

Effects of Alloying Elements on the Pitting Corrosion of Stainless Steels

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Effects of alloying elements on the pitting corrosion resistance of 17Cr-16Ni steels with and without 4% Mo were evaluated by the corrosion rate in 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4% NaCl added with hydrogen peroxide and by the polarization measurement in 0.1N NaCl+0.1-0.25N Na_2SO_4 at 40°C. The elements, the content of which was varied, were carbon, nitrogen, silicon, phosphorus, sulfur, manganese and nickel. The supplementary alloying elements were aluminum, titanium, vanadium, cobalt, copper, zirconium, niobium, tin and tungsten. Tungsten, like silicon, was found beneficial in minimizing the pitting corrosion if added together with molybdenum. Carbon was favorable if no chromium carbides were formed. Copper added to the Mo-free steel was beneficial, but not effective in the Mo-bearing steel. Manganese was proved to be harmful in both Mo-free and Mo-bearing steels, but increasing its content more than that of ordinary stainless steels did not enhance its harmful effect. The very favorable effect of nitrogen was also recognized. The effects of the other alloying elements are summarized in a table. The more noble the electrode potential at a relatively high c.d., *i.e.* 10mA/cm², in anodic polarization curves measured in sodium chloride solution, the lower was the corrosion rate in the ferric chloride test if a second phase was absent. The presence of a second phase increases especially the corrosion rate in ferric chloride solution. It was indicated that the alloying to increase the passivating ability of the steel would shift the pitting potential to the more noble direction by passivating the depassivated sites before they can grow as ordinary pits.

1. Introduction

About one fifth of the wet corrosion failure cases of stainless steel equipments in the chemical industry are caused by pitting corrosion.^{1,2)} Controlling metallurgical factors is one of the most practical measures to minimize this kind of failure, and, therefore, several new types of stainless steels claimed to be resistant to pitting corrosion are being developed. These new stainless steels contain generally a large amount of chromium in combination with molybdenum. The effects of alloying elements on the pitting corrosion of stainless steel are summarized in review articles.^{3,4)} Although the effects of chromium and molybdenum are well recognized by many investigators, the effects of the other alloying elements are not well established yet. Especially a combined effect of two or more elements has not been clarified. In this investigation the effects of several alloying elements on the pitting corrosion of austenitic stainless steels with and without molybdenum were evaluated by several experimental condi-

tions, and the results obtained through different methods were compared one another.

2. Experimental

The nominal composition of the base steel, to which various kinds of elements were added is as follows: 0.03% C, 0.02% N, 0.5% Si, 1.5% Mn, 0.005% P, 0.01% S, 17% Cr, 16% Ni, and 0% or 4% Mo. The amount of the elements other than chromium, nickel and molybdenum were determined as above so that these steels could be manufactured by the same process as in the case of ordinary austenitic stainless steels, such as Types 304 and 316. The amount of these elements was varied in a certain range as shown in the upper half of Table 1, in the lower half of which the elements added to the base steel are shown. The air-melted ingots were hot worked to bars of 13 mm in diameter by swaging, heat treated at 1050°C for one hour and water quenched. The specimens polished with 500 grit paper were submitted to immersion tests in 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 4% NaCl added with 0.15% H_2O_2 at 40°C. The duration of the tests was 24 hours.

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Table 1. Amount of alloying elements added to 17Cr-16Ni-(4Mo) steels.* (wt%)

Alloying elements	17Cr-16Ni steel	17Cr-16Ni-4Mo steel
C	0.005-0.1	
N	0.02-0.2	
P	0.005-0.1	
S	0.01-0.1	
Ni		10-20
Si	0.5-2.5	0.25-1.5
Mn	0.05-6	0.1-6
Ti, Zr, Nb, Al	up to 2	up to 1
V, Mo, W	up to 4	up to 1
Co	-	up to 3
Cu	up to 2	up to 4
Sn	up to 0.2	up to 0.2

* The composition of the base steels:
 17Cr-16Ni steel—0.03C, 0.02N, 0.5Si, 1.5Mn, 0.005P, 0.01S, 17Cr, 16Ni.
 17Cr-16Ni-4Mo steel—17Cr-16Ni steel+4Mo.

The pitting corrosion resistance was estimated by weight loss. The anodic polarization was measured in deaerated 0.1N NaCl containing sodium sulfate at 40°C by using a potentiostatic potential step rate of 50 mV every two minutes. In order to distinguish the differences among the effects of various alloying elements clearly the amount of sodium sulfate added to 0.1N NaCl was varied according to base compositions, namely 0.25N for Mo-free steels and 0.1N for Mo-bearing ones. The specimen for polarization measurement was mounted in epoxy resin after passivation treatment in 15% HNO₃+2% HF and the surface of 1 cm² was polished with 500 grit paper immediately before the measurement. The passivation treatment before mounting prevented any corrosion from occurring at the interface between the metal and the resin. If crevice corrosion was observed in the specimen after the test, the data obtained from it were omitted. The critical current density for passivation was measured in 1N H₂SO₄+0.05N NaCl at 40°C, in order to find if there would exist any correlation between the passivation ability in the acid and the pitting corrosion resistance of the steel. The cathodic polarization of the tested steels was also measured in 100 g/liter Fe₂(SO₄)₃·xH₂O+0.7 g/liter FeSO₄·7H₂O at 40°C.

3. Results

The dependence of the corrosion rate in the

ferric chloride solution and the pitting potential* in 0.1N NaCl added with sodium sulfate on alloying elements is shown in Figs. 1-4. As to the Mo-free steel, carbon, nitrogen, copper and molybdenum minimize the corrosion rate in the ferric chloride solution and also shift the pitting potential to the more noble direction. Tungsten and vanadium showed similar effects, but to a lesser degree. Although titanium increased the pitting potential, it was detrimental in the ferric chloride test. On the other hand zirconium, nickel and silicon were found beneficial in the ferric chloride test, but they had no appreciable influences on the pitting potential. Niobium, manganese, aluminum and sulfur were detrimental in both the ferric chloride test and the polarization test. Decreasing the manganese content of the base alloy to less than 0.1 per cent was very beneficial. Addition of tin (up to 0.2%) and phosphorus (up to 0.1%) showed little effect.

As to the Mo-bearing steel, manganese, alumi-

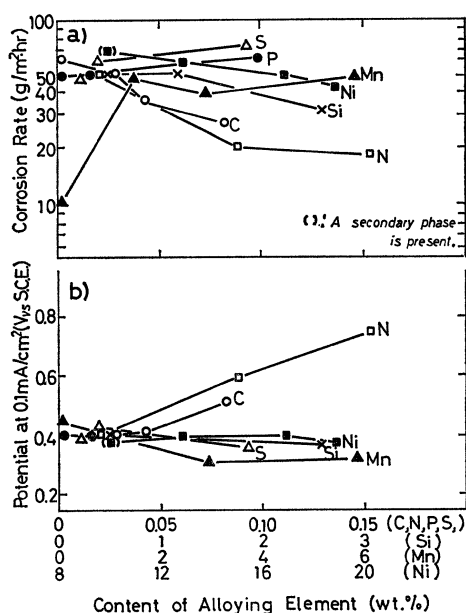


Fig. 1. Effects of alloying elements in 17Cr-16Ni steels on: a) the corrosion rate in 10% FeCl₃·6H₂O at 40°C, and b) the potential at 0.1 mA/cm² in anodic polarization curves in 0.1N NaCl+0.25N Na₂SO₄ at 40°C. (I) (Effects of the variation of the amount of the elements present in the base steel).

* In this paper the electrode potential at the c.d. of 0.1 mA/cm² in the anodic polarization curves was expressed as a "pitting potential."

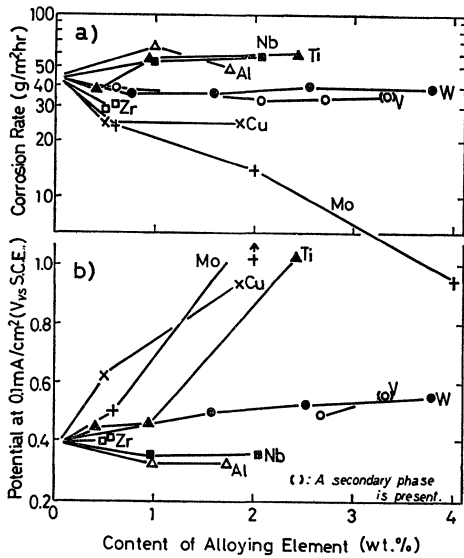


Fig. 2. Effects of alloying elements in 17Cr-16Ni steels on: a) the corrosion rate in 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 40°C, and b) the potential at 0.1 mA/cm² in anodic polarization curves in 0.1 N NaCl+0.25 N Na₂SO₄ at 40°C. (II) (Effects of supplementary alloying elements).

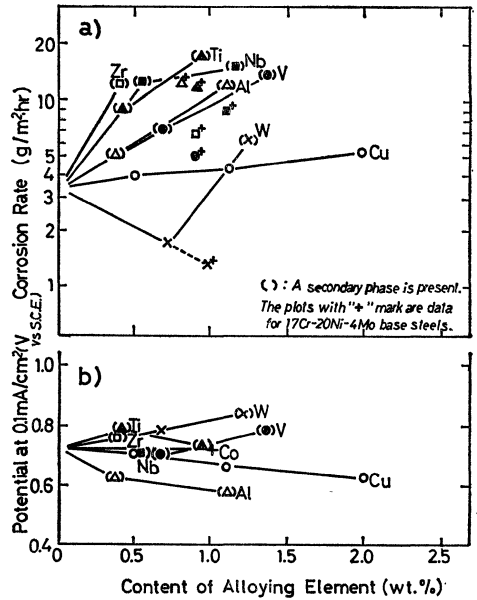


Fig. 4. Effects of alloying elements in 17Cr-16Ni-4Mo steels on: a) the corrosion rate in 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 40°C, and b) the potential at 0.1 mA/cm² in anodic polarization curves in 0.1 N NaCl+0.1 N Na₂SO₄ at 40°C. (II) (Effects of supplementary alloying elements).

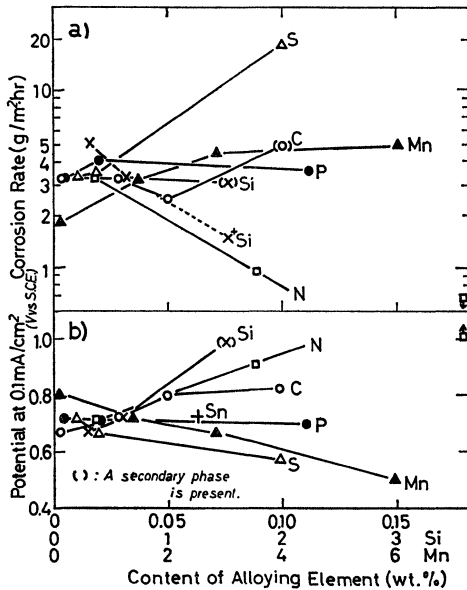


Fig. 3. Effects of alloying elements in 17Cr-16Ni-4Mo steels on: a) the corrosion rate in 10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 40°C, and b) the potential at 0.1 mA/cm² in anodic polarization curves in 0.1 N NaCl+0.1 N Na₂SO₄ at 40°C. (II) (Effects of the variation of the amount of the elements present in the base steel).

num, carbon, nitrogen and sulfur behaved in the same way as in the Mo-free steel. Copper in combination with molybdenum reduced pitting corrosion resistance estimated by the above tests, but it did not seem to impair the resistance in the 4% NaCl immersion test. Tungsten added together with molybdenum was beneficial in all the test conditions. However, the corrosion rate in the ferric chloride solution increased when specimens contained ferrite, sigma or carbide in the microstructure. The absence of these phases should lower the corrosion rate as indicated by the data with the 17Cr-20Ni-4Mo steel in Fig. 4, except for aluminum, which was detrimental whether ferrite or sigma phase is present or not. The presence of a second phase itself did not have, however, an appreciable influence on the pitting potential.

The effects of alloying elements on the pitting corrosion resistance of the stainless steels evaluated in different conditions are summarized in Table 2, together with the results by other authors.³⁻⁸⁾ The qualitative data in 4% NaCl added with hydrogen peroxide are given in this table.

Table 2. Effects of alloying on pitting corrosion resistance of austenitic stainless steels.*

Group	Alloying element	Own experiments						Literature ³⁻⁸⁾
		Mo-free steel			4% Mo steel			
		Anodic polar.	FeCl ₃	NaCl	Anodic polar.	FeCl ₃	NaCl	
IIa	Be		—					
IIIa	Ce		—**					—
IVa	Ti	+	—	?	0	—	?	—, 0, +
	Zr	0	+	?	0	—	?	0
Va	V	+	0, +	?	0	—	?	+
	Nb	—	—	?	0	—	?	—, 0
	Ta							0
VIa	Cr	+	+	+	+	+	+	+
	Mo	+	+	+				+
	W	+	0, +	?	+	+	+	0
VIIa	Mn	—	—	—	—	—	—	0, +
	Re							+
VIII	Co				0	+	0	
	Ni	0	+	?				+
Ib	Cu	+	+	+	—	—	+	
IIIb	Al	—	—	?	—	—	—	
IVb	C	+	+	+	+	+	+	
	Si	0	+	?	+	+	+	—, 0, +
	Sn	0	0	0	0	0	0	
Vb	N	+	+	?	+	+	?	+
	P	?	0	?	0	0	?	
VIb	S	—	—	—	—	—	—	—
	Se							—

* +: effective, 0: no effect, —: detrimental, ?: The effect is not clear. Anodic polar.: Anodic polarization in 0.1N NaCl+0.1–0.25N Na₂SO₄ at 40°C. FeCl₃: 10% FeCl₃·6H₂O at 40°C. NaCl: 4% NaCl+0.15% H₂O₂ at 40°C

** Ce+La misch metal.

4. Discussion

4.1. Relation between the Corrosion Rate in the Ferric Chloride Test and the Pitting Potential

The relation between the corrosion rate in the ferric chloride test and the electrode potential at a relatively high current density, *i.e.* 10 mA/cm², in the anodic polarization curves in sodium chloride solution is shown in Figs. 5 and 6. There exists a general tendency that the steel with lower corrosion rate shows a more noble potential at the above current density, though there are some exceptions.

The steel with 2.4% Ti in Fig. 5 shows a much greater corrosion rate in the ferric chloride test than expected from the anodic polarization. This is attributed to its greater depolarizing effect on the cathodic reaction in the ferric-ferrous system⁶⁾ ($\beta_c=0.08$) than the other elements ($\beta_c=0.11-0.14$). The plots for the steels with a second phase in Fig. 6 deviate also to the upper direction except for aluminum-alloyed steels. The presence of some secondary phases did not change, however, the cathodic polarization in the ferric-ferrous

system significantly. It is probable that the chromium and molybdenum depletion, which might be produced in the vicinity of the second phase, accelerates the pitting corrosion, especially in the ferric chloride solution. If the depleted zone is very small it will not influence the polarization behavior appreciably.

A negative deviation from the general relation is recognized in Fig. 5 for the steel whose manganese content is lower than the base steel. According to microscopic examinations, some of the inclusion particles in the base steel were attacked in the ferric chloride solution. When the same steel was immersed, however, in an acidified ferric chloride solution, almost all the inclusion particles were easily attacked. Table 3 shows the corrosion resistance of inclusions in 10% ferric chloride with 3.5% hydrochloric acid as a function of the manganese content. The manganese-chromium sulfide with relatively high chromium content, chromite and silica seem to be immune even in the acidified ferric chloride. In the steel with

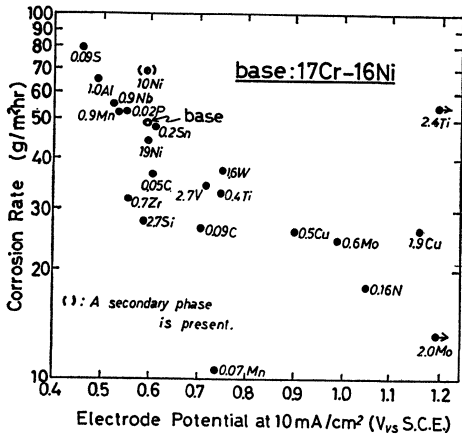


Fig. 5. Relation between the corrosion rate of 17Cr-16Ni steels with various alloying elements in 10% FeCl₃·6H₂O and the electrode potential at 10 mA/cm² obtained from anodic polarization curves in 0.1 N NaCl+0.25 N Na₂SO₄ at 40°C.

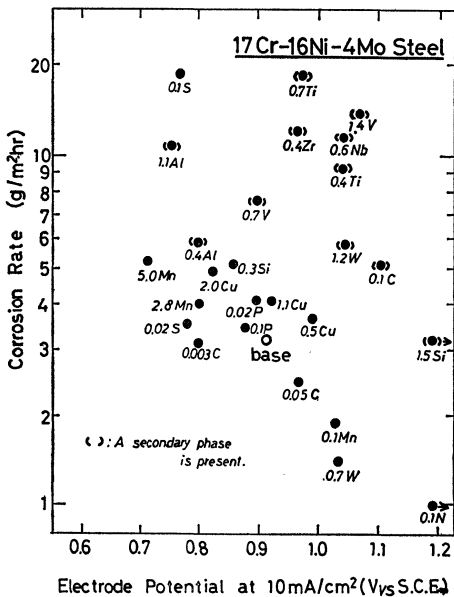


Fig. 6. Relation between the corrosion rate of 17Cr-16Ni-4Mo steels with various alloying elements in 10% FeCl₃·6H₂O and the electrode potential at 10 mA/cm² obtained from anodic polarization curves in 0.1 N NaCl+0.1 N Na₂SO₄ at 40°C.

0.04% Mn no inclusion is attacked in this medium. But when the manganese content is increased to 0.47%, manganese silicate is formed. This is attacked by the same solution. If the manganese content is further increased, the chromium content in the manganese-chromium sulfide is reduced,

Table 3. Corrosion resistance of inclusions in 17Cr-16Ni-0.5Si-0.03S steels with various amounts of manganese. Tested in 10% FeCl₃·6H₂O+3.5% HCl.*

Type of inclusion	Mn content (%)				
	0.04	0.47	1.13	1.67	2.30
(Cr, Mn)S	R	R	C	C	C
(Cr content in the sulphide)**	(35%)	(28%)	(8.5%)	(6%)	(4.5%)
Cr ₂ O ₃ -SiO ₂	R	R	—	—	—
MnO-SiO ₂	—	C	C	C	C

* R: Resistant, C: Corroded.

** Determined by electron micro-probe analysis.

ed, and it will become attacked by the acid solution. It can be supposed from these results that if the steel contains little manganese, the number of secondary pits, which are produced by the acidified solution flowed out of the originally formed pits, is less than that of the steel with 1.5% Mn. If the size of the inclusion is smaller than that of the micro pit which can be easily passivated before it grows to a stable pit, the inclusion itself seems to have not an appreciable effect on the polarization curve. The small inclusion site might be passivated after the inclusion has been dissolved.

Figure 7 is a schematic representation of the relation between the corrosion rate in the ferric chloride test and the polarization in the sodium chloride solution.

4.2. Relation between the Pitting Potential and the Critical Current Density for Passivation in the Acid

It has been often observed during anodic polarization measurement of stainless steels in sodium chloride solution that small pits are produced and again passivated in the potential range where stably growing pits are not formed.⁹⁻¹²⁾ Similar phenomena were observed in the present experiment. It is assumed from these phenomena that the steel easily passivated, *i.e.* the steel with lower critical current density for passivation, should have a more noble pitting potential. In Figure 8 the relation between the pitting potential and the critical current density for passivation in the acid is shown. This figure does not contradict the above assumption. Favorable alloying elements to pitting corrosion resistance may help towards passivating the micro pit before it can

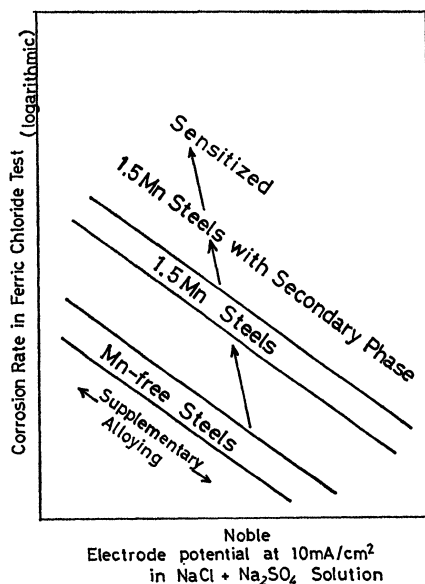


Fig. 7. Relation between the corrosion rate in the ferric chloride test and the electrode potential at a relatively high c.d., e.g. 10 mA/cm², in the polarization curves in sodium chloride solution as influenced by the manganese content and microstructures of the stainless steels. (Schematic).

become larger than a certain critical size, and accordingly shift the pitting potential to the more noble direction. Only the plot for the steel with 0.16% N fairly deviates from the general relation. According to our previous study,¹³⁾ nitrogen increases the pitting corrosion resistance of austenitic stainless steels not only by stabilizing austenite as insisted by M. A. Streicher,⁵⁾ but also by consuming proton in the depassivated site (or pit) to produce ammonium ion, and thus preventing the lowering of pH in it and passivating it before it can grow as an ordinary pit. The effect of nitrogen would be therefore greater if the elements with high passivating ability, such as chromium, molybdenum and nickel, are present in the steel. Table 4 gives the analysis of ammonium ion in the

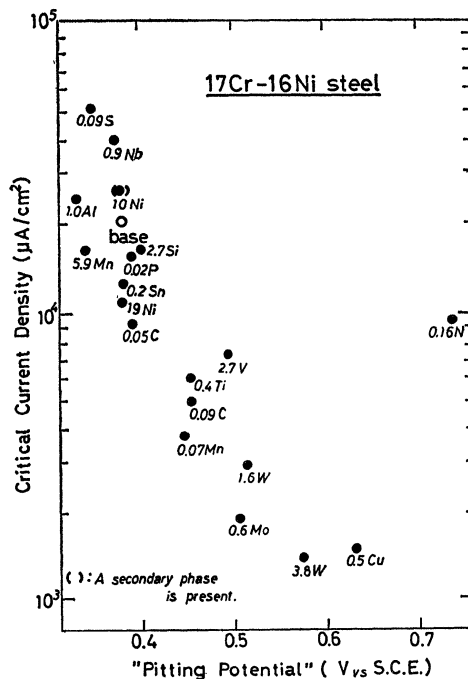


Fig. 8. Relation between the pitting potential* of 17Cr-16Ni steels with various alloying elements in 0.1 N NaCl+0.25 N Na₂SO₄ and the critical current density for passivation in 1 N H₂SO₄+0.05 N NaCl at 40°C.

* Potential at the c.d. of 0.1 mA/cm² in anodic polarization curves.

solution after the pitting corrosion test of nitrogen containing steels. It is indicated that nitrogen goes into solution as ammonia and is present as ammonium ion. Nitrogen was beneficial not only for stable austenitic stainless steels but also for ferritic-austenitic stainless steels.¹³⁾

5. Conclusion

It was found that tungsten, like silicon, was a very beneficial alloying element to pitting corrosion resistance of the stable austenitic stainless steel if added with molybdenum. Carbon was

Table 4. Analysis of ammonium ion in the solution after pitting corrosion test in 20% FeCl₃·6H₂O.

Base steel	N* (wt%)	Weight loss (mg)	Amount of N in the corroded metal (calculated from weight loss) (mg)	Amount of N present as NH ⁺ in the test solution analyzed by Kjeldahl method (mg)	Test condition
25Cr-22Ni-1.5Mo	0.018	2891	0.52	0.4	40°C, 24 hr
25Cr-22Ni-1.5Mo	0.130	1704	2.22	2.5	40°C, 24 hr
17Cr-22Ni-1.5Mo	0.184	1402	2.58	2.3	R.T., 144 hr

* Nitrogen content soluble in concentrated hydrochloric acid.

also beneficial if it did not form carbides. Manganese was harmful and its influence was greater if the sulfur content was higher, but increasing the manganese content more than that of conventional stainless steels did not enhance its harmful effect. Copper was favorable to the Mo-free steel, but not effective to the Mo-bearing one. The very favorable effect of nitrogen was again recognized in the stable austenitic stainless steel. The effects of the other alloying elements on the stable austenitic stainless steels are summarized in Table 2.

The more noble the electrode potential at a relatively high c.d., *i.e.* 10 mA/cm², in anodic polarization curves in sodium chloride solution, the lower is the corrosion rate in the ferric chloride solution if a second phase is absent. The presence of a second phase, such as carbide and sigma, in the austenite accelerates especially the corrosion rate in the ferric chloride test, but it has not an appreciable influence on the anodic polarization in sodium chloride solution. It was indicated that the alloying to increase the passivating ability of the stainless steel would shift the pitting potential to the more noble direction.

(Received October 11, 1974)

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