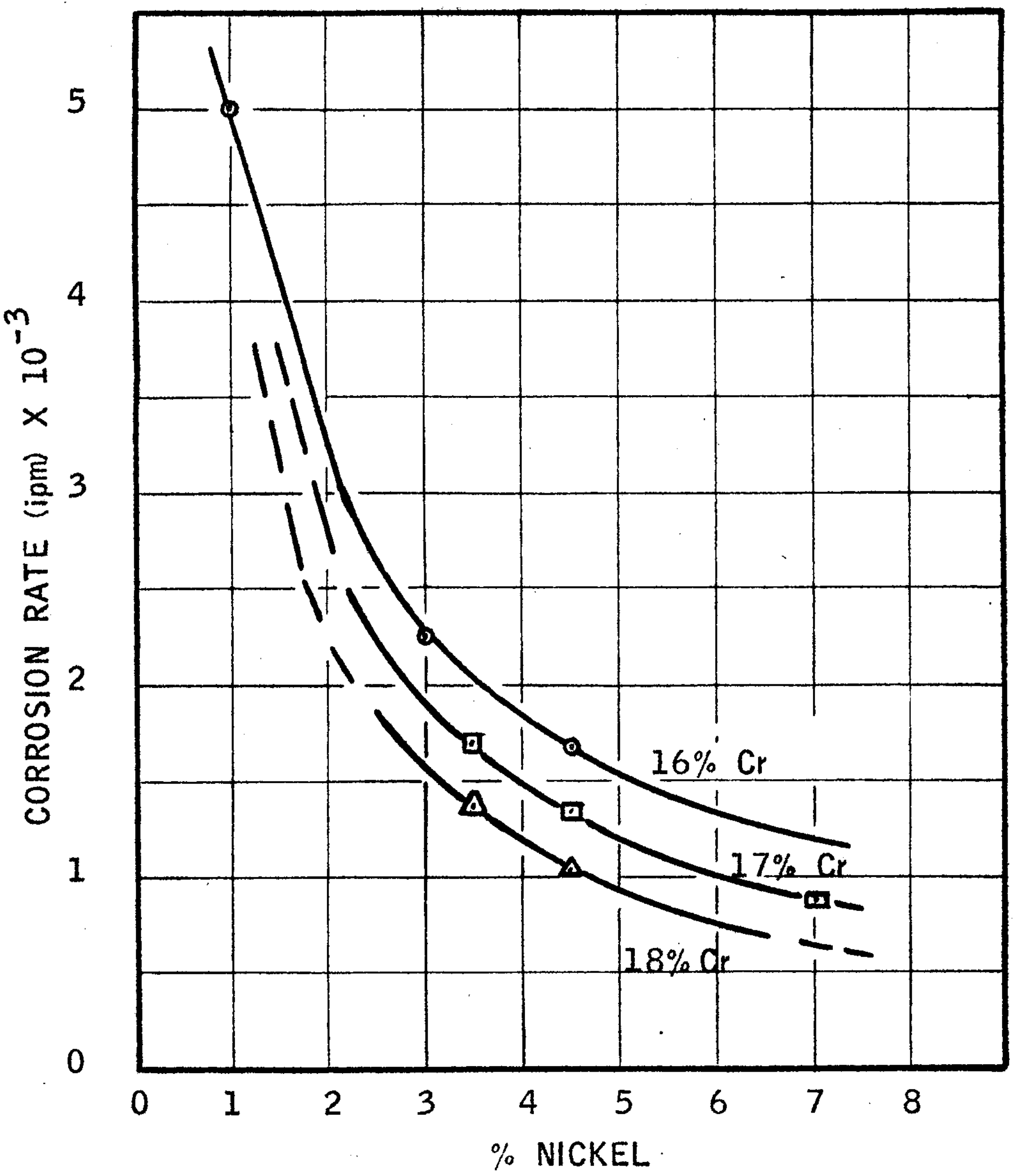


FIG. 6 EFFECT OF NICKEL & CHROMIUM ON CORROSION IN BOILING 65% NITRIC ACID. MANGANESE VARIED BETWEEN 1 & 18%. (8)

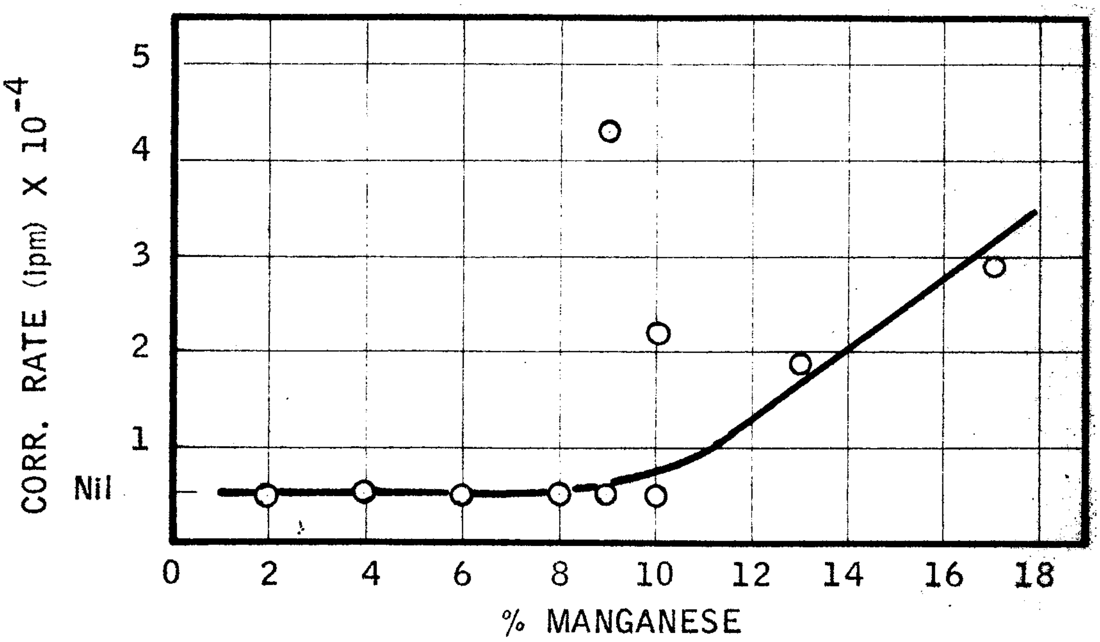


FIG. 7 EFFECT OF MANGANESE ON CORROSION RATE IN 10% BOILING PHOSPHORIC ACID. ALLOY CONTAINING 17 - 18% Cr; 4 - 5% Ni. (15)

corrosion resistance of a 17-18% chromium, 4-5% nickel alloy. At greater concentrations manganese increases the corrosion rate of the alloy. This effect is similar to that experienced with nitric acid. The minor role played by manganese in influencing corrosion rate is also shown in Figure 8. This is a plot of chromium content versus corrosion rate at a constant nickel content (4-5%) with the manganese content noted at the data points. The advantage gained by keeping chromium above 16% is very evident. Within the limited range of compositions tested (4-6%) the nickel content does not appear to significantly affect the corrosion resistance.

As with the strong oxidizing acids, the substitution of a portion of the nickel with manganese is not significant. The chromium content is most critical and must be above 16% to obtain good resistance. These conclusions are also presented by others (10,16,17).

Reducing, inorganic acids - sulfuric acid. Resistance to corrosion by these acids can be shown by the resistance to 10% sulfuric acid. Binder and Thompson (8) have studied the effect of substituting manganese for nickel and the resulting corrosion rates for the alloys. The results are presented in Figure 9. The corrosion rate varies greatly with the nickel content. The greatest variation is from 0.1 mils per month at 9% nickel to 1.2 mils per month at 3% nickel, both at 1% manganese. On the other hand, the variation in corrosion rate at a given nickel content varies only slightly with the manganese content. In general the greater the ratio of manganese to nickel the greater the corrosion rate. Binder and Thompson also point out that chromium from 16 to 18% has less effect on reducing corrosion than does increasing the nickel from 3.5 to 4.5%.

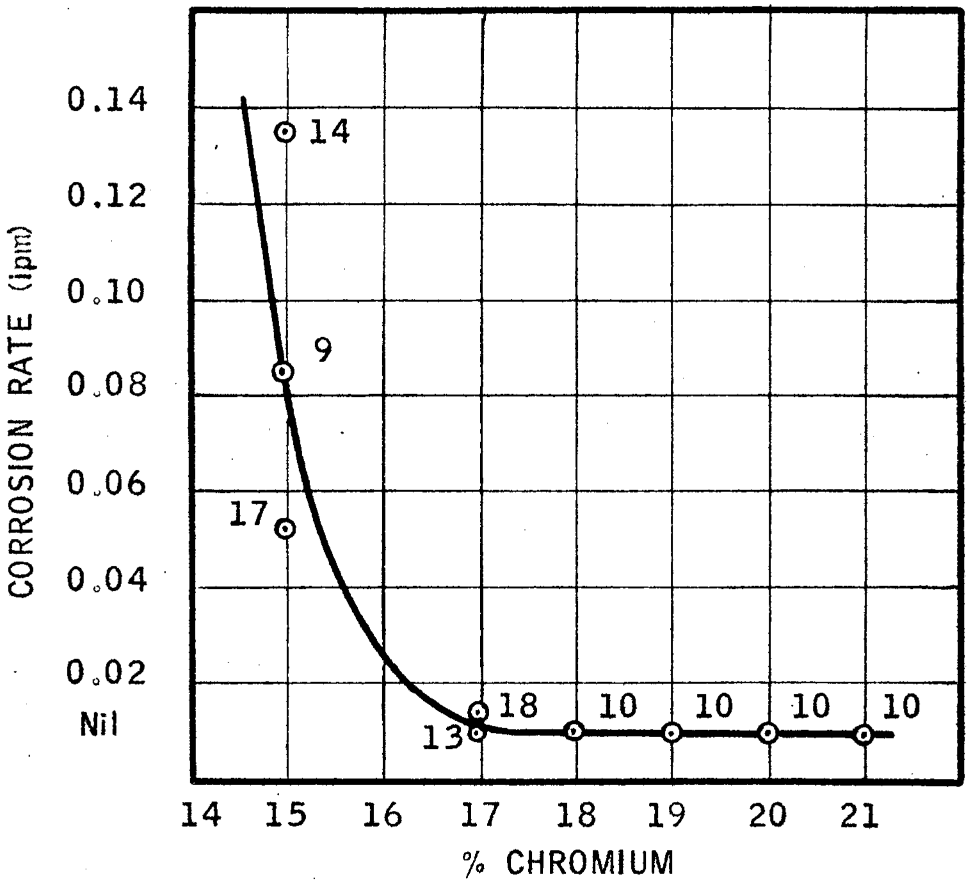


FIG. 8 EFFECT OF CHROMIUM ON CORROSION RATE IN 10% BOILING PHOSPHERIC ACID.

MANGANESE CONTENT (%) NOTED BY DATA POINTS. NICKEL - 4 to 5%

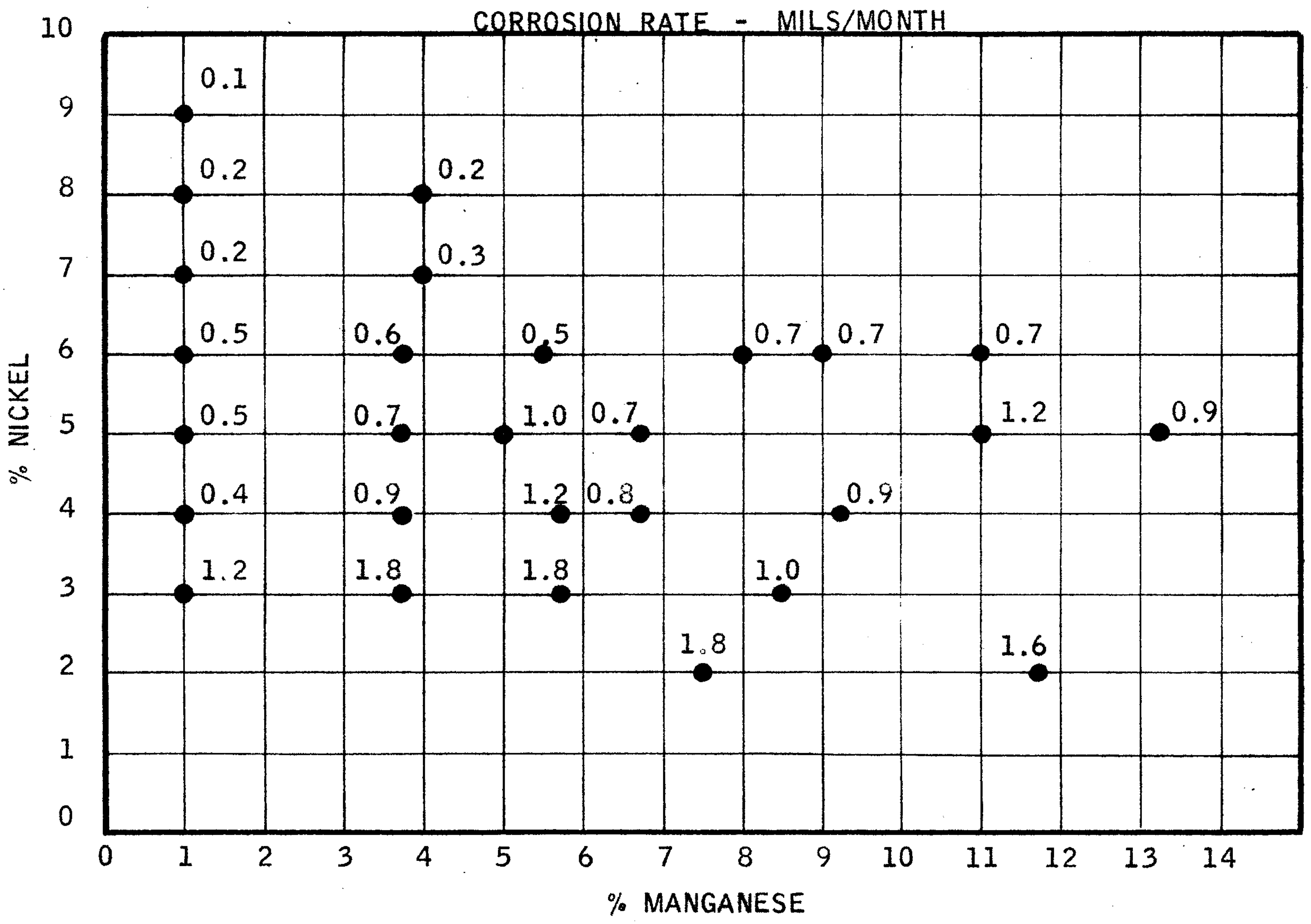


FIG. 9 EFFECT OF NICKEL AND MANGANESE ON CORROSION RATE IN 10% SULFURIC ACID. TEMPERATURE - 70°C, AIR-FREE. 18% Cr, 0.05 - 0.08% C, & 0.12 - 0.15% N. (8)

This general effect of nickel is also shown by others (17) who report that the Type 201 and 202 alloys are not as resistant as the Type 301 alloy and that the same is true of the very low nickel alloys (11). Parks (18) claims that the addition of manganese will lower the corrosion resistance of the straight chromium alloys. This is not supported by the data presented here. From the data available, it appears that the substitution of manganese for nickel does not produce an alloy with comparable corrosion resistance in the reducing, inorganic acids.

Mild, oxidising, organic acids - glacial acetic acid. Comparative data are available for a number of alloys in boiling glacial acetic acid. These are presented in Figure 10 to show the effect of manganese on an alloy containing 17-18% chromium and 4-5% nickel. The addition of manganese decreases the corrosion resistance. There is, however, quite a spread in the data and only that which appears to be consistent is presented.

Figure 11 indicates that chromium has a much greater effect on the corrosion resistance. Increasing the chromium from 16 to 19% decreases the corrosion rate from 0.008 to 0.0004 ipm. It was not possible with the data available to plot the effect of chromium at constant manganese and nickel contents. The influence of these constituents may effect the relationship shown, particularly data points 9, 10, & 11 which are at high manganese contents. The data plotted in Figure 10 show that this high manganese content will increase the corrosion rate. But the variation indicated should only be about 3 mils per month which would be insignificant on the scale used in Figure 11. It is interesting to note the relative independence of corrosion rate with nickel content. Data

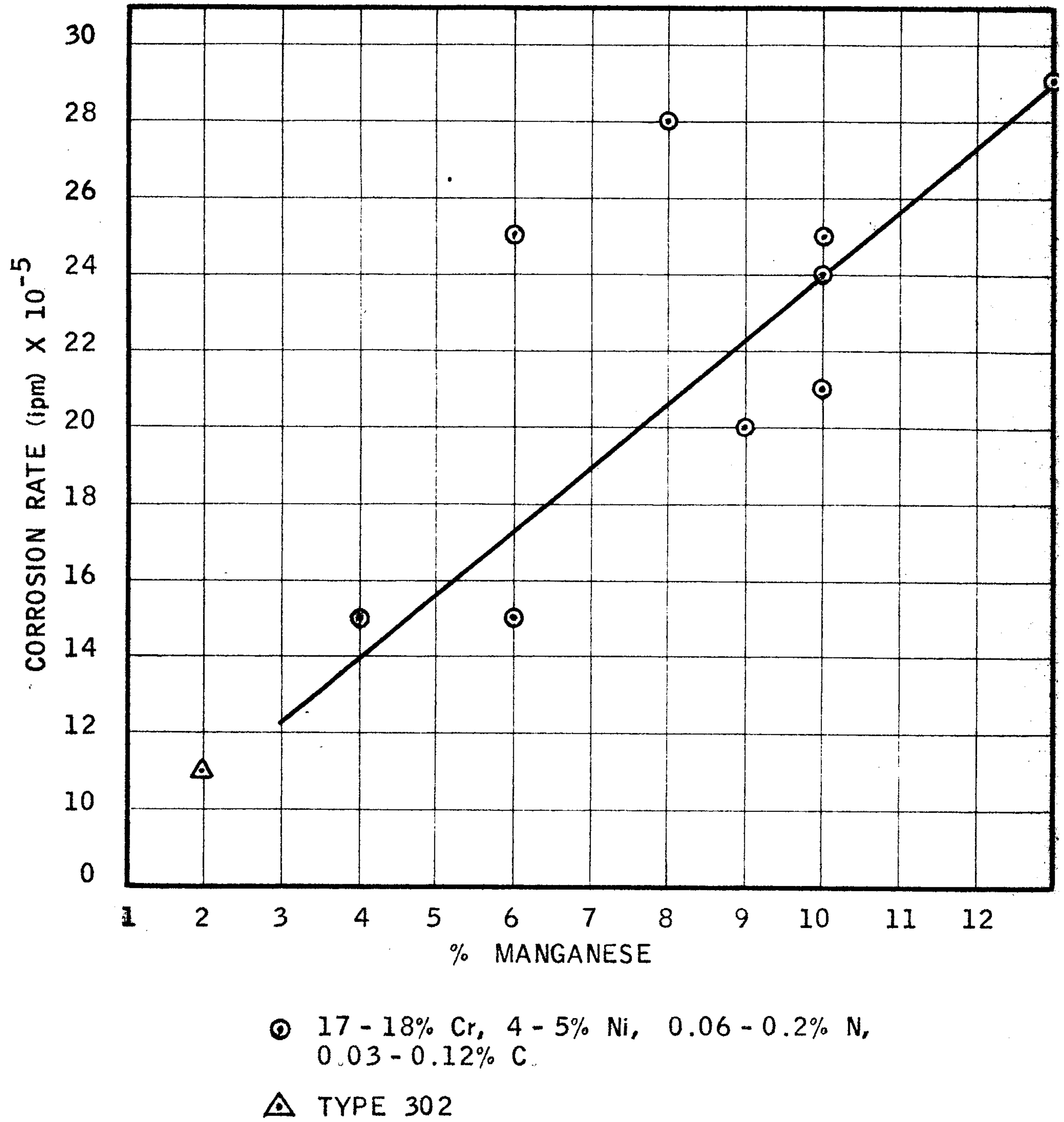


FIG. 10 CORROSION RATE IN BOILING GLACIAL ACETIC ACID AS A FUNCTION OF MANGANESE CONTENT. (15)

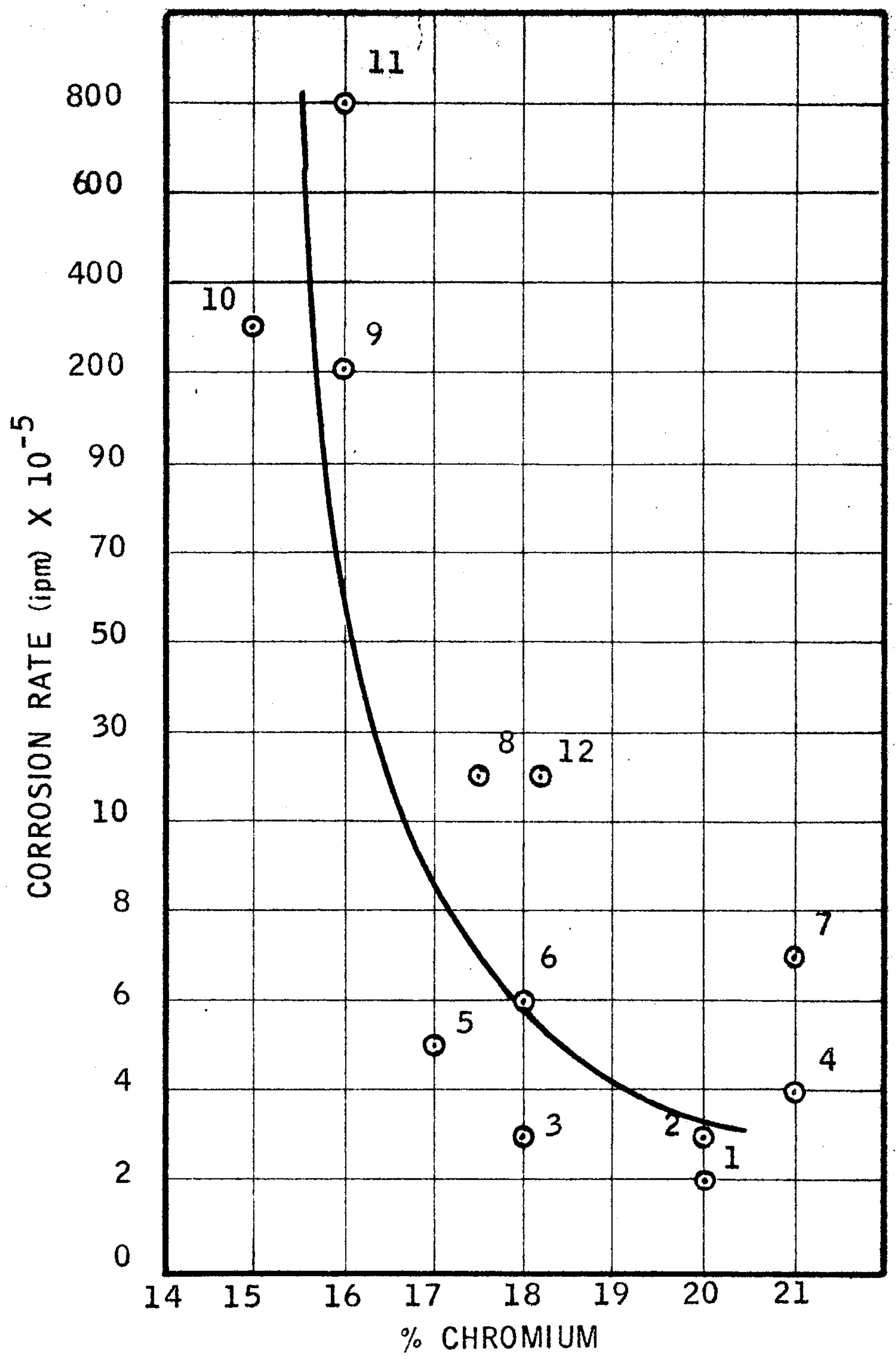


FIG. 11 EFFECT OF CROMIUM CONTENT ON CORROSION IN ACETIC ACID (GLACIAL, BOILING) (15)

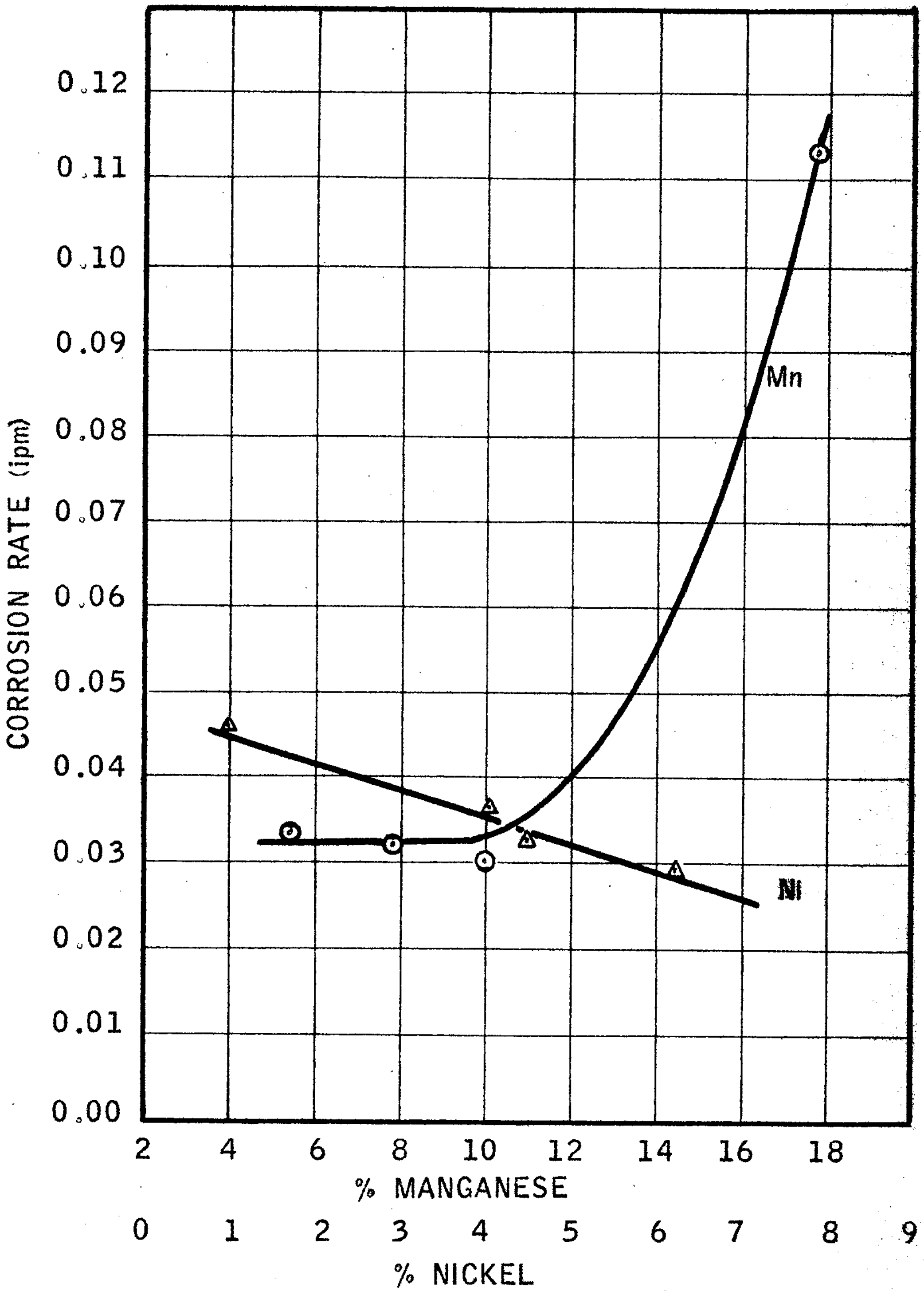
NO.	1	2	3	4	5	6	7	8	9	10	11	12
[illegible].	5	4	5	4	2	6	4	4	1	6	1	9
Mn	9	9	9	10	10	7	10	10	15	14	15	1

points 9 & 10 are for similar alloys containing 1 and 6% nickel. Similarly, data point 12 which is an 18 Cr - 8 Ni alloy shows a higher rate than a 18 Cr - 6 Ni - 7 Mn alloy. These apparent descrepancies lead one to question this data. The data of others (11, 19, 10, 12) indicate that the Types 201 & 202 and the low nickel alloys are as resistant to acetic acid as are the 18% chromium - 8% nickel and 12% chromium alloys.

Neutral, aggressive, organic acids - lactic acid. The effect of both manganese and nickel in boiling 50% lactic acid are shown in Figure 12 (15). As found in other environments manganese in concentrations less than 11% has no effect on the corrosion resistance of an alloy containing 17% chromium - 4% nickel. At concentrations greater than 11%, manganese will greatly increase the corrosion rate. Nickel, in an alloy containing 17% chromium and 6 - 10% manganese improves the corrosion resistance as the concentration is increased from 1 to 7%. The improvement is significant by comparison to other environments. It would be expected from these data that a reduction in nickel would seriously affect the corrosion resistance of the alloys. Manganese in the concentrations proposed (5.5 to 10%) for the chromium-manganese-nickel alloys should not in itself affect the corrosion resistance.

Inorganic bases - potassium hydroxide. Data for this reagent is meager. The only data found was that of Hatscher (11) on room temperature tests in 5% potassium hydroxide. He reported that two steels containing 15 - 16% Cr, 0.5% Ni & 16 - 18% Mn were as resistant as AISI Types 301 and 430 alloys. However, none showed a measurable corrosion rate.

Atmospheric corrosion. Although there is much information



● EFFECT OF MANGANESE CONDUCTED WITH STEELS CONTAINING 17% Cr & 4% Ni.

△ EFFECT OF NICKEL CONDUCTED WITH STEELS CONTAINING 17 - 18% Cr & 6 - 10% Mn.

FIG. 12 EFFECT OF MANGANESE & NICKEL ON CORROSION RATE IN BOILING 10% LACTIC ACID. (15)

published on this, there is little quantitative data available on the corrosion resistance of various compositions. Flint and Taft (20) have published the results of exposure tests at Birmingham, England. The results of this industrial exposure of 18% Cr, 10% Mn, 2% Ni; 17% Cr; and 18% Cr, 8% Ni alloys are given in Table 3. It can be seen from this that the manganese steel is intermediate to the straight chrome steel and the chromium-nickel steel. Others (21,22,23,24,11) report that Types 201 and 202 alloys and the high chromium-high manganese alloys are as resistant to both industrial and marine atmospheres as Types 301, 302 and 304 alloys.

Since the addition of 12% chromium will make iron stainless in the atmosphere, it is not expected that the addition of manganese will alter the resistance. The qualitative data reported support this. Only in severe marine exposure are the low nickel, high manganese alloys inferior to Types 301 and 302 alloys. This may result from the presence of a duplex austenite-ferrite structure present in the alloys tested.

Oxidation resistance. There has been considerable data published on the comparative oxidation resistance of AISI Types 201, 202 & 304 alloys. But the data on the effect of various manganese contents is rather limited. Only three authors treat the subject (25,26,27). Unfortunately, they were treating the effect of so many variables that it is difficult to obtain a clear picture of the role manganese plays. Table 4 presents the data of Brown (26). This shows that the addition of 10 to 14% manganese to a 20% chromium alloy increases the oxidation rate considerably. (The molybdenum and tungsten additions should have no effect on the oxidation rate (2).) It should be noted, however, that

TABLE 3

ATMOSPHERIC CORROSION OF CHROMIUM-MANGANESE-NICKEL AUSTENITIC STAINLESS STEELS (20)

Composition Cr	Mn	Ni	Surface Condition	Time days	Ave. Corr. Rate (mdd)	Max. Depth of pits (in.) Upper Surface	Lower Surface	Ave. No. pits/cm^2 Upper	Lower
18	10	2	Pickled	566	-	0.002	0.0035	20	18
18	10	2	Polished	510	0.23	0.003	0.003	20	25
17	-	-	Pickled	566	-	0.003	0.005	10	30
17	-	-	Polished	510	0.09	0.005	0.0045	10	30
18	-	8	Pickled	566	-	0.002	0.0015	5	2
18	-	8	Polished	510	0.06	0.003	0.001	12	10

TABLE 4

OXIDATION RATES FOR VARIOUS CHROMIUM; CHROMIUM-MANGANESE; AND CHROMIUM-NICKEL ALLOY STEELS (26)

Composition							Weight Gain*	
Mn	Cr	Ni	C	Si	Mo	W	1835°F	2015°F
0.48	26.16	-	0.26	0.50	-	-	9.33	22.7
14.64	22.39	-	0.24	0.63	-	-	66.7	96.3
9.36	21.10	-	0.20	0.66	2.66	-	62.7	98.4
10.03	18.90	-	0.13	0.42	-	2.02	-	91.5
0.60	19.18	8.62	0.26	0.52	-	-	11.7	264.
0.36	17.58	24.75	0.34	2.70	-	-	2.90	14.6

*grams/meter^2

a 10% manganese-18% chromium alloy is inferior to a 9% nickel-19% chromium alloy at 1835°F but is more resistant at 2015°F.

It is interesting to note the effect of nickel on oxidation resistance as reported by Brown. At 1835°F a 9% nickel - 19% chromium alloy is about as resistant as a 26% chromium alloy and a 25% nickel - 18% chromium alloy is considerably better. However, at 2015°F the 9% nickel - 19% chromium alloy shows an extremely high rate (264 grams/meter^2) while the 12% chromium and the 25% nickel - 18% chromium alloys have increased only a slight amount to 22.7 and 14.6 grams/meter^2 respectively.

Table 5 gives the data of Harder & Gow (27) on the effect of manganese at the lower temperatures of 1400 and 1600°F. These data show that at a constant chromium and nickel content, the best resistance is obtained with 10% manganese. For the 6% chromium - 8% nickel and the 10% chromium - 4% nickel alloys the increase in oxidation rate for both higher and lower manganese contents is appreciable. Monypenny (25) shows that the maximum rate of attack occurs at 10% manganese. His data was based on seven alloys containing 20% Cr and either 0.1 or 1.0% C at 1800°F (1000°C).

Typical results from comparative tests of Types 204 and 304 alloys are shown in Figure 13. Type 204 alloy has the same oxidation rate as Type 304 alloy up to about 1500°F. Above this temperature the Type 204 alloy oxidizes at a much more rapid rate. Figure 14 shows the weight gain as a function of time. At 1250 and 1450°F both the Types 204 and 304 alloys form a protective scale as shown by the decrease in rate of weight gain with time. At 1650°F the Type 204 alloy continues to gain weight with time indicating that the oxide scale is not protective and

TABLE 5

OXIDATION RATES FOR VARIOUS CHROMIUM-MANGANESE-NICKEL ALLOY SYSTEMS (27)

Composition					Weight loss*	
Mn	Cr	Ni	Si	C	1400°F	1600°F
5	6	4	1	0.31	0.090	0.374
10	6	4	2	0.47	0.096	0.295
15	6	4	1	0.29	0.121	0.295
5	6	8	1	0.30	0.078	0.314
10	6	8	2	0.31	0.065	0.256
15	6	8	1	0.31	0.117	0.577
5	10	4	1	0.30	0.067	0.189
10	10	4	2	0.50	0.010	0.003
15	10	4	1	0.31	0.032	0.201
3	10	8	2	0.33	-	0.045
5	10	8	2	0.30	0.0021	0.015
10	10	8	2	0.59	0.005	0.004
15	10	8	1	0.32	0.015	0.157
1	12	6	1	0.53	0.004	0.049
4	12	6	1	0.50	0.121	0.066
8	12	6	1	0.49	0.004	0.023
10	12	6	2	0.50	0.0015	0.003
3	12	8	2	0.33	-	0.007
8	12	8	2	0.33	-	0.007
3	12	10	2	0.33	-	0.011
5	12	10	2	0.33	-	0.006
4	18	6	2	0.40	0.0015	0.0015
6	18	6	2	0.30	0.002	0.0015
1	24	12	1	0.38	0.001	0.002

*grams/inch^2/day

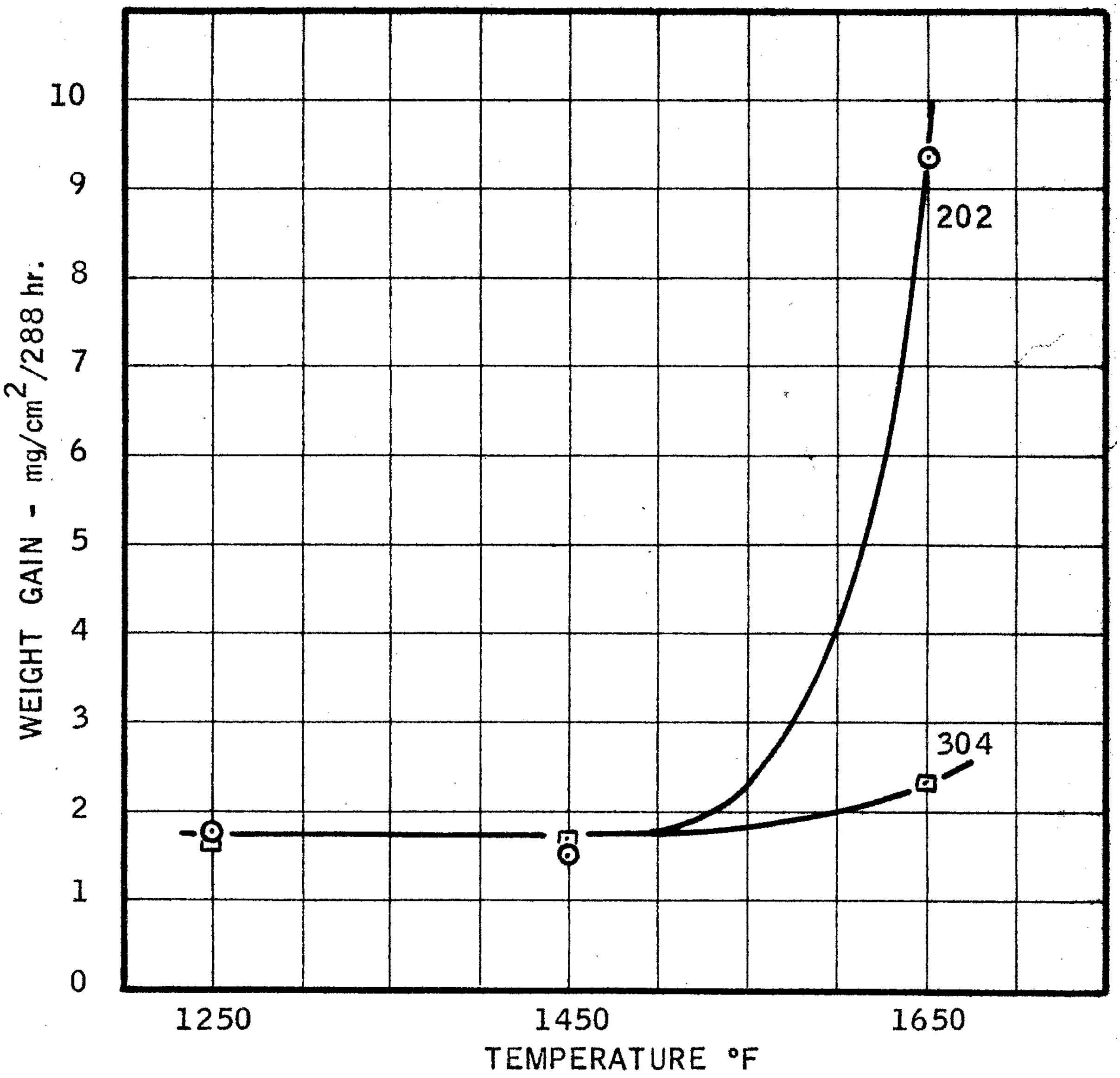


FIG. 13 COMPARITIVE OXIDIATION RATES OF TYPE 202 AND TYPE 304 ALLOY STEELS. (31)

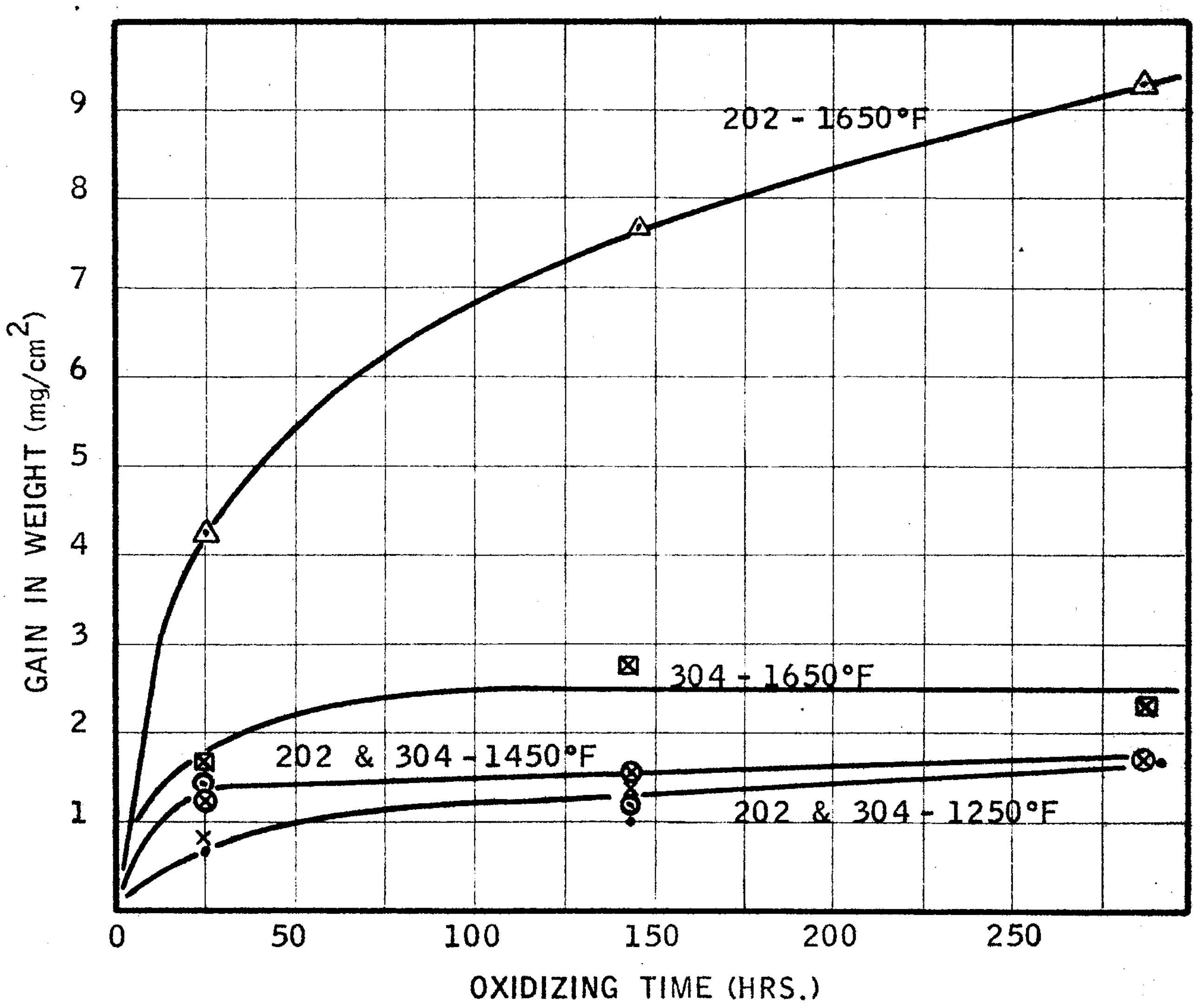


FIG. 14 OXIDATION RATES OF TYPES 202 & 304 ALLOY STEELS AS A FUNCTION OF TIME. (31)

excessive oxidation occurs.

Based on these data the substitution of manganese for a portion of the nickel will reduce the maximum allowable temperature for long time exposure of the alloy. The temperature limit should be about 1500°F for long life. This conclusion is backed by others (24,28,21,29, 30) who agree on this general temperature range, but offer no data.

<u>High temperature sulfur</u>. Everyone talks about this system but no one has done much about it. There are many references (5, 28, 32, 4, 22, 25, 29) to the good resistance of the manganese bearing steels to sulfur attack. This is, most likely, based on theoretical analysis of the alloy. Simply, nickel is not resistant to sulfur, therefore if it is replaced with manganese more resistant to sulfur, the resistance of the alloy will be improved. The picture is summed up neatly by Monypenny (3) who states, ". . . it may be noted that little experimental evidence in support of this (resistance to sulfur) appears to have been published."

Harder and Gow (27) have presented limited data on experimental alloys in oxidizing and reducing sulfurous environments at 1400 and 1600°F. A summary of this data is presented in Table 6. At a given concentration of chromium and nickel, manganese has no significant effect. The effects of increasing chromium and nickel are much more significant.

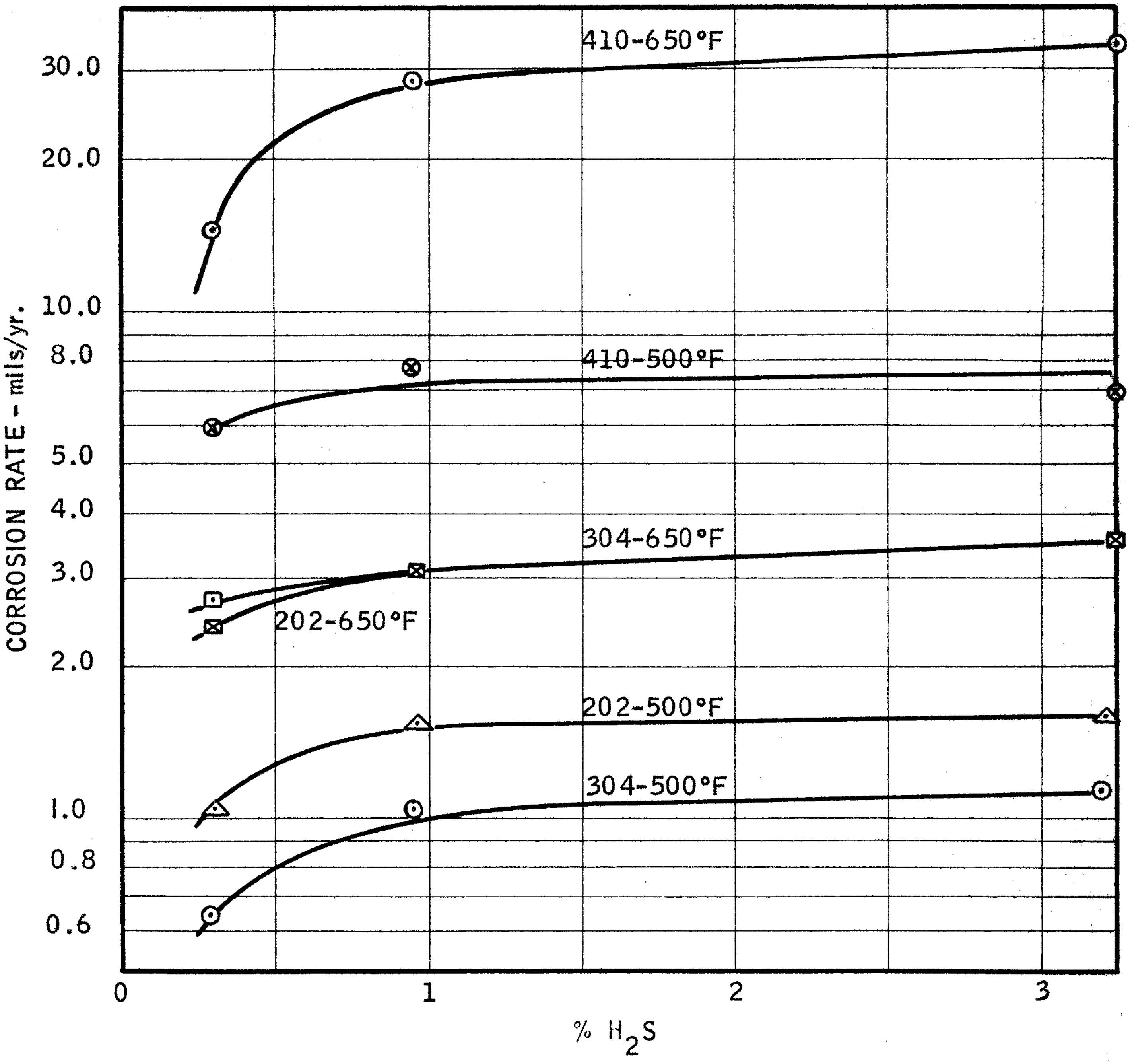
Figure 15 shows the comparative corrosion rates for Types 410 (12% Cr), 202 and 304 alloy steels exposed to hydrogen sulfide. The environment contained 50% hydrogen, 0.3 to 3.5% hydrogen sulfide and the balance methane at 200 psi. The Type 202 alloy is comparable to Type 304 alloy at a temperature of 650°F but is inferior at 500°F. Both

TABLE 6

CORROSION RATES FOR CHROMIUM-MANGANESE-NICKEL ALLOY STEELS IN SULFUROUS ATMOSPHERES (27)

Composition %				Weight Loss - grams/in^2/day			
				Oxidizing-Sulfur		Reducing-Sulfur	
					B	C	D
Mn	Cr	Ni	Si	220 grains	200 grains	104 grains	19 grains
3	10	8	2	0.179	0.302	-	0.00063
5	10	8	2	0.205	0.273	-	-
6	10	8	2	-	-	0.0115	0.00170
8	10	8	2	0.158	-	-	-
3	12	8	2	0.099	-	0.0117	0.00047
5	12	8	2	0.032	0.214	-	-
6	12	8	2	-	0.158	-	0.00160
8	12	8	2	0.063	-	0.0113	-
8	10	8	2	0.158	-	-	-
8	12	8	2	0.063	-	0.0113	-
1	18	8	1	-	0.110	0.0183	0.006
1	25	12	1	0.0023	0.008	0.0019	0.00057

No.	Temp. °F	Time (hr)	CO_2	O_2	CO	H	H_2O	S(grains)	N	Remarks
A	1600	100	12.4	8.0	-	-	4.6	220	bal	X'cess air
B	1600	100	5.9	0.0	4.6	3.5	4.0	200	bal	)Deficiency of
C	1400	100	9.0	0.0	5.5	4.7	5.1	104	bal	)air for complete
D	1400	100	7.0	0.0	6.4	5.1	3.8	19	bal	)combustion



TEST CONDITIONS: TIME 190 HRS.
ATMOSPHERE: 50% H_2, H_2S, BAL. CH_4

FIG. 15 CORROSION OF TYPES 410, 202 & 304 ALLOY STEELS IN HYDROGEN SULFIDE. (31)

steels are considerably better than the Type 410 alloy. This environment has been shown to be particularly aggressive to the straight chromium steels with data reporting the 12% Cr alloy no more resistant than the carbon steels.

From the limited data available, the substitution of manganese for nickel does not improve the resistance of the alloy to sulfur corrosion. In general these data show manganese to decrease the resistance of the alloy to sulfur attack. In hydrogen sulfide the presence of manganese may be more beneficial at higher temperatures. This should be investigated further to determine if the manganese alloy is more resistant or whether the nickel alloy was less resistant.

Intergranular Corrosion. The austenitic chromium-manganese-nickel steels are susceptible to intergranular corrosion (34,8,6,35,18,33). Franks, Binder and Thompson (35) analyzed a H_2SO_4 - $CuSO_4$ solution in which a 15.2% Cr, 11.8% Mn, 2.1% Ni, 0.12% C, 0.5% Cu alloy exhibited intergranular attack after being heated for 1 hour at 1300°F (725°C). The analysis showed chromium to be present in the solution in lower quantities than in the steel indicating that the chromium content of the steel adjacent to the grain boundaries was decreased as a result of the heat treatment. Chromium was present in the grain boundaries as chromium carbide. The analysis also showed manganese to be present in the solution in slightly larger quantities than in the steel. Grimshaw (34), presenting limited data, suggests that the addition of both manganese and copper will increase the resistance of the alloy to intergranular corrosion by 10% $CuSO_4$ - H_2SO_4.

The most systematic study of the susceptibility of the austenitic chromium- manganese-nickel stainless steels has been made by Binder, Thompson and Bishop (35). They determined the effect of carbon on alloys containing 18.25% Cr, 7-11% Mn, 4-10% Ni, 0.4% Si, 0.22% N and 0.010-0.043% C. The intergranular corrosion tests were conducted on specimens heated 30 minutes at 2000°F (1075°C) and air cooled, then reheated 1, 6, and 24 hrs. at 1200°F (650°C), 100 hrs. at 1000°F (550°C), 8 weeks at 750°F (400°C) and 16 weeks at 570°F (300°C). The test solutions consisted of boiling 65% nitric acid, 10% nitric acid - 3% hydrofluoric acid at 158°F (70°C) and boiling, acidified, copper sulfate solution.

It was found that the maximum carbon content at which the alloy retains its immunity under the conditions of test is related to the sum of the manganese and nickel contents. This is similar to the relationship that exists in the 0.03% carbon austenitic chromium-nickel steels. This is shown in Figure 16 for alloys heated for 6 hours at 1200°F (650°C). It can be noticed that the carbon limit decreases as the sum of the manganese and nickel increases. The carbon limits for 1, 6 and 24 hours at 1200°F (650°C) are shown in Table 7. None of the steels exhibited intergranular attack after heating for 16 weeks at 570°F (300°C) or for 8 weeks at 750°F (400°C). As predicted by the tests at 1200°F (650°C), complete immunity to attack was shown by alloys containing 0.025% C and manganese plus nickel less than 14% in the 100 hr. test at 1000°F (350°C).

These conclusions agree with the data presented by Renshaw and Lula (15) and de Sy (33). Renshaw and Lula presented data on ten alloys containing 17-20% Cr, 8-10% Mn, 4-5% Ni, 0.11-0.40% Ni and 0.017-0.11%C. Allegheny-Ludlum have published (13) data on the resistance of two

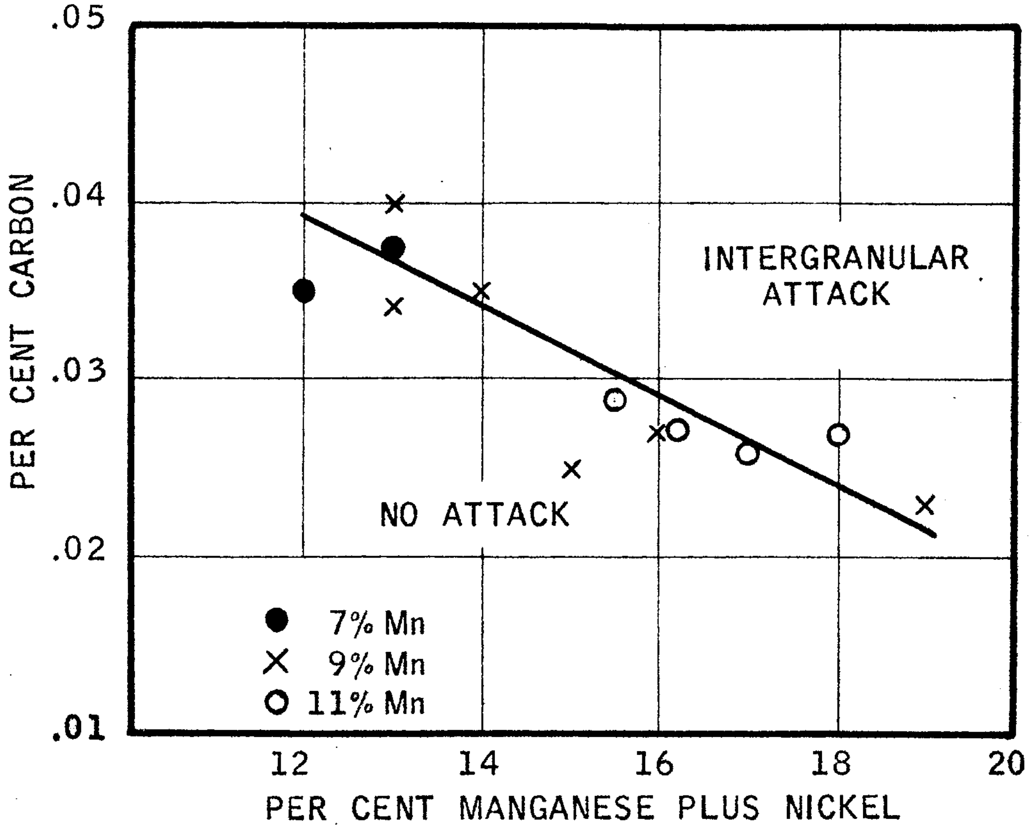


FIGURE 16 RELATIONSHIP BETWEEN CARBON LIMIT FOR IMMUNITY TO INTERGRANULAR CORROSION AFTER 6 HOURS AT 650°C. AND THE MANGANESE - PLUS - NICKEL CONTENT OF THE STEEL DETERMINED FROM TESTS IN BOILING 65% NITRIC ACID. (35)

TABLE 7

CARBON LIMIT FOR IMMUNITY TO INTERGRANULAR CORROSION (35)

Heating Time at 650°C	% (Mn Ni)	% Carbon Limit Boiling 65% HNO_3 Acid	 10% HNO_3-3% HF @ 70°C	 Boiling Acidified $CuSO_4$ Solution
1 hour	14	0.050	0.040	0.050
1 hour	18	0.035	0.030	0.040
6 hour	14	0.035	0.030	0.030
6 hour	18	0.025	0.020	0.020
24 hour	14	0.025	0.020	0.020
24 hour	18	0.020	0.015	0.015

experimental alloys which tends to confirm these conclusions. One is a 204L composition containing 0.03%C with 7.5/10.0% Mn, 5/7 Ni, & 17/19 Cr which resisted attack by boiling 65% HNO_3 after being heated to 1200°F for 24 hours. A CM alloy containing 0.15% C with 13/18 Mn, 1 Ni, and 14/17 Cr, was rapidly attacked after only 2 hour exposure to 1200°F. Flint and Toft have reported (20) that an alloy containing 0.08% C, 10.5% Mn, 1.9% Ni and 17.5% Cr was rapidly attacked after sensitizing at 1200°F (650°C) for 2 hours.

The only data in real conflict with these conclusions was presented by Binder and Thompson in an earlier paper (8) with Franks. Twenty four alloys containing 3.5-4.5% Ni, 7-9% Mn, 16-18% Cr were tested after heating to 1200°F (650°C) for 20 minutes and 1000°F (550°C) for 2 hours. Exposure to 65% boiling nitric acid showed that no attack would occur on those heated to 1000°F (550°C) if the carbon was less than 0.1%. Those exposed to 1200°F (650°C) showed accelerated attack if the carbon was at 0.1%. Lowering carbon to 0.06% significantly reduced the rate of attack. However, these results are not in direct contradiction since the sensitizing time was short compared to the previous tests quoted.

Based on the work of Binder et. al., to attain immunity to intergranular attack the carbon content must be less than 0.025% if the sum of the manganese plus nickel is 14 and 0.020% if the manganese plus nickel equals 18. Columbium and titanium can not be used to stabilize the manganese steels as with the chromium-nickel steels. They will remove carbon and nitrogen from the alloy with the formation of delta ferrite. This may lead to hot-working difficulties and a general reduction in corrosion resistance of the alloy. In low nickel steels, titanium causes the austenite to transform to low temperature ferrite and the steel may lose its non-magnetic properties.

CORROSION ENGINEERING OF THE CHROMIUM-MANGANESE-NICKEL AND THE CHROMIUM-MANGANESE AUSTENITIC STAINLESS STEELS

It has been shown that the substitution of manganese for nickel will not seriously affect the corrosion resistance of the chromium-nickel austenitic stainless steels in a great many environments. These alloys appear to be a new class of steels that will find an application in industry. They have a slight cost advantage of about five cents per pound over the chromium-nickel grades. This section will cover the corrosion resistant properties of the manganese containing austenitic stainless steels now available. The compositions and designations are given on page 12, but will be repeated in the specific discussion below.

A compilation of the corrosion data available for these alloys is presented in Table 8 on pages 56 to 63. In some cases the data of separate investigators were not in agreement and the best reconciliation was made. As with all corrosion data presented in this manner, one must consider the corrosion rates presented only an indication of the rate that may be experienced in a given exposure. The effect of temperature variations, exposure time, velocity, contaminants, etc. may cause these rates to vary considerably.

AISI Type 201 - 0.15max%C, 16/18%Cr, 3.5/5.5%Ni
5.5/7.5%Mn, 0.25max%N

AISI Type 202 - 0.15max%C, 17/19%Cr, 4/6%Ni, 7.5/10%Mn 0.25max%N

These two alloys will be discussed together as they have similar characteristics. In most corrosive environments they show equivalent corrosion resistance, probably because the difference in alloy content is small. It has been shown that in many environments no change in corrosion resistance was noted at manganese contents up to about 10%. Both of these alloys contain less than 10% manganese. The nickel limits overlap for the two alloys, so, while it is possible to have a difference of 2.5% in nickel it is not probable.

Compared to the 18% chromium - 8% nickel alloys, Types 301, 302 and 304, the Types 201 and 202 alloys have equivalent resistance in most environments, as shown in Table 8. In the stronger acids, such as sulfuric and oxalic, these alloys are inferior. In a number of organic compounds, the Types 201 and 202 alloys are superior to Types 304 and 316 alloys, the most resistant of the 18% chromium- 8% nickel grades. In all cases reported the Types 201 and 202 alloys are superior to the 17% chromium (Type 430) alloy except when neither corroded.

Based on the data of Binder, Thompson and Bishop (35) these alloys should experience intergranular attack after heating to 1200°F for as little as one hour. The carbon content of 0.15% max. is greatly in excess of the 0.025% carbon limit for steels containing manganese plus nickel less than 14%. In earlier tests Franks, et. al. (8) had shown that the Types 201 and 202 compositions containing 0.10% carbon were rapidly attacked when heated for as little as 20 minutes at 1200°F and exposed to boiling 65% nitric acid. Renshaw and Lula (15) present data to show that the carbon limit should be anout 0.06%. All investigators agree that intergranular attack will occur at the carbon level permitted in these alloys. When using these alloys, the same precautions must be taken as with the Types 301 and 302 alloys to avoid intergranular corrosion. It has been found (6) that a knife-line attack occurred on welded specimens of Types 201 and 202 alloys similar to that with the Types 301 and 302 alloys.

The Types 201 and 202 alloys do not have the oxidation resistance of the chromium - nickel grades. Figure 17 presents the oxidation resistance of these alloys. It can be seen that the Types 201 and 202 alloys are equivalent to the Type 304 alloy at temperatures below 1400°F. Above this temperature the rate increases more rapidly than with either Types 301 or 304. For applications where oxidation is a factor the alloys will find limited application. Due to some inconsistancies in the data, it would be advisable to test the alloy at temperatures above 1400°F before plant scale application is made.

The superior resistance to high temperature sulfur attack of the manganese containing alloys has been reported quite widely. However, the data in support of this is lacking. From the limited data found (27,31) Figure 15, it can be concluded that the Types 201 and 202 alloys will be no more resistant than the chromium-nickel alloys. Much additional work is required before definite conclusions can be made.

The austenitic stainless steels are not known for their resistance to sea water corrosion. The manganese containing alloys likewise are not resistant to attack by sea water. Alloysof the Type 201 composition were tested in flowing sea water at Kure Beach, N. C., for 191 days.

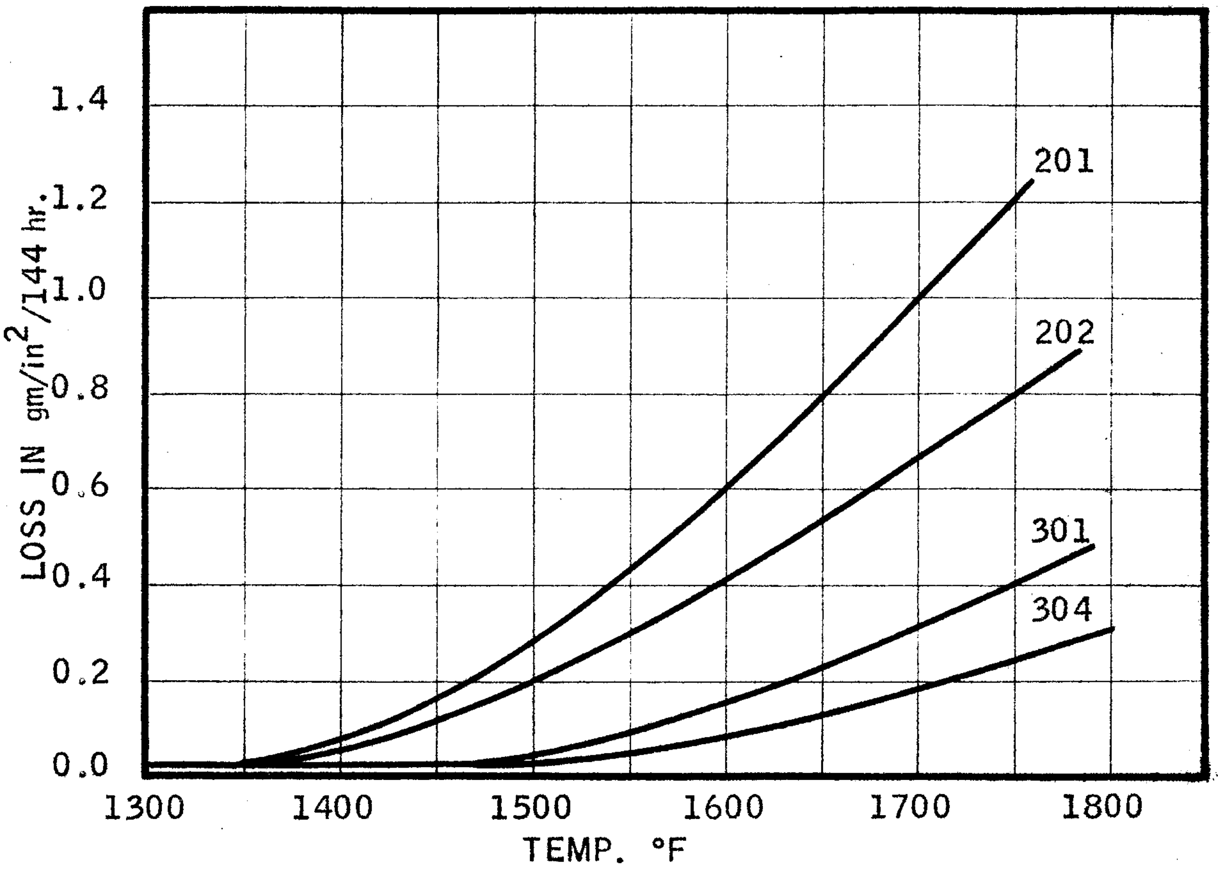


FIG. 17 OXIDATION RATES OF TYPES 201, 202, 301 & 304 ALLOY STEELS. (8)

The weight loss was slightly higher than for Type 302 alloy but both specimens were perforated at the end of the test. The addition of manganese has not helped the corrosion resistance of the austenitic stainless steels in this environment.

The atmospheric corrosion resistance is similar to that experienced with the Types 301, 302 or 304 alloys. Figure 18 shows test panels that have been exposed for 10 months to a marine atmosphere at Kure Beach, N. C. The similarity of test panels shows that the Types 201 and 202 alloys will be suitable in applications where Types 301, 302 and 304 are now used.

The new manganese containing chromium-nickel austenitic stainless steels, Types 201 and 202, appear to fill a number of applications where the chromium-nickel alloys are now used. The alloys have sufficient corrosion resistance to be called stainless steels, although they will not fill all the applications where the chromium-nickel alloys are now used.

204 Stainless Steel - 0.08max%C, 7.5/10.0%Mn, 17/19Cr,
4/6%Ni, 0.25max%N

204L Stainless Steel - 0.03max%C, 7.5/10.0%Mn, 17/19%Cr,
4/6%Ni, 0.25max%N

Although these steels are designated by the producer (a) with a number similar to those used by the AISI these compositions have not been accepted by the AISI to date. By comparing the compositions to those for Types 201, 301, 202, 302 and 304, it is evident that they follow the existing pattern and would be proposed as a substitute for the Type 304 alloy. Since they differ from the Type 202 alloy by only

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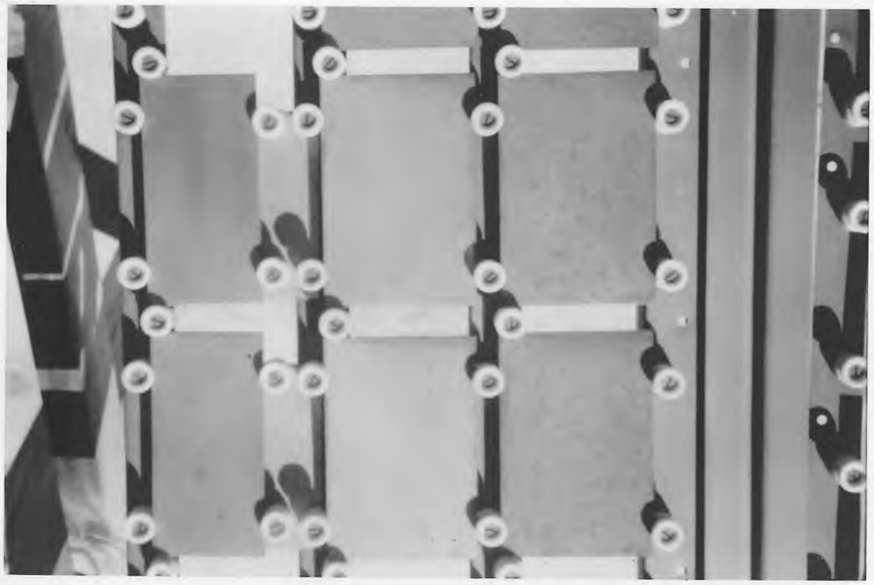
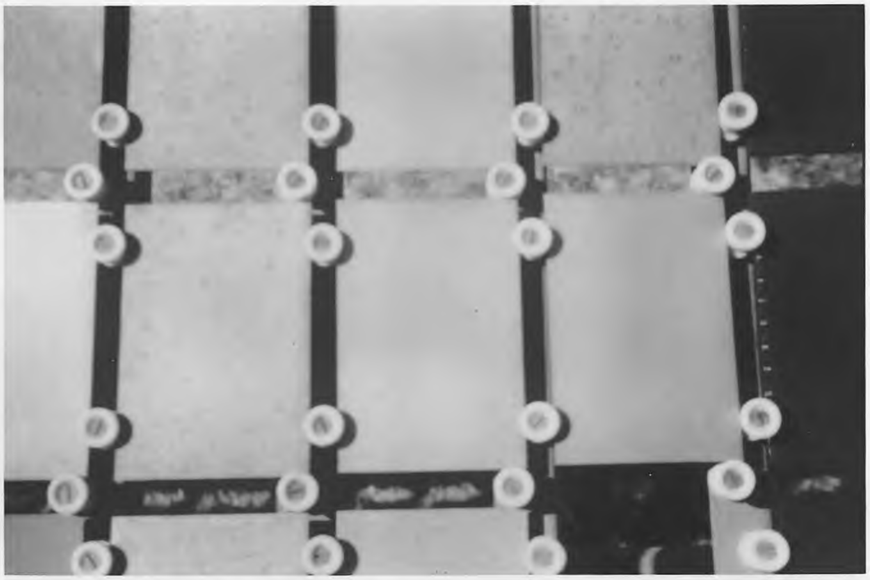
(a) Allegheny Ludlum Steel Corp.



Type 304 Type 302 Type 202
At 80 feet from the sea.



Type 202 Type 302
At 800 feet from the sea.

FIG.18 TYPES 302, 304, 201 AND 202 ALLOYS EXPOSED
9 MONTHS TO MARINE ATMOSPHERE AT KURE BEACH, N.C.

a lower carbon content, they would be expected to have a corrosion resistance similar to that for the Type 202 alloy. The lower carbon content will decrease the amount of grain boundary carbide precipitation and increase the resistance to intergranular attack. Based on the data of Renshaw (15) the alloys should be very resistant, but the data of Binder (35) would show them to be susceptible to intergranular corrosion. The use of these alloys where intergranular corrosion is a major factor should be approached on the same basis as with Type 304 alloy.

Chromium-Manganese Austenitic Stainless Steels Containing Less Than 1% Nickel

There are no "standard" alloys in this classification although several are being produced. Listed below are the designations and composition of these alloys.

DESIGNATION	COMPOSITION %				
	C	Mn	Cr	Ni	N
Tenelon	0.10max	14.5	17	—	0.40
TRC	0.08	14.5	15min	1.0	0.20
CM	0.15max	13/18	14/17	1.0	0.25
CMN	0.65	12	25	—	0.45

The general corrosion resistance of these alloys varies between that of the Types 201 and 202 alloys and Type 430 (17%Cr) alloy. The resistance to various chemicals is given in Table 8. In general these alloys are as resistant as the higher nickel grades in the mildly corrosive atmospheres but are decidedly inferior in the moderate to severe corrosives. This is the combined result of reducing nickel and increasing manganese. It has been shown that the nickel content is critical in the more severly corrosive atmospheres. Lowering the nickel will increase the corrosion rate. Manganese in most atmospheres was shown to have little effect at concentrations below 10%. Above this, corrosion resistance was lowered. With the combined effect of reducing nickel to less than 1% and increasing manganese to about 14% the alloy definitely loses some of its corrosion resistance.

The corrosion resistance of these alloys depends upon the stability of the structure. They are all austenitic in the annealed condition. However, as pointed out earlier, the austenitic structure at these high chromium and low nickel contents is dependent upon the balance between carbon and nitrogen in the alloy. It has been found with alloys such as TRC that considerable delta ferrite is formed during rolling. Its presence will decrease the corrosion resistance of the alloy. The Tenelon alloy is claimed to be resistant to ferrite formation during rolling operations. Before using these alloys where mild corrosives are involved, samples of fabricated parts of the alloy should be tested.

As would be expected from the high carbon content of these alloys, they are susceptible to intergranular corrosion. Exposure to boiling, 63% nitric acid after heating to 1200°F for 2 hours has produced severe attack of the alloy. Samples of TRC alloy have been sensitized at 1200°F for 1 hour and have been completely embrittled as measured by the Strauss Test (19). These alloys would be expected to show intergranular attack in the heat affected areas adjacent to welds unless subsequent heat treatment were possible. It has also been shown (19) with the TRC alloy that cold working the alloy will increase the susceptibility to sensitization. A sample of annealed TRC showed no carbide precipitation after heating for 5 minutes at 1300°F. After cold rolling to a reduction of 9 and 20%, heating to 1300°F caused the precipitation of carbides. This points up again the value of having a stable austenitic structure in the alloy. It is most desirable to retain the austenitic structure in the fabricated product.

Little data is available on the oxidation resistance of these alloys although some of the alloys do have superior high temperature mechanical properties (12). The oxidation resistance is not expected (36, 29, 2) to be as good as the chromium-nickel or the chromium-manganese-nickel alloys. The resistance should be equivalent to that of the straight chromium alloys containing the same amount of chromium. Although these alloys were first used in Germany for furnace covers (19) it is not anticipated that they will have application as heat resistant alloys. In addition, by virtue of their lower nickel content these alloys will be more susceptible to the formation of the sigma phase (5) than the Types 201 & 202 alloys.

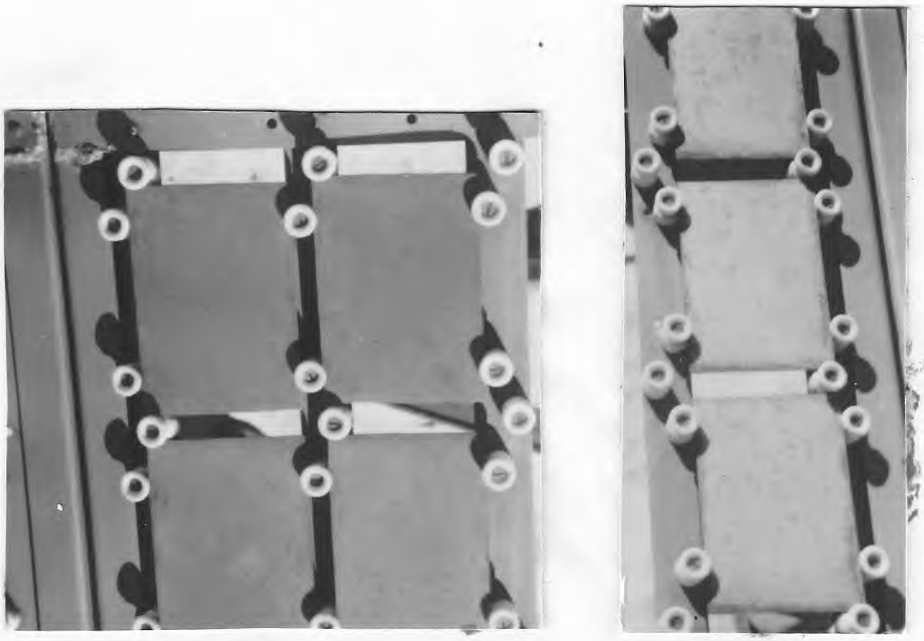
No data is available on the high temperature sulfur resistance of these alloys. Contrary to the reports of may, the limited data available shows that replacement of nickel with manganese does not improve the alloy. Lacking data on the low nickel alloys, it must be assumed they would be no more resistant than the Type 430 alloy.

As with the Types 201 and 202 alloys, the very low nickel grades are not resistant to sea water. Tests on a 10% Mn, 18% Cr, 0.16% Ni, 1% Cu alloy showed it to corrode at a rate three times that of Types 304 alloy and to be perforated at the end of the test when Type 304 showed only minor pitting (19). These alloys are not suitable where resistance to sea water is required.

For atmospheric exposures these steels should be as resistant as the chromium-nickel alloys. As pointed out earlier little quantitative data is available of the corrosion rates experienced. Exposure tests and commercial applications of these alloys for periods up to nine years in marine and industrial atmospheres has shown these alloys to be comparible to the Types 301 and 302 alloys. In severe marine exposures as represented by the 80 foot lot at Kure Beach, N. C., these alloys are not as resistant as the Types 301 and 302 alloys. Figure 19 shows panels of TRC and Tenelon now on test at the Kure Beach exposure site of the International Nickel Company.

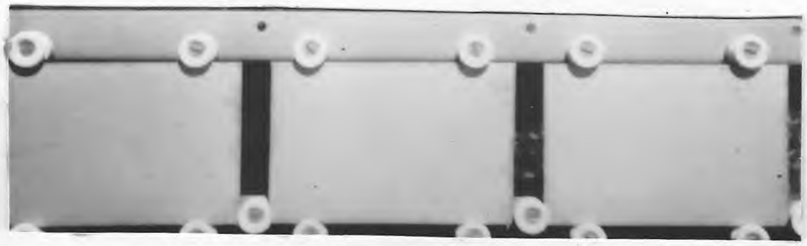
Service experience of the low nickel alloys has been quite favorable. These alloys have been used in the construction of railroad cars and automotive truck trailers. It has been reported (21) that the Budd Co. has had these steels in use for 15 years with no evidence of corrosion due to normal atmospheric conditions or common cleaning solutions. These steels are completely suitable where atmospheric resistance is required.

The low nickel, chromium-manganese austenetic stainless steels are applicable where only mild corrosives are present. They will fill the need for the Types 301 and 302 alloys where the corrosion resistance of the Type 430 alloy is adequate, but does not have the necessary physical properties. The majority of these applications would involve exposure to the atmosphere where a non-tarnishing surface is required. The alloy does not have sufficient corrosion resistance to be used in industrial equipment where corrosion resistance is required. There is little data on these alloys for industrial environments. The data available



TRC TENELON

Exposed 80 feet from the sea.



TENELON

Exposed 800 feet from the sea.

FIG. 19 TRC AND TENELON EXPOSED TO MARINE ATMOSPHERE AT KURE BEACH, N.C.

indicate that the alloy may be suitable in a limited number of environments. Before plant scale application is made, tests should be conducted on fabricated parts to verify the resistance of the alloy to be used.

TABLE 8

CORROSION RATES FOR THE CHROMIUM-MANGANESE-NICKEL, CHROMIUM-NICKEL, AND CHROMIUM STAINLESS STEELS.

TABLE 8-a CORROSION RATE (inches per month)

Media	Conc. %	Temp. ^{o}F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Acetic Acid	5	Room	nil		nil			nil	TRC nil		11,19
	10	Boiling					nil	nil	TRC nil		19
	60	158	0.00001		0.00001	0.00001		0.000017	0.00001 TRC	Tenelon 0.00001	10,16,12
Glacial Acetic Acid: Vapor		Boiling	0.0004	0.0010			0.0004		TRC 0.0020		15
Liquid		Boiling	0.00025	0.00024			0.00011		TRC 0.0021		15
Glacial Acetic Acid	15	Boiling		0.0000			0.0000				16
Acetic Acid-Acetic Anhydride Mixture	-	-					ipy 0.0039	0.0024	Type 316 ipy	18-5-5 ipy 0.0025	37
Crude Acetic Acid-Acetic Anhydride Mixture	-	-					ipy 0.0484		Type 316 ipy 0.0175	18-5-5 ipy 0.0675	37
Ammonium Chloride	5	Room	nil		nil			0.00002	TRC nil		19
Aluminum Chloride	5	Room	nil		nil			nil	TRC nil	18-10-2 nil	20,19

18-5-5 = 18.27%Cr, 5.23%Mn, 5.21%Ni, 0.05%C, 0.12%N
18-10-2 = 18%Cr, 10%Mn, 2%Ni

TABLE 8-b CORROSION RATE (inches per month)

Media	Conc. %	Temp. °F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Aluminum Sulfate	5	Room	nil		nil			nil	TRC nil		19
Calcium Chloride	5	Room			nil			nil*	TRC nil*		*Slight Pitting 11
Calcium Hypochlorite	5	Room	nil		nil			0.00004	TRC nil		19
Citric Acid	20	Boiling					nil	nil	16-16-1 nil		109
	25	Boiling		nil			nil				16
Crude Diethyl sulfate-vapor	-	122		ipy 0.0171			ipy 0.0083				37
-Liquid	-	122		ipy 0.0183			ipy 0.0087				37
Crude dimethoxy-butane	-	266		ipy 0.0002			ipy 0.0002		Type 316 ipy 0.0002		37
Dichlorophenoxyeth- and isopropyl benzoate	Conc.	248					nil		Type 347 nil	18-5-5 nil	37

16-16-1 = 16%Cr, 16%Mn, 1%Ni

TABLE 8-c CORROSION RATE (inches per month)

Media	Conc. %	Temp. °F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Dioxane plus 0.1% Water & 8% HCl	-	Room					ipy 0.0068		Type 316 ipy 0.0035	18-5-5 ipy 0.0030	37
Dioxane plus 8% HCl		Room					ipy 0.0065		Type 316 ipy 0.00.8	18-5-5 ipy 0.0048	37
Dry Dioxane purged with dry HCl during test		212					ipy 0.0053		Type 316 ipy 0.0047	18-5-5 ipy 0.0062	37
Formaldehyde	22.8	878		< 0.0001			<0.0001	0.0001			aerated. 38
	35	185		<0.0001			<0.0001	<0.0001			aerated. 38
	35	185		<0.0001			<0.0001	<0.0001			non-aerated. 38
	39	235		<0.0001			<0.0001	<0.0001			non-aerated. 38
	37 to 48	120		<0.0001			<0.0001	<0.0001			non-aerated. 38
Glutaric Anhydride Distillation-Liquid		313		ipy 0.023			ipy 0.045		Type 316 ipy 0.005	18-5-5 ipy 0.030	37

TABLE 8-d CORROSION RATE (inches per month)

Media	Conc. %	Temp °F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Glutaric Anhydride Distillation-Vapor		431.6		ipy 0.0002			ipy 0.0072		Type 316 ipy 0.0045		37
Hydrochloric Acid	2	120					0.0008	0.0064	16-16-1 0.2160		19
Lactic Acid	5	86	0.00001		0.00001	0.00001		0.00001			16,12
	10	Boiling					<0.0001	0.0002	16-16-1 0.0001		19
	15	Boiling		nil			nil				16
	50	Boiling	0.0373	0.0317			0.0940		15-41-1 0.0358	20-6-8 0.0278	15
Magnesium Chloride	5	Room	nil		nil			0.00003	TRC nil		19
Nitric Acid	5	Room	nil		nil			nil	TRC nil		11,19
	5	Boiling	0.00003		0.00003	0.00003		0.00013	TRC 0.00007	Tenelon 0.00007	12
	65	Boiling	0.0014	0.0014	0.00084			0.0040	TRC 0.0050		15,8,9, 10,16

15-14-1 = 16%Cr, 15%Mn, 1%Ni
20-6-8 = 20%cr, 9%Mn, 5.5%Ni

TABLE 8-e CORROSION RATE (inches per month)

Media	Conc. %	Temp. °F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Oxalic Acid	5	Room	nil					nil	TRC nil		19
	10	200	0.0243	0.0235			0.0065		15-$\overset{14}{41}$-1 0.0358	20-6-8 0.0278	15
Pentanedione Distillation Vapor	-	-		ipy 0.0090			ipy 0.0026		Type 316 ipy 0.0004		37
Liquid	-	-		ipy 0.0361			ipy 0.0136		Type 316 ipy 0.0020		37
Perfluorobutyryl Chloride in Freon		32		ipy 0.0009			ipy 0.0006		Type 316 ipy 0.0003		37
Phosphoric Acid	5	Room	nil		nil			nil	TRC nil		19
	10	86	0.00001		0.0001	0.00001		0.00001	TRC 0.00001	Tenelon 0.00001	10,12
	10	Boiling	nil	nil			nil		15-14-1 0.053	20-6-8 nil	15,14
	40	Boiling					0.0004	0.0004	16-16-1 0.0005		19
	50	Boiling		0.0003			0.0001				10

TABLE 8-f CORROSION RATE (inches per month)

Media	Conc. %	Temp. °F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Potassium Hydroxide	5	Room	nil		nil			nil	TRC nil		11,19
Reaction making amino - ethyl hydrogen sulfate	-	194		ipy 0.0179			ipy 0.0231		Type 316 ipy 0.0132		37
Salt spray	20	Room			nil			mild attack	mild attack		11,23
Sodium Chloride	5	Room			nil			nil**	nil**		**slight pitting 11
Sodium Hypochlorite	0.10	160					gm/in^2 0.0002	gm/in^2 0.00064	Type 316 gm/in^2 0.00014	16-17-1 gm/in^2 0.000136	19
Sodium Sulfate	Conc.	Room	nil		nil			nil	TRC nil		19
Sulfuric Acid	2	120					<0.0001	<0.0001	16-16-1 0.0002		19
	5	Room	nil		nil			0.0025	TRC 0.00283		11,19
	5	86	0.013		0.001	0.001		0.390	TRC 0.390	Tenelon 0.200	12
	10	158	1.1	1.0	0.2				TRC 2.8		8

TABLE 8-g CORROSION RATE (inches per month)

Media	Conc. %	Temp. °F	Type 201	Type 202	Type 301	Type 302	Type 304	Type 430	Other	Other	Remarks & References
Sulfurous Acid Vapor	Conc.	Room	0.0004*	0.0004*			0.0007*		15-14-1 0.0121*	20-6-8 0.0006*	15
Liquid	Conc.	Room	0.0003*	0.0002*			0.0004*		15-14-1 0.0647*	20-6-8 0.0007*	15
Tartaric Acid	30	Boiling		nil			nil	nil	16-16-1 nil		11,16,19
Zinc Chloride	5	Room	nil		nil			nil	TRC nil		19
Acrylonitrite and Water		221		nil			nil		Type 316 nil	18-5-5 nil	37

*grams loss per 28 days

BIBLIOGRAPHY

References

1. Compilation by the American Stainless Steel Producers.

2. Bennett, E. V., "Low Nickel Austenetic Stainless Steels" Materials Advisory Board Staff Study, Rept. No. MAB-45-SM, National Research Council.

3. Monypenny, J. H. G., Stainless Steels in Industry, Vol. 1 Stainless Iron and Steel, Chapman & Hall, Ltd., London (1951).

4. Gurzberg, Z., W. A. Alexandcrova & L. S. Gelderman, "Properties of Corrosion Resisting Chromium-Manganese and Chromium-Nickel-Manganese Steels" Archiv für das Eisenhüttenwesen V. 8, September 1934, pp. 121-123.

5. Sully, A. H., Manganese Academic Press, Inc., New York, 1955, 305 pp.

6. Lincoln, R. A., "Nickel Restrictions Bring Use of New Stainless Steels" Iron Age V.171, No. 20, May 14, 1953, p. 139.

7. Everhart, J. L., "Chromium-Manganese Stainless Steels" Materials and Methods V. 39, No. 3, March 1954, pp. 92-94.

8. Franks, R., W. O. Binder & J. Thompson, "Austenitic Chromium-Manganese-Nickel Steels Containing Nitrogen" Transactions, American Society for Metals, V. 47, 1955, pp. 231-250.

9. Carney, D. J., "High-Nitrogen Steels: New Stainless Family" Steel V. 137, November 7, 1955, pp. 138, 140, 144.

10. Hall, A. M., & D. B. Roach, "New Stainless Steels" Materials & Methods, April, 1956, p. 137.

11. Hatschek, R. L., "New Austenitic Stainless Good Alternate for 18-8" The Iron Age, V. 171, March 12, 1953, pp. 135-138.

12. ______, "Nickel-Free Austenitic Stainless Steels", Materials & Methods, January, 1957, pp. 104-105.

13. ______, "The Chromium-Nickel-Manganese Austenitic Stainless Steels" Allegheny Ludlum Steel Corp., 1956, 10 pp.

14. Snair, G. L., Jr., & [illegible]. G. Renshaw, "The Corrosion Resisting Properties of the New Chromium-Nickel-Manganese Austenitic Stainless Steels" Paper Presented at the 13th Annual Conference, National Association of Corrosion Engineers, St. Louis, Missouri, March 11-15, 1957.

15. Renshaw, W. G., and R. A. Lula, "The Corrosion Properties of Chromium-Nickel-Manganese Austenitic Stainless Steels" Paper Presented at the 59th Annual Meeting, American Society of Testing Materials, June 17-22, 1956.

16. ________, "New Stainless Steels Containing 17% Chromium- 4% Nickel-6% Manganese and 18% Chromium - 5% Nickel - 8% Managnese" American Iron and Steel Institute, Contribution to the Metallurgy of Steel, No. 47, May 1955, 10 pp.

17. Huddle, F. P., "Nickel Conservation with High - Manganese Stainless Steels" Metals Progress, V. 8, No. 6, 1955, p. 100.

18. Parks, J. M., "Chromium-Manganese 'Stainless' Irons", Metals & Alloys, V. 17, 1943, pp. 330-335, 539-543.

19. Private Communication, The Budd Company.

20. Flint, G. N., and L. H. Toft, "Properties of a High-Manganese Austenitic Stainless Steel" Metallurgia, V. 51, No. 305, March, 1955, pp. 125-129.

21. ________, "How to Use the New Low Nickel Austenitic Stainless Steels" Steel Processing, V. 42, July, 1956, pp. 404-406.

22. Beckett, F. M., "Rustless Chromium-Manganese Steels Have Deep-Drawing Qualities" Iron Age, V. 125, 1930, pp. 1468-1470

23. Gray, A. G., "New Stainless Stretches Nickel" Steel, V. 132, March, 9, 1953, pp. 94-97.

24. Paret, R. E., "Fabrication of Low-Nickel, High-Manganese Stainless Steels" Metals Progress, V. 69, No. 5, May 1956, pp. 55-57.

25. Monypenny, J. H. G., "Chromium Manganese Steels as Heat Resistant Steels" Metallurgia, V. 17, January, 1938, pp. 93-96

26. Brown, M. P., "Heat Resisting Steels Without Nickel" Metal Progress, V. 39, 1941, pp. 336-338.

27. Harder, O. E. and J. T. Gow, "An Emergency Heat-Resistant Alloy" Transactions, American Society for Metals, V. 32, 1944, pp. 409-482.

28. Schmidt, M. and W. Lamarche, "Heat Resisting Chromium-Manganese Steels as Substitutes for Chromium-Nickel Steels" Metals & Alloys, V. 13, 1944, p. 805.

29. Krivobok, V. N., "Permanency of the Stainless Steels" Metal Progress, V. 34, 1938, p. 223.

30. ______, "Research Results for Higher Manganese Stainless Steels," Steel Processing, V. 42, January, 1956, p. 42.

31. Private Communication, Esso Research and Engineering Co.

32. Legat, H. J., "Austenitic Cr-Mn Steels are Unusually Creep Resistant" Metal Progress, V. 33, 1938, p. 284.

33. deSy, A. I., "Chromium-Manganese Stainless Steels" Metals and Alloys, V. 11, 1940, p. 38.

34. Grimshaw, L. C., "Manganese and Copper Additions to '18 and 8' - Armstrong Metal" Metals & Alloys, V. 6, 1935, p. 264.

35. Binder, W. O., J. Thompson and C. R. Bishop, "Intergranular Corrosion Resistance of Low-Carbon Austenitic Chromium-Manganese-Nickel Steels" Paper Presented at the 59th Annual Meeting, American Society of Testing Materials, June 17-22, 1956.

36. Kluke, R, "Einfluss von Manganzusätzen bis 20% auf Gefüge und Eigenschaftern von Gusslegierungen mit 30% Cr" Arch. Eisenhüttenwesen, V. 11, June, 1938, pp. 615-618

37. Private Communication: Electro-Metallurgical Co.

Additional Literature

Brown, D. I., "New Stainless Passes its Tests" *The Iron Age*, V. 171, No. 1, January 1, 1953, p. 228.

Bruhl, F., "Gefüge und Eigenschaften von Chrome-Mangan-Stählen mit Gehalten bis 1%C, 15%Mn, und 30%Cr" *Arch. Eisenhuttenwesen,* V. 10, December 1936, pp. 243-255. Abst. *Metals & Alloys,* V. 8, 1937, p. 572.

Carney, D. J., "Nickel-Free and Low Nickel Austenitic Stainless Steels" *Blast Furnace and Steel Plant,* V. 43, December 1955, pp. 1377-1380.

Franks, R., "Effects of Special Alloy Additions to Stainless Steels," *Transactions,* American Society for Metals, V. 27, 1939, p. 505.

Franks, R. and W. O. Binder, "Cold Rolled Stainless in Aircraft" *Mechanical Engineering,* V. 64, 1942, p. 589.

Franks, R., W. O. Binder and C. M. Brown, "High Manganese Austenitic Steels" *The Iron Age,* V. 150, October 1, 1942, pp. 51-57.

Hinkle, G. W., "Making 200-Type Stainless" *Steel,* V. 139, July 9, 1956, pp. 94-96.

Kendall, V. V., "Corrosion and Corrosion-Resistant Metals & Alloys" *Metals & Alloys,* V. 8, 1937, p. 313.

Liberman, L. and P. Strelts, "Nickel Free Heat Resistant and High Strength Steels" *Kach. Stal.*, V. 5, No. 4, 1937, pp. 11-21. Abst. *Metals & Alloys V.9,* 1938, p. 112.

Mack, D. J., "High-Manganese Stainless Steels" *Metals & Alloys,* V. 18, November 1943, pp. 1081-1084; September 1943, pp. 507-512.

Paret, R. E., "Experience with High Manganese Stainless Steels" *Metals Progress,* June, 1956.

Rohn, W., "Acid Resistance of Vacuum Melted Alloys Containing Nickel" *Chemical & Metallurgical Engineering,* V. 34, July, 1927, pp. 417-420.

_______, "Chromium-Manganese Stainless - A Composite" *Metals & Alloys,* V. 16, 1942, pp. 960-966.

_______, "Low-Nickel Austenitic Stainless Standardized" *American Machinist,* V. 100, April 23, 1956, pp. 126-128.

_______, "Nickel-Free Austenitic Stainless Steels," *Materials & Methods,* January, 1957, p. 104.