

Pitting Corrosion of Metals

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Introduction

Among the different forms of localized corrosion, pitting is encountered most often in technologically important metallic materials. Carbon steels, low alloy and stainless steels, nickel base alloys, aluminum, titanium, copper, and many other metals and their alloys may suffer severe pitting in different environments, especially in those containing chloride ions. For example, pitting has been observed in seawater desalination units and gas and oil refineries, and in the salt, chemical process, marine and shipping, and pulp and paper industries. Pitting also occurs in different water cooled systems, for example, those used in the nuclear industry and in central heating systems.

Because pitting is widespread and damaging, it has been a matter of great concern to industry for more than 30 years. Many investigations have been performed by scientists in research and development institutions all over the world, and they are continuing their investigations to determine what conditions lead to pitting and how the basic mechanisms of pitting work and to develop effective methods of protection.

These investigations have established the influence of both external (environment composition, temperature, electrode potential) and internal parameters (alloy composition, heat treatment, surface preparation, etc.) on pitting corrosion. Inhibitors for a wide variety of metals and commercial alloys have been found.

It has been established that pitting is, ironically, a detrimental side effect of the beneficial phenomenon of passivity. As a matter of fact, metals and alloys that are in their passive state and in contact with aggressive media are prone to pitting. Therefore, the behavior of passivating films and their improvement or damage under certain chemical and/or electrochemical environmental conditions are of great importance. Predicting passive film behavior and pitting in diverse environments proved to be extremely complex, however. The recent use of highly sophisticated techniques such as automatic ellipsometry, Auger electron spectroscopy, and x-ray photospectroscopy for surface film examination permitted the discovery of interesting correlations between the composition and structure of the alloy and surface film, and the protective ability of the latter. This opened up a promising avenue for predicting how the alloy composition as well as the heat and surface treatments should be modified to improve resistance to pitting and other forms of localized corrosion, which are also associated to the properties of passive films.

Despite the progress made in understanding the role of passivity in pitting, many questions remain unanswered. One reason for this is the still inadequate characterization of the nature of passive films and their interaction with various electrolytes. The existing theories of pitting are all based on the perceived relationship of pitting to the localized breakdown of passivity, yet they still do not explain all aspects of this type of corrosion.

This problem has become even more complicated lately because it was found that pitting could also occur in the absence of aggressive anions such as chlorides. Under certain conditions, pitting of carbon steels may occur in not only the presence of the sulfate ion in aqueous solution at room temperature, but also in high temperature oxygenated pure water (with impurity levels lower than a few ppm). This suggests that mechanisms other than those operating in chloride solutions may be responsible for pitting.

Obviously, more research is needed before practical and scientific questions can be answered successfully and the results applied to the problems encountered in the field.

The purpose of this book is to give a comprehensive and critical picture of the state of knowledge in pitting corrosion science based on most of the available literature and on personal experience derived from laboratory work.

It is my hope that this book will be useful to scientists conducting research as well as to engineers confronted with localized corrosion problems.

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creasing potential and film thickness, while others maintain that the opposite is true.⁵² Yolken, et al.,⁴⁹ found a significantly smaller number of protons in anodic films grown at potentials below 0 V_{SCE} than they did at higher potentials, and Konno and Nagayama¹⁶ showed that the ratio of H₂O molecules to individual iron cations decreased from 1.8 to 0.7 when the potential was shifted from -0.2 to 0 V_{SCE}. Above 0 V, the decrease in water content was less pronounced, the ratio being approximately 0.4 at 1 V_{SCE}. Above 0.2 V, water is thought to be present only in the outer portion of the film; below 0 V, it is present in the inner and outer portions.¹⁶

Stainless Steels

Investigation of the composition and structure of oxide films on stainless steels is much more difficult than in the case of iron because the films are thinner, their chemical composition is even more complicated, and they cannot be reduced cathodically. Therefore, chemical and electrochemical methods are of limited value for studying passivity of stainless steel.

A major part of the information available on composition and structure of passive films on stainless steels has been obtained with spectroscopic techniques, particularly x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Other methods such as ion scattering spectroscopy (ISS) and secondary ion mass spectrometry (SIMS) also provide valuable data.

The XPS method was used to study the composition and structure of oxide films on iron-chromium alloys.⁵⁶⁻⁵⁹ For example, Hashimoto, et al.,⁵⁶ used this method to compare films formed on Fe-30Cr and Fe-30Cr-2Mo alloys during passivation in 1M KCl. They did not find any substantial difference in the film composition, which was primarily hydrated chromium oxyhydroxide. Molybdenum was deficient in the passive film on the Mo-containing steel. In another study,⁵⁸ it was found that the chromium content of the passive film formed in deaerated 1M H₂SO₄ increased drastically in an alloy with approximately 13% Cr. The high corrosion resistance of Cr rich Fe-Cr alloys was attributed to the protective nature of chromium hydroxide, which was shown to be the main constituent of passive films on alloys with at least 12.5% Cr.

Olefjord and Fischmeister⁵⁷ reported some differences between the composition of films formed on iron base alloys containing 4 to 30% Cr in dry oxygen and those formed in oxygenated water at 25 to 70 C. For varying periods of exposure to dry oxygen, the average composition of film corresponded to that of the alloy, but depletion of chromium later occurred in the outermost portion of the film, and there was a slight enrichment at the metal/oxide interface. In the case of the aqueous environment, however,

prolonged exposure led to chromium enrichment primarily in the outermost portion of the film. The passive film was thought to consist of two layers: an outer layer of $\text{Cr}(\text{OH})_3$ and an inner one of iron-chromium oxide ($\text{Fe}_{1-x}\text{Cr}_x\text{O}_4$).

Using ISS, Frankenthal and Malm⁶⁰ studied the composition of air-formed oxide films on a series of Fe-Cr alloys (5 to 25% Cr). They found that the film composition changed continually with depth. At the air/oxide interface, the film contained little or no chromium and appeared to be either oxygen rich or deficient in iron. Immediately beneath the surface layer, the Cr content increased sharply, reached a peak, and then decreased to the level of Cr in the bulk alloy. At its maximum, the Cr content was two to three times higher than that of the alloy.

Similar results were reported by Tjong, et al.,⁶¹ who studied passive films formed in borate buffer solution (pH 8.4) on iron based alloys containing 3, 9, 12, and 18% Cr. Both the AES and SIMS techniques were used. For the Fe-3Cr alloy passivated in the potential range of 0.65 to 1.45 VSHE, the Auger spectra showed negligible Cr content in the passive layer. For the other alloys studied, the percentage of chromium passed through an apparent maximum within the film.

Ensling, et al.,⁷⁵ studied oxide films formed on martensitic Fe-16.5Cr and austenitic 18Cr-8Ni stainless steels in oxygen-free water at 295 C. Using Mössbauer spectroscopy, they found nonstoichiometric magnetite in both alloys. On Incoloy 800, however, a nickel ferrite ($\text{Ni}_{0.8}\text{Fe}_{2.2}\text{O}_4$) was formed.

The structure of passive films on Fe-Cr alloys was determined by McBee and Kruger,⁶² who used the electron diffraction technique, while Ambrose and Kruger measured the film thickness (Table 2.3). It follows from both of these studies that the film thickness decreases and noncrystallinity of the film increases with increasing Cr content.

In a study of passive films on AISI 316 stainless steel in 1M NaCl + 0.1M Na_2SO_4 solution (pH 7) at a constant potential of 442 mVSHE, depletion of Fe and Ni in the film relative to that in the substrate was observed, but the film was Cr enriched.⁶³ Neither Si nor Mo enrichment was found in the film. These findings contradict the results of Rhodin.^{64,65} Using a microchemical method to study the composition of films isolated from the substrate, Rhodin found that passive films on a similar alloy contained approximately 14 wt% Si and 4.2 wt% Mo. However, it should be emphasized that in Rhodin's experiments, the oxide film formed in a 5% KNO_3 + 0.5% $\text{K}_2\text{Cr}_2\text{O}_7$ solution.

Using AES, Barnes, et al.,⁶⁶ obtained results that differed from those of Lumsden and Staehle.⁶³ On mill-finished 316 stainless steel which had

TABLE 2.3 — Variation in Limiting Film Thickness (as a function of Cr Content) and Crystallinity of Passive Films on Fe-Cr Alloys

Cr (%)	Degree of Crystallinity of Passive Film ⁽¹⁾	Limiting Film Thickness ⁽²⁾ (Å)
0	Well-oriented spinel	36
5	Well-oriented spinel	27
12	Poorly oriented spinel	21
19	Primarily noncrystalline	19
24	Completely noncrystalline	18

⁽¹⁾According to Ambrose and Kruger, unpublished data.

⁽²⁾Reference 117.

received no subsequent surface treatment, they found a Mo content of close to 14%, which was significantly higher than the content in the alloy (2%). Mo enrichment was also found on the surface of AISI 304 stainless steel which contained Mo only as a residual element.

Okamoto, et al.,⁶⁷ used XPS to study the composition of the passive film on 18Cr-8Ni steel after exposure to sulfuric acid solution at various potentials. Figure 2.2 gives the ratios of peak height for Cr(LIII) and Ni(LIII) to that for Fe(LIII) against the potential of the passivation treatment. A remarkable increase in the concentration of Cr and Ni relative to Fe is observed at 0.4 V for the film formed in 60 minutes. The same ratio of Ni(LIII) to Fe(LIII) was found after 2 hours of passivation. However, the Cr:Fe ratio decreased with increasing passivation times at potentials higher than 0.4 V, whereas the ratio increased at potentials lower than 0.4 V. The results therefore indicate that film composition depends on passivation conditions, particularly the potential.

The XPS and AES methods were used by Olefjord and Elfstrom⁶⁸ to study oxide films on austenitic stainless steels passivated in 0.1M HCl + 0.4M NaCl solution. The film formed in the passive region consisted primarily of chromium oxide. Iron was preferentially dissolved even during passivation. Mo enrichment was observed in a highly Mo alloyed (6% Mo) steel. Ni was present only to a small extent in the film.

In summary, chromium enrichment occurs in the passive film and in the form of hydroxide. With increasing Cr content, the film becomes amor-

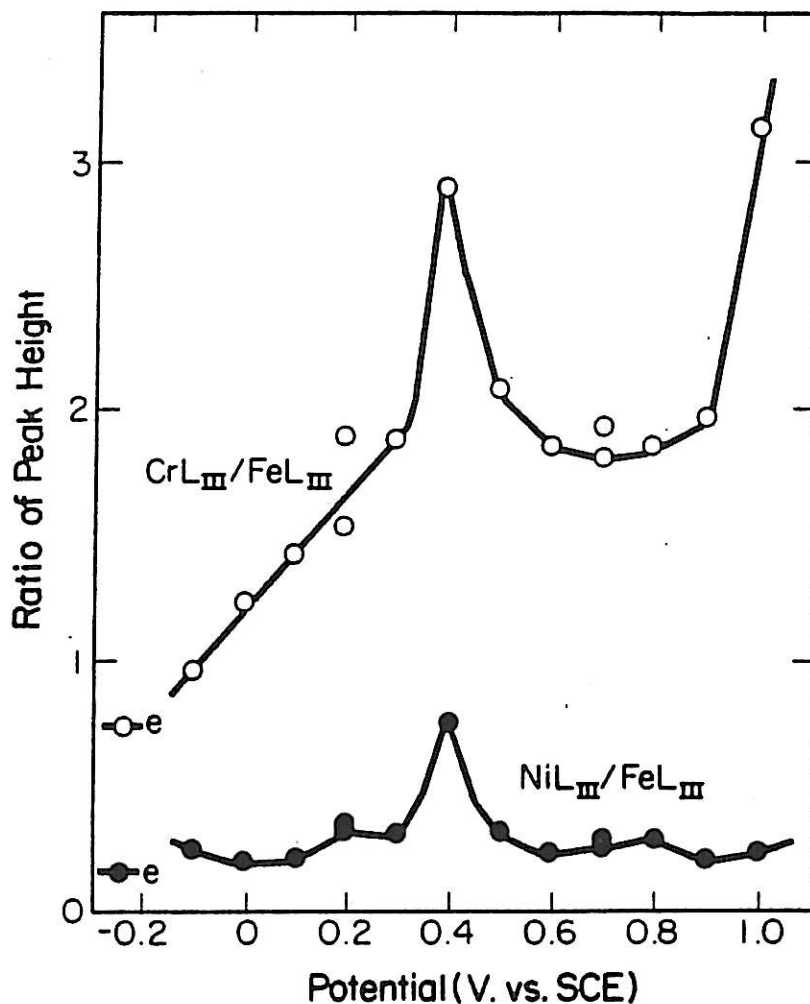


FIGURE 2.2 — Changes in the peak height ratio of Cr:Fe and Ni:Fe for 18Cr-8Ni stainless steel passivated at various potentials in 1N H₂SO₄ for 1 hour. [SOURCE: G. Okamoto, et al., J. Japan Inst. Met., Vol. 38, p. 117 (1974), reprinted with permission.]

phous, and its thickness decreases.

The results of tests to determine the Mo content in films have been inconsistent. While some investigators have observed Mo enrichment in the film relative to the Mo content of the alloy, most authors have found a reduction or even depletion of this element in the film (see Chapter 8 under *Effects of Cr and Mo on the Resistance of Steels to Pitting*).

The composition of the film seems to be significantly affected by the conditions (environment, potential, time, temperature) in which the film develops. If the dissolution rate of a given component of the steel at the given potential and in the given solution greatly exceeds the dissolution rate of other elements, this component undergoes selective dissolution. Preferential dissolution of iron in Fe-Cr alloys causes the formation of a chromium enriched film.

The composition and structure of oxide films formed on the surface of

stainless steels in aqueous solutions at high temperatures have been studied by different investigators, but with contradictory results.

Nakayama and Kitada⁶⁹ used x-ray spectroscopic analysis and electron diffraction to study films formed in deionized water at 300 C. On mechanically polished surfaces, they found a corundum-type iron oxide in which Cr content increased with increasing distance from the external surface of the film. On chemically polished surfaces, a spinel-type oxide was found; its external layers were rich in iron and nickel.

Nakayama and Oshida⁷⁰ investigated changes in the composition of films formed in water at 300 C with 8 ppm dissolved oxygen. After exposure for one hour, a corundum-type oxide was detected, whereas after 24 hours, a spinel-type oxide was present. The composition was assumed to be $(\text{Cr,Fe})_2\text{O}_3$ or $\alpha\text{-Fe}_2\text{O}_3$, and $\text{NiO}(\text{Cr,Fe})_2\text{O}_3$, respectively.

Ishihara, et al.,⁷¹ found a cubic spinel-type oxide identified as Fe_3O_4 and NiFe_3O_4 in aerated water at more than 250 C. Below 225 C, the film was composed of $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 .

Fuji, et al.,⁷² obtained the following structure of the oxide film in sodium sulfate solutions at 250 C: at about -0.63 and -0.3 VSHE, a spinel-type oxide; and at $+0.4$ VSHE (above the transpassive peak), a corundum-type oxide. Under open circuit conditions in deaerated solution, the oxide film exhibited a spinel structure, and in the presence of oxygen, a corundum-type structure, which corresponds to the results obtained under controlled potential.

Castle and Clayton^{73,74} used XPS to study the composition and thickness of oxide films on 18Cr-8Ni stainless steel exposed to water at temperatures from 40 to 200 C. At lower temperatures (40 and 80 C), the film was 1.5 nm thick, and its thickness was only slightly dependent on temperature. The kinetics of film growth at lower temperatures were logarithmic, but at 200 C, the film grew almost linearly with time. The film composition, on the other hand, depended on temperature. Below 120 C, there was little segregation of Cr and Fe in depth profile, whereas at 200 C, marked segregation of these elements was found. At low temperatures, the outer layer was rich in OH^- . At higher temperatures, however, the outer layer was rich in Fe and composed of hydrated oxides. The composition of the inner layer was assumed to be $\gamma\text{-Fe}_2\text{O}_3$ and Cr_2O_3 .

It appears that below 200 C, a thin protective oxide film exists on steel surfaces in contact with water or sodium sulfate solution. At higher temperatures, this film rebuilds, the kinetics of its growth changing from a slow logarithmic rate to a more rapid rate; the resulting film is less protective than the one formed at lower temperature. It appears that the crystalline structure of the oxide film (whether spinel or corundum) does not significantly affect the film's protective properties.

stronger chemisorption of chloride ions on the metal surface, causing easier breakdown of passivity. The pit number also increases with increasing temperature because at higher temperatures, more sites are susceptible to pit nucleation. An increase in temperature accelerates the transport of reagents and reaction products to or from the electrode. However, the effect of temperature on transport rate is considerably less than its effect on the chemisorption of chloride ions and on the ionization of metal. Therefore, the changes in electrolyte concentration inside pits occur more rapidly with increasing initial current density in pits. These concentration changes lead to increased concentration polarization, and to ohmic polarization, when salt layers or other corrosion products are deposited in pits. Consequently, inhibition of the metal dissolution, both by transport processes and decreases of the current density in pits vs exposure time, are more pronounced at higher temperatures.

It is notable that at certain temperatures, pitting can occur without chloride ions in the solution, which is presumably related to some changes in film structure at these temperatures.

The Influence of Surface Condition

The metal surface state is known to affect pitting susceptibility. The more homogeneous the surface is, both chemically and physically, the higher the pitting potential, the lower the pit number, and the better the metal resistance to pitting.¹¹⁷ Surface roughness, caused by local "weak" points in the protective oxide film, where a critical Cl^- concentration can be attained, or by inhomogeneities resulting from surface preparation, can increase the number of active sites for pit nucleation.¹¹⁸

Streicher¹¹⁹ found that the number of pits per unit area is higher on steel pickled in nitric + hydrofluoric + hydrochloric acids at 70 C than on steel pickled and passivated in nitric acid + potassium dichromate solution. These measurements were performed after the current density was increased from 0 to 3 mA/cm² and held for 5 min at this value. The results are listed in Table 9.5.

Isaacs and Kissel¹²⁰ studied the effect of exposure time on active pit propagation on AISI 304 stainless steel in 0.4M FeCl_3 solution of pH 0.9, using a scanning reference electrode to measure the number of active pits. Both the number of active pits and the rate at which their growth was decreased (because of passivation) depended on the steel surface treatment. Pitting resistance decreased in the following order: electropolished + cathodically polarized > abraded with 600 grit SiC > abraded + oxidized at 250 C for 16 h > electropolished > electropolished + oxidized at 110 C

TABLE 9.5 — Effect of Surface Preparation and Heat Treatment on Pitting of Stainless Steels in 0.1M NaCl at 25 C⁽¹⁾

Steel AISI Type	Code	Pits/cm ² ⁽²⁾		
		Pickled	Passivated	Ground ⁽⁴⁾
304	ER-2	7.4	3.4	3.1
304 ⁽³⁾	ER-2 ⁽³⁾		3.3	5.0
316	EW-5	7.3	0.46	0.0
316 ⁽³⁾	EW-5 ⁽³⁾		0.76	
316L	FH-3	5.0	0.17	1.2
316L ⁽³⁾	FH-3 ⁽³⁾	3.5	1.4	1.5
321	FF-7		2.4	3.9
321 ⁽³⁾	FF-7		1.5	0.5
347	EX-2		2.9	6.7
347 ⁽³⁾	EX-2 ⁽³⁾		2.5	6.4

⁽¹⁾SOURCE: M. A. Streicher, J. Electrochem. Soc., Vol. 103, p. 375 (1956), reprinted with permission.

⁽²⁾Average of 10 runs.

⁽³⁾Heated 1 h at 1250 F.

⁽⁴⁾Ground to 120-grit finish.

for 24 h > electropolished + oxidized at 165 C for 24 h > electropolished + oxidized at 240 C for 24 h > electropolished + oxidized at 250 C for 24 h. The authors concluded that surface preparation influenced film thickness. The thinnest films form on surfaces that have been cathodically treated. The film thickness on electropolished surfaces is intermediate between that on surfaces cathodically treated and air oxidized (oxidation above 100 C). Film thickness is expected to increase with oxidation temperature. Above 250 C, the pitting resistance decreases again, probably because of some changes in the film properties.

Defrancq¹²¹ found that, for iron and steel, reproducibility of E_{np} determination increased with increasing surface roughness. This effect was not, however, attributed to the occurrence of flaws or imperfections in the oxide film, but to an increased energy of metal cations, resulting in their dissolution at relatively lower potentials.

Manning, et al.,¹²² studied the effect of surface roughness on pitting potential of single-phase and duplex AISI 304L stainless steel. For mechanically prepared specimens in rectangular form, experiments were conducted using samples with and without prepassivation. The pitting

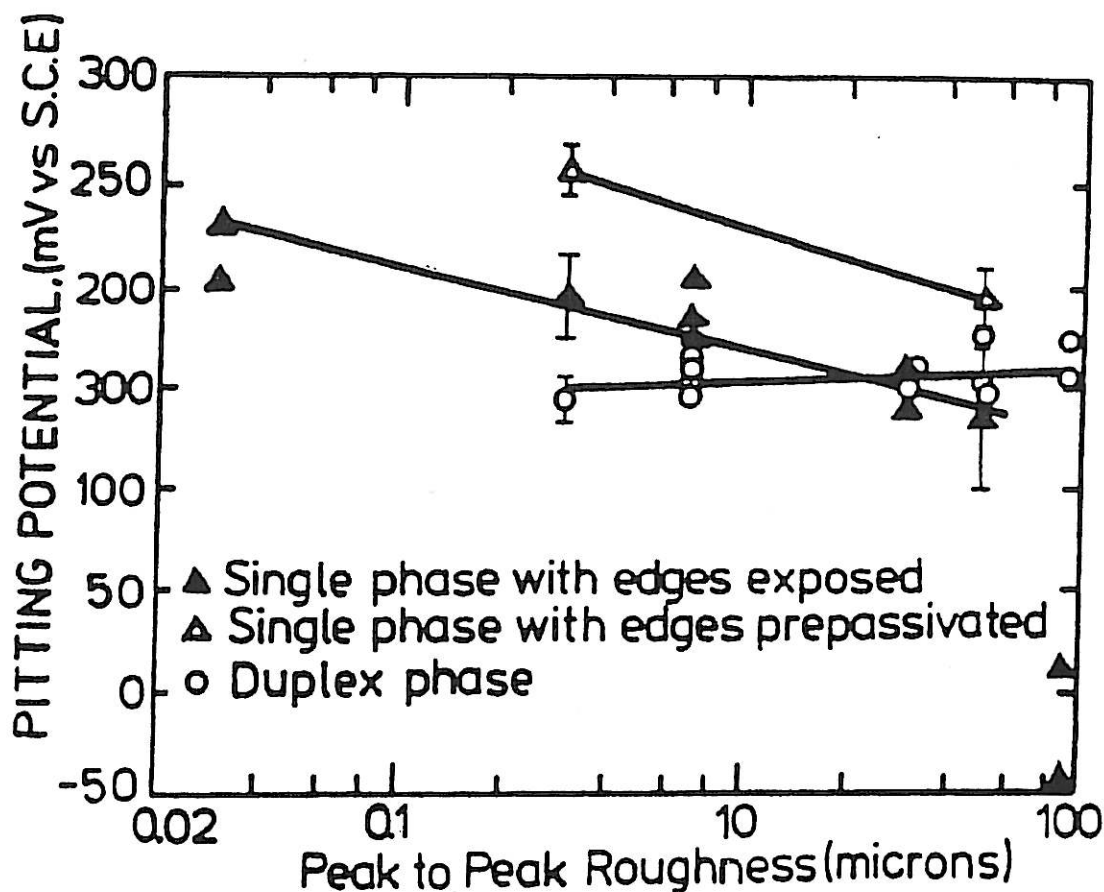


FIGURE 9.33 — Pitting potentials of single-phase and duplex AISI 304 stainless steels in 1M NaCl solution vs surface roughness. [SOURCE: P. E. Manning, D. J. Duquette, W. F. Savage, *Corrosion*, Vol. 35, No. 4, p. 151 (1979).]

potential of single-phase steel decreased monotonously with increasing surface roughness. This effect was not observed for duplex steel (Figure 9.33). The authors concluded that the different behavior of single and duplex steel was primarily connected with sulfidic inclusions. In this respect, it is notable that a difference was observed between E_{np} for samples with prepassivated edges polished with 80 grit paper with scratches both parallel and perpendicular to the rolling direction. The edge effect observed on single-phase steel with edge-passivated and edge-exposed specimens was related to the greater amount of inclusion/matrix interfaces in the transverse edges of the specimens. In this case, pits were initiated on inclusions, while in the duplex steel, pits were nucleated at γ/δ interfaces, and there was no surface roughness effect. A more positive E_{np} was obtained for specimens polished with diamond paste, and a more negative effect was found for specimens pickled in nitric + hydrochloric acid (Table 9.6).

Synderberger¹²³ investigated the influence of surface condition on pit initiation and crevice corrosion of many austenitic and ferritic stainless steels. A

TABLE 9.6 — Pitting Potential Data for Surface Treatments of Single and Duplex Phase AISI 304L Stainless Steel⁽¹⁾

Treatment Number	Peak to Peak Roughness (μm)	Pitting Potential (mV vs SCE)							
		Edge Exposed		Single Phase		Duplex Phase			
		No. of Tests	Ave.	Edge Passivated	No. of Tests	Ave.	Edge Exposed	No. of Tests	Ave.
5.	0.03	2	216						
4.	0.3	5	196 \pm 20	5	255 \pm 11	5	145 \pm 11		
9.	0.3	2	198			1	173		
6.	0.7	2	180			2	150		
3.	0.7	2	184			2	163		
8.	3.0	2	150			2	155		
1.	5.0	5	135 \pm 5	5	193 \pm 18	2	150		
2.	5.0	5	135 \pm 21	5	137 \pm 12	2	164		
7.	9.0	2	- 18			2	165		

1. 80 grit paper with scratches parallel to the rolling direction.
 2. 80 grit paper with scratches perpendicular to the rolling direction.
 3. 240 grit paper.
 4. 600 grit paper.
 5. 3 μm diamond paste.
 6. Electropolished.
 7. Pickled in 25% HNO₃, 25% HCl, 50% H₂O.
 8. Pickled in 15% HNO₃, 5% HCl, 2% HF, 78% H₂O.
 9. Pickled in 15% HNO₃, 2% HF, 83% H₂O.
- ⁽¹⁾SOURCE: T. Shibata, T. Takayama, Corrosion, Vol. 33, No. 7, p. 243 (1977).

beneficial effect of pickling in 10% HNO₃ + 1% HF, and also in 10% H₂SO₄ solution, was found. Passivation in 25% HNO₃ also produced a positive effect. This beneficial surface treatment effect was attributed to the removal of sulfidic inclusions emerging on the surface, which were sites for discrete pit nucleation. In fact, much higher resistance to crevice corrosion in 0.1% NaCl + 0.1% K₃Fe(CN)₆ was obtained for AISI 304, AISI 316, and 20Cr-25Ni-4.5Mo-5Cu steels with normal and low (0.2%) Mn contents than for steels with higher percentages of Mn and sulfidic inclusions.

Crolet, et al.,¹²⁴ found pitting was dependent on surface treatment; crevice corrosion was found independent of surface treatment.

Studying the effect of experimental procedure on E_{np} for different alloys in 4% NaCl + 0.01M HCl at 70 C as a function of scan rate, Manning¹²⁵ obtained data given in Table 9.7. At a low scan rate, the E_{np} values for differently prepared specimens are close to each other. This indicates that during slow scan, the differences in the properties of the initial film formed at corrosion potential disappear.

Shibata and Takayama^{126,127} obtained large differences in E_{np} evaluated statistically for AISI 304 stainless steel specimens prepared in

**TABLE 9.7 — Effect of Experimental Procedure
on the Pitting Potential as a
Function of Scan Rate⁽¹⁾**

Material	Test Type ⁽²⁾	Pitting Potential (mV vs SCE)		
		0.36 V/h	5.0 V/h	50.0 V/h
Alloy 20	A	236	253	276
Alloy 20	B	260	400	351
Alloy 825	A	209	88	1
Alloy 825	B	235	260	270
20Cb-3 alloy	A	160	63	20
20Cb-3 alloy	B	175	175	265

⁽¹⁾SOURCE: T. Shibata, T. Takeyama, Proc. 19th Symp. on Corros. and Protection, Japan Soc. of Corros. Eng., p. 23, 1978, reprinted with permission.

⁽²⁾Test Type A—2 min at corrosion potential and potentiodynamic test was begun in the cathodic region (−300 mV vs SCE). Test Type B—1 h at corrosion potential and potentiodynamic test was begun at the corrosion potential.

E_{NP} = potential for pitting propagation

various ways. The E_{NP} values measured in 3.5% NaCl increased in the following order: electropolished < 2/0 emery polished < 6/0 emery-polished < electropolished and passivated in 20% HNO₃ at 35 C for 1 h < passivated < emery-polished and passivated as above. Comparing the behavior of AISI 304 and 316 stainless steels polished with 2/0 emery paper with those etched in 30% H₂SO₄ at 35 C for 10 min, the authors¹²⁶ found that etching apparently generated a larger scatter than emery polishing. This was concluded from the line slopes of the normal probability of pitting vs E_{NP} . The steepest slope indicated the least dispersion. This scatter of experimental results in E_{NP} determination was higher for AISI 316 steel (Figure 3.14 in Chapter 3).

As reported by Asami and Hashimoto,¹²⁸ surface treatment appears to affect the chromium content in the passive film. It is shown in Figure 9.34 that the Cr content in the surface film examined by XPS increases in the following order: dry polishing < wet polishing < HF etching < 10% HNO₃ etching < 30% HNO₃ passivation treatment. Selective iron dissolution and preferential chromium oxidation occurs during surface treatment, causing impoverishment of the surface film in iron and enrichment in chromium. When the Cr content in the surface film is larger, both the pit-

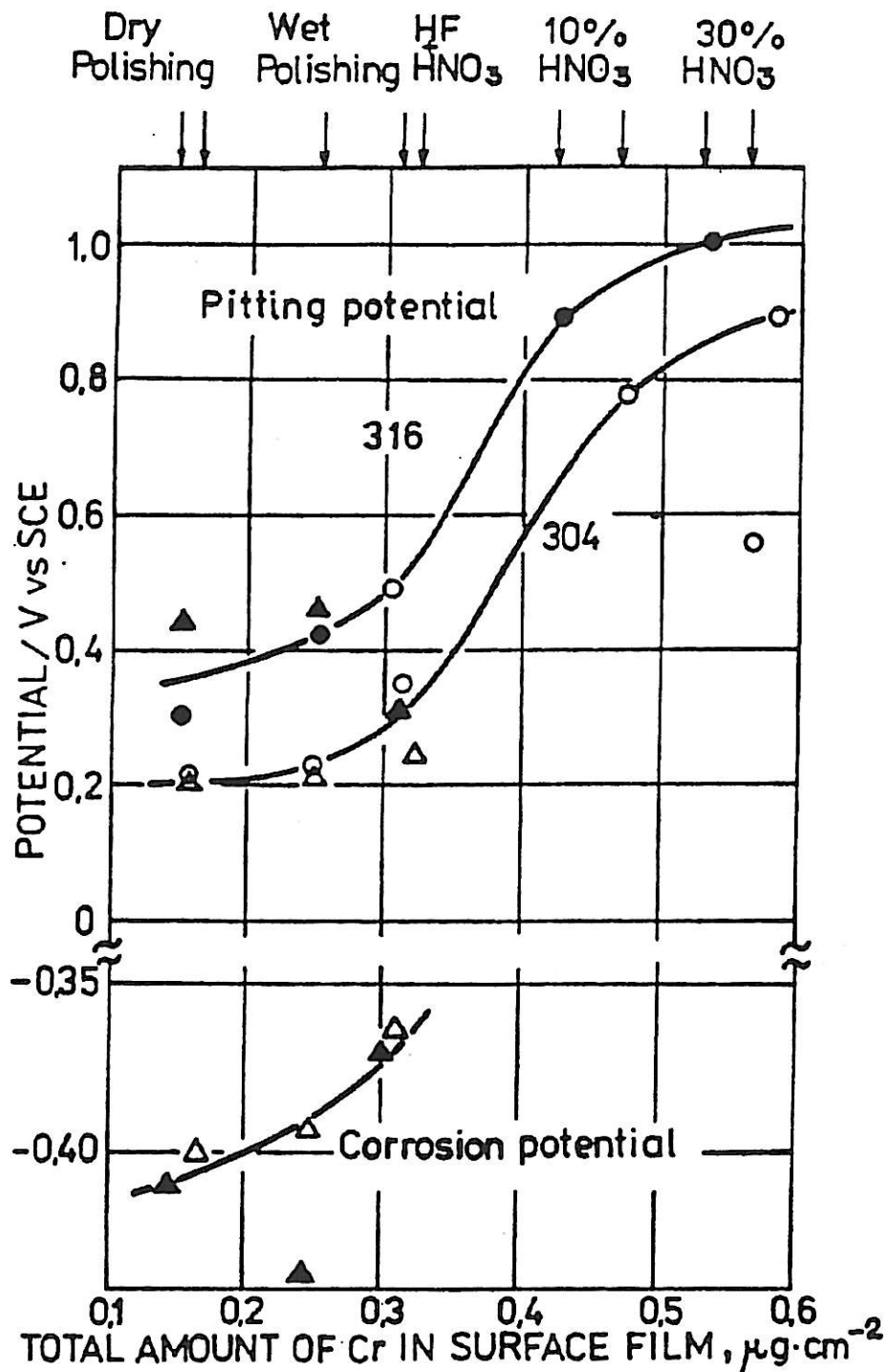


FIGURE 9.34 — Relationship between pitting potential and corrosion potential in 3.5% NaCl and total amount of Cr in the surface film. Data for E_{np} follow Reference 127 (○ for AISI 316, and ○ for AISI 304 steel) and Reference 129 (▲ for AISI 316 and △ for AISI 304 steel). Data for the corrosion potential are after Reference 124 (▲ for AISI 316 and △ for AISI 304 steel). [SOURCE: K. Asami, K. Hashimoto, Corros. Sci., Vol. 19, p. 1007 (1979), reprinted with permission.]

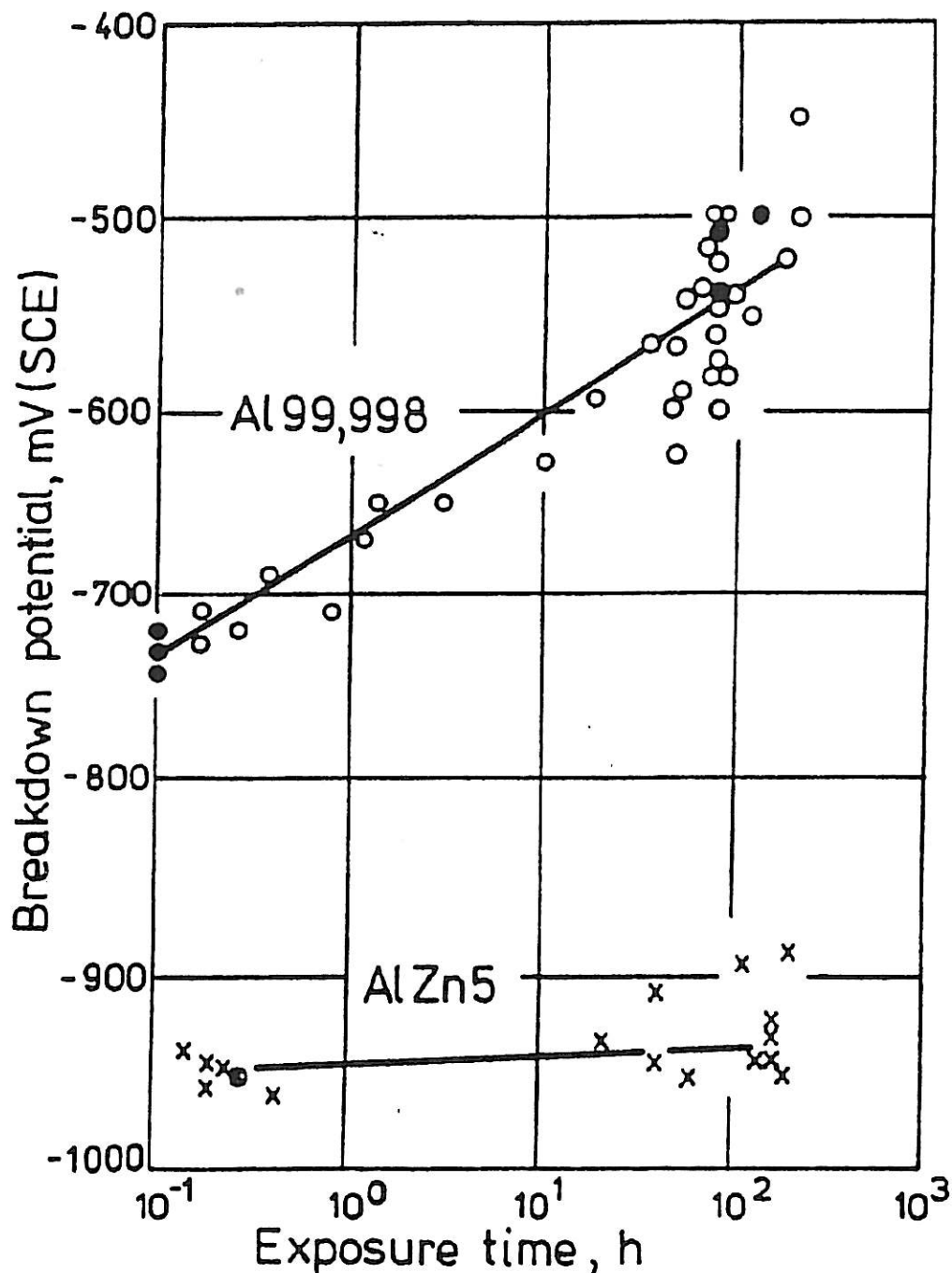


FIGURE 9.35 — Effect of exposure time for pure Al and Al-5Zn Alloy to artificial seawater on pitting potential at 30 C: scan rate 1200 or 100 mV/h. [SOURCE: H. Ginsberg, W. Huppertz, *Metall.*, Vol. 26, p. 565 (1972), reprinted with permission.]

ting potential and corrosion potential are more noble. Clearly, E_{corr} depends on the composition of the oxide film on steel; E_{np} is influenced by the film protective ability and the steel composition.

Ginsberg and Huppertz¹³⁰ studied the influence of exposure time in artificial seawater on E_{np} of similarly prepared specimens of Al and Al-5Zn alloy. They found a linear dependence of E_{np} on exposure time for Al and independence of E_{np} on time for the Al-5Zn alloy (Figure 9.35). These

results suggest that exposure to seawater induces changes in the structure and thickness of the oxide film on Al, but does not cause similar effects in the Al-5Zn alloy.

In general, the passive film quality is the most important parameter affecting the pitting resistance of various metals and alloys. On the other hand, the quality of passive films is a complex function of metallurgical and environmental factors and is strongly affected by every type of surface preparation and treatment.

Solution Flow

The effect of the flow velocity of chloride solutions on pitting potential of metals and alloys was investigated by several researchers. The results of these studies can be divided into two groups: (1) studies wherein no effect was noted; and (2) studies wherein some insignificant influence of flow rate on E_{np} was established.

Sato, et al.,¹³¹ studied the pitting effect of rotation speed of an electrode of 18Cr-8Ni stainless steel in 0.2M NaCl + 0.1M Na₂SO₄ solution. Changes in rotation speed (0 to 5000 rpm) affected neither E_{np} , nor induction time for pit nucleation. From these results, it was concluded that the pit nucleation process is not controlled by any mass transfer and that pit nucleation occurs inside the passive film.

Castro and Wilde¹³² also reported that E_{np} of iron in LiCl solution was independent of the rotational velocity.

Mansfeld and Kenkel¹³³ did not find a definite effect of rotation on E_{np} and E_{pp} for AISI 304 stainless steel in 3.5% NaCl. Both of these potentials were determined from the forward and backward sweeps of polarization curves measured at a scan rate of 1.8 V/h. A rotating cylinder was used at angular velocities ranging up to 196 rad/s (186 cm/s).

Rozenfeld, et al.,¹⁰⁹ found that E_{np} for 99.99% Al and aluminum alloys with 5% Cu, Mg, or Zn does not depend on the rate of disc rotation (0 to 300 rpm). Other authors^{4,134} also reported that stirring had no discernible effect on E_{np} of Al.

Postlethwaite, et al.,⁹⁸ did not observe any effect of solution flow on E_{np} of Zircaloy 2, but the current density decreased with increasing flow velocity, indicating that the pitting attack decreased.

No effect of stirring on E_{np} was observed for Ti,¹³⁵ but for discs of a Ti-6Al-4V alloy immersed in NaCl solution, E_{np} shifted¹³⁶ from 1.8 V at zero speed to 4.3 V at 5000 rpm.

Riskin and Turkovskaia¹³⁷ noted that E_{np} of 18Cr-8Ni stainless steel in NaCl solution was shifted to more positive values when the elec-

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